METALLOGRAPHY

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BY

CECIL H. DESCH

D.Sc. (Lond.), Ph.D. (Würzb.), Hon. LL.D. (Glas.), F.R.S.

LATE SUPERINTENDENT, METALLURGY DEPARTMENT, NATIONAL PHYSICAL LABORATORY

FORMERLY PROFESSOR OF METALLURGY, UNIVERSITY OF SHEFFIELD

WITH ILLUSTRATIONS

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PREFACE TO THE SIXTH EDITION.

THE fourth edition of this book appeared after a relatively long interval, and the progress of the subject made a thorough revision of the text necessary. For the fifth edition an appendix was added, supplementing the information in the text. The same plan has been adopted in the present edition, further notes being added in the appendix, but many passages in the text have also been revised and recent references inserted. The abbreviations used in the references are, as before, mainly those of " British Chemical Abstracts," and all temperatures are expressed in Centigrade units.

For Chapters IX and X, dealing with X-ray methods of investigation, the writer is indebted to his former colleague at the National Physical Laboratory, Prof. G. D. Preston, now of Dundee, and he also wishes to thank other members of the Laboratory staff for fruitful discussion and for the use of photographs, the Department of Scientific and Industrial Research for permission to use several diagrams from papers issued by the Laboratory, the makers of microscopes named in the text for the use of blocks for illustrations of apparatus, and Miss M. Le Pla, B.Sc., for the preparation of the Index.

WIMBLEDON, *January*, 1944.

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CHAPTER I.

INTRODUCTION.

METALLOGRAPHY may be defined as the study of the internal structure of metals and alloys, and of its relation to their composition, and to their physical, chemical and mechanical properties. It is a branch of physical chemistry, since the internal structure depends on the physical and chemical conditions under which the solid metal or alloy is formed, and the study of structure presents itself as a department of the study of equilibrium in heterogeneous condensed systems. Whilst, however, physical chemistry concerns itself in general only with the nature and relative quantity of the phases in a system, and with the transformations of energy which accompany chemical changes, metallography takes into account a further variable, namely, the arrangement of the component particles in space. It is thus intimately connected with crystallography.

The consideration of metals and alloys as a class apart from other mixtures and solutions which obey the same physico-chemical laws is partly an historical accident, and arises partly from the great importance of the metals in technical practice. The needs of practical metallurgy, especially in the iron and steel industries, have been the motive of the earliest, and of many of the most important metallographic investigations. The study of structure has proved itself an indispensable auxiliary to chemical analysis in the scientific control of the metallurgical industries, an auxiliary of which the applications become more extensive and more important every year. But from the standpoint of pure science, the identity of the relations in metallic and non-metallic systems must not be overlooked. Geologists and mineralogists make use of the methods and results of metallography to study the formation and metamorphosis of igneous rocks, whilst light has been thrown from the same source into the hitherto obscure region of the cements and slags,[1] and the science is capable of still further extension.

The word "metallography" was formerly used[2] to signify the description of metals and their properties. In this sense it is obsolete, although an isolated example of its use is found as late as 1871.[3]

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[1] This subject is reviewed by F. M. Lea and the author in "The Chemistry of Cement and Concrete," London, 1935.

[2] The earliest instance of its use given in the "New English Dictionary," Oxford, is dated 1721.

[3] T. A. Blyth, "Metallography as a Separate Science," London, 1871.

Its reintroduction to designate the microscopic structure of metals and alloys dates only from 1892,[1] since when it has been generally accepted, gradually receiving an extension of meaning to include investigations by other than microscopical means.

The examination of metals by means of the microscope, so recent as a method of systematic research, was nevertheless practised by several of the older investigators. As far back as 1665 Robert Hooke, in his "Micrographia," described the appearance of lead crystallizing from its alloy with silver, and further described and drew the magnified surface of a polished steel razor blade, adding some thoughtful remarks on the nature of polish.[2]

Réaumur, in 1722,[3] employed the microscope to examine the fractured surfaces of steel and of white and grey cast iron, founding on the results which he obtained a method of distinguishing between irons subjected to different thermal treatments. An extract will show the nature of his observations :—

> P. 392 : "Si on examine les unes et les autres fontes au microscope, les fontes bien blanches y parôitront toujours d'une tissure compacte, on y pourra observer quelques lames plattes parsemées, mais beaucoup plus petites que celles de l'acier, la même loupe qui fait apercevoir celles dont sont composés les grains d'un acier trempé peu chaud, ne feroit pas appercevoir celles-cy. Les fontes grises paroissent au microscope d'un tissu tellement spongieux, que tout semble un amas d'especes de crystalisations, ou si l'on veut de brossailles, des especes de vegetations chimiques, faites d'une infinité de branchages entrelassés, mais composés chacun de petites lames agencées les unes sur les autres."

Réaumur suggests in the same work, one of the most important in the early history of iron, a polyhedral arrangement of the crystals, and puts forward a theory to explain the hardening effect of quenching steel. The very numerous drawings testify to the careful character of his observations.

In 1775 a French ironmaster, Grignon, described and illustrated crystals of iron found growing into the cavities of castings.[4]

The microscopical examination of fractured surfaces is of very limited application, and is unsuitable for systematic study. The way towards a better method was opened by the discovery of Widmanstätten, Director of the Royal Porcelain Works, in Vienna, that certain meteorites when cut and polished develop a distinct

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[1] F. Osmond, *Rapport présenté à la commission des méthodes d'essais des matériaux*, February, 1892.

[2] Robert Hooke, "Micrographia ; or Some Physiological Descriptions of Minute Bodies made with Magnifying Glasses, with Observations and Enquiries Thereon," London, 1665.

[3] R. A. F. de Réaumur, "L'Art de convertir le fer forgé en acier, et l'art d'adoucir le fer fondu," Paris, 1722.

[4] Grignon, "Mémoires de Physique, sur l'Art de Fabriquer Le Fer," etc., Paris, 1775.

and characteristic structure when oxidized by heating in air.[1] The experiment was made at the suggestion of C. von Schreibers, and Widmanstätten found that etching with nitric acid gave even better results. He did not publish any account of the experiments, but they were described by Schweigger and others.[2] Widmanstätten's figures being visible without magnification, the process was not extended to metals having a more minute structure, and metallography made no further progress for many years. Paul Annosow examined etched surfaces of Oriental damascened steel blades by means of the microscope in 1841.[3] In 1864 H. C. Sorby, of Sheffield, who may also be regarded as the founder of the modern science of microscopical petrography, was led from the study of rocks and meteorites to that of iron and steel. His early publications on the subject were confined to brief notes,[4] although his specimens and photographs, exhibiting the constituents of iron and steel, were shown in Sheffield and at the Bath meeting of the British Association. Sorby was successful in devising a suitable technique for the preparation and examination of microscopic sections, and his later publications[5] contain photomicrographs which have hardly been surpassed in excellence by later workers. Sorby is certainly entitled to the credit of being the founder of metallography, although his early observations remained almost unnoticed for twenty years, by which time similar results had been attained by workers in other countries, none of whom, however, approached him in technical skill.

Attempts had been made[6] to examine metals by cutting thin sections similar to those used in the study of rocks. It is not possible to examine such sections by transmitted light, however thin they may be cut, and the plan was therefore adopted of subjecting them to the attack of reagents, so as to dissolve out certain constituents, leaving the residue in the form of a spongy network. This method is not very valuable, and beyond demonstrating the fact that iron or steel containing carbon has a cellular structure, little information was obtained by its means.

In 1878 the first communications from the Charlottenburg Testing Laboratory appeared.[7] The work of Martens was inde-

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[1] This name has been very variously spelt. L. J. Spencer (*Min. Mag.*, 1933, **23**, 329) states that the family name is Widmanstetter, but enquiry in Austria shows that the investigator himself used the form Widmanstätten, which is therefore retained.

[2] J. S. C. Schweigger, *Schweigger's J.*, 1813, **7**, 174; C. von Schreibers, "Meteorische Stein- u. Metallmassen," i, 20, Vienna, 1820.

[3] N. Belaiew, "Sur les précurseurs de la Métallographie," *Rev. Métall.*, 1914, **11**, 221; *J. Roy. Soc. Arts*, 1921, **69**, 833.

[4] *Proc. Sheffield, Lit. Phil. Soc.*, 1864, Feb.; *Brit. Assoc. Rep.*, 1864, ii, 189.

[5] *Engineer*, 1882, **54**, 308; *J. Iron Steel Inst.*, 1886, i, 140; 1887, i, 255.

[6] F. Osmond and J. Werth, *Compt. rend.*, 1885, **100**, 450; *Ann. Mines*, 1885, [viii], **8**, 1.

[7] A. Martens, *Z. Ver. deut. Ing.*, 1878, **22**, 11, 206, 480; 1880, **24**, 398; *Glaser's Annalen*, 1880, **7**, 476; *Stahl u. Eisen*, 1882, **2**, 423; *Verh. Ver. Bef Gewerbefl.*, 1882, 233.

pendent of that of Sorby but fell far behind it in experimental skill. He was followed by Wedding,[1] Stein,[2] and Osmond.[3] All these investigators, confining themselves at first to iron and steel, aimed at the discovery of a means of controlling the quality and composition of manufactured products. The arrangement of iron and steel crystals in ingots had been determined macroscopically as early as 1868,[4] and the extension of this knowledge to the microscopic structure was followed by very numerous investigations in this direction.

THE STUDY OF ALLOYS.

The further progress of metallography is intimately connected with the study of the nature of metallic alloys. The word *alloy*, or its equivalent form *allay*, was originally used to mean an intimate association of two or more metals and is so employed by Chaucer. Its special and restricted use to denote base metal added to gold or silver, for the purpose of working or coining, is of later origin, and is etymologically incorrect. The present use of the word is in accordance with its original signification.

It was long a matter of controversy whether alloys were to be regarded as chemical compounds or as mechanical mixtures. Perhaps the earliest researches directed towards the immediate solution of the problem are those of Levol,[5] who by the systematic examination of series of alloys of progressively changing composition, was able to show that only a few alloys remain homogeneous throughout the process of crystallization, all others being capable of separation into more fusible and less fusible parts. A few alloys proved to be exceptions to this rule, having a constant melting-point, and retaining the same composition throughout the processes of freezing and melting. In the alloys of silver and copper a mixture in the proportions represented by the formula Ag_3Cu_2 was found to have this property, and was considered by Levol to be a definite compound. We now know that this is incorrect, and that Levol's alloy is the eutectic mixture of the two metals, which do not form an intermetallic compound. Nevertheless, the research marks a distinct advance in the knowledge of alloys.

The view that alloys are to be regarded as solidified solutions, which may or may not contain compounds according to circumstances, is due to Matthiessen.[6] The method of investigation which he adopted was the study of physical properties, such as density, electrical conductivity, and thermo-electric power, comparing together alloys

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[1] H. Wedding, *J. Iron Steel Inst.*, 1885, i, 187; *Stahl u. Eisen*, 1886, **6**, 633.

[2] S. Stein, *ibid.*, 1888, **8**, 595. [3] F. Osmond and J. Werth, *loc. cit.*

[4] D. Tschernoff, *Mém. Soc. techn. Russ.*, April, 1868.

[5] A. Levol, *J. Pharm. Chim.*, 1850, [iii], **17**, 111; *Ann. Chim. Phys.*, 1852, [iii], **36**, 193; 1853, [iii], **39**, 163.

[6] A. Matthiessen, *Brit. Assoc. Rep.*, 1863, 37; *Trans. Chem. Soc.*, 1867, **20**, 201. Later references are given in Chapter XIV.

containing varying quantities of the same component metals, and seeking for any discontinuous changes of properties which might mark the presence of compounds. The work of Matthiessen was the starting-point of the application of physical chemistry to the study of alloys. It was followed by many similar determinations of conductivity, etc.[1]

After the discovery of Raoult's law of the depression of freezing-point of solutions, the study of alloys from this point of view was suggested by the fact that alloys very frequently melt at a lower temperature than their components. In the same year, the depression of the vapour-pressure of mercury produced by the addition of other metals was studied by Ramsay,[2] and the depression of the freezing-point by Tammann,[3] and by Heycock and Neville.[4] Complete curves, showing the change of freezing-point on passing from one end to the other of a series of binary alloys, were published for a number of pairs of metals by Kapp [5] and Heycock and Neville.[6]

The application of the theory of phases of Gibbs [7] to alloys was suggested by Jüptner [8] and by Le Chatelier.[9] Its first important application was made by Roozeboom [10] in a famous paper, in which the results obtained in the thermal examination of iron and steel by Roberts-Austen [11] were utilized in the construction of a complete diagram of the thermal equilibrium of iron and carbon. This diagram has formed the basis of all the subsequent discussions of the iron-carbon system, and although it has been found necessary to modify it in a number of particulars, its general outline has been preserved in all the schemes proposed by later workers. Roozeboom adopted the hypothesis of the existence of three allotropic modifications of iron, stable within different ranges of temperature, originally propounded by Osmond,[12] and this hypothesis has been retained, although it has undergone much modification.

The possible types of solid solutions or mixed crystals in binary systems had been reviewed from the theoretical standpoint of the phase rule by Roozeboom in 1899.[13] The first important application

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[1] G. Kamensky, *Proc. Phys. Soc.*, 1883, **6**, 53; *Phil. Mag.*, 1884, [v], **17**, 270; V. Strouhal and C. Barus, *Abh. k. böhm. Ges. Wiss.*, 1884, [vi], **12**, No. 14; C. Barus, *Amer. J. Sci.*, 1888, [iii], **36**, 427. See Chapter XIV.

[2] W. Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 521.

[3] G. Tammann, *Z. physikal. Chem.*, 1889, **3**, 441.

[4] C. T. Heycock and F. H. Neville, *Trans. Chem. Soc.*, 1889, **55**, 666.

[5] A. Kapp, *Ann. Physik*, 1901, [iv], **6**, 754.

[6] *Phil. Trans.*, 1897, **189**, A, 25.

[7] See "The Phase Rule," by A. Findlay, in this series.

[8] H. von Jüptner von Jonstorff, *Stahl u. Eisen*, 1899, **19**, 23.

[9] H. Le Chatelier, *Compt. rend.*, 1900, **130**, 85.

[10] H. Bakhuis Roozeboom, *Z. physikal. Chem.*, 1900, **34**, 437; *J. Iron Steel Inst.*, 1900, ii, 311.

[11] W. C. Roberts-Austen, "5th Rep. to Alloys Research Committee," *Proc. Inst. Mech. Eng.*, 1899, 35.

[12] F. Osmond, *Mém. Artill. Marine*, 1887, **15**, 573; *J. Iron Steel Inst.*, 1890, i, 38; *Compt. rend.*, 1890, **110**, 242, 346.

[13] *Z. physikal Chem.*, 1899, **30**, 385, 413.

of his teaching to alloys other than those of iron was made by Heycock and Neville in their study of the copper-tin alloys, in which the method of quenching from determined temperatures was introduced as a method of research.[1] The same paper also contains photomicrographs which represent the highest degree of accuracy and technical perfection then attained. The application of microscopical methods to alloys other than those of iron was at first confined to a few alloys, such as the brasses and the alloys of gold,[2] but its subsequent development has been very rapid. The school of metallographers founded in Paris by Osmond and Le Chatelier contributed largely to the advancement of the study. In 1901 a number of memoirs dealing with the structure and constitution of alloys, most of which had previously appeared in the *Bulletin de la Société d'Encouragement*, were collected in a volume which had a great influence in extending the knowledge of metallographic methods and results.[3] In England the Alloys Research Committee, under the guidance of Roberts-Austen, conducted experiments the results of which were embodied in an important series of reports from 1891 onwards.[4] The work of the committee was transferred to the National Physical Laboratory in 1904, and was actively continued, being until 1931 under the direction of W. Rosenhain.[5] Two disciples of Sorby, J. E. Stead and J. O. Arnold, were chiefly responsible for the application of metallographic methods in the steel industry.

In the year 1903 a memoir by G. Tammann appeared,[6] the first of a long series of contributions from the Göttingen laboratory. These included a survey of a large number of binary metallic systems, the object being to establish regularities between alloys of different metals. The materials were often impure, and the experimental methods were not comparable with those of Heycock and Neville, so that the diagrams then put forward have mostly needed much alteration on later revision, but the work stimulated interest in alloy systems, and soon included valuable studies of the properties of metals.

The further progress of metallography will be dealt with in greater detail in the chapters allotted to its respective departments. Its

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[1] *Phil. Trans.*, 1902, **202**, A, 1. This method had been employed in the study of steels by H. M. Howe in 1893, *Trans. Amer. Inst. Min. Eng.*, **23**, 466.

[2] G. Guillemin, *Compt. rend.*, 1892, **115**, 232; G. Charpy, *ibid.*, 1893, **116**, 1131; 1895, **121**, 494; 1896, **122**, 670; F. Osmond and W. C. Roberts-Austen, *Phil. Trans.*, 1896, **187**, A, 417; J. O. Arnold and J. Jefferson, *Engineering*, 1896, **61**, 176; T. Andrews, *ibid.*, 1898, **66**, 411, 541, 733; 1890, **67**, 87; H. Le Chatelier *Bull. Soc. d'Encourag.*, 1896, [v], **1**, 559; J. E. Stead, *J. Soc. Chem. Ind.*, 1897, **16**, 200, 506; 1898, **17**, 1111; H. Behrens, "Das mikroskopische Gefüge der Metalle u. Legierungen," Leipzig, 1894.

[3] "Contribution à l'Étude des Alliages," Paris, 1901.

[4] *Proc. Inst. Mech. Eng.*, 1891, 543; 1893, 102; 1895, 238; 1897, 31; 1899, 35; 1901, 1211 (W. Campbell); 1904, 7 (W. Gowland).

[5] See H. C. H. Carpenter, R. A. Hadfield, and P. Longmuir, *Proc. Inst. Mech. Eng.*, 1905, 857; H. C. H. Carpenter and C. A. Edwards, *ibid.*, 1907, 57; W. Rosenhain and F. C. H. Lantsberry, *ibid.*, 1910, 119; W. Rosenhain and S. L. Archbutt, *ibid.*, 1912, 319.

[6] *Z. anorg. Chem.*, 1903, **37**, 303.

growth has been so rapid as to require special organs to serve for the collection and comparison of the results obtained by workers in different countries. The *Metallographist*, established in America as an international medium in 1898, continued to serve this purpose until 1903, when it became merged in a publication devoted to the iron and steel industries. Another central organ, the *Internationale Zeitschrift für Metallographie*, appeared from 1911 till 1918, publishing papers in English and French as well as German. The attempt to found an international journal has not been repeated. English researches have mainly appeared in the *Journal of the Iron and Steel Institute* (founded 1869), the *Journal of the Institute of Metals* (1908), and the *Transactions of the Faraday Society* (1903). In Germany the *Zeitschrift für anorganische Chemie*, *Stahl und Eisen*, *Archiv für Eisenhüttenwesen* (1927), *Zeitschrift für Metallkunde*, *Metallwirtschaft*, and *Mitteilungen des Kaiser Wilhelm Instituts für Eisenforschung* (1920) have been the principal media. In the United States the *Transactions of the American Institution of Mining and Metallurgical Engineers* contain much of the published work,[1] and the American Society for Steel Treating (1920), the title of which was altered in 1934 to that of the American Society for Metals, issues *Transactions*, in which many important papers on metallography appear. In France there is only one principal organ, the *Revue de Métallurgie* (1904), and there are several Russian journals. The *Science Reports of the Tôhoku University* contain a large proportion of the Japanese work. It is characteristic of metallographic studies, however, that material has frequently to be sought in periodicals devoted to chemistry, physics, crystallography, engineering, geology, or other allied subjects, and this fact makes it essential that the relevant literature should be thoroughly abstracted. Very comprehensive abstracts are issued by the Institute of Metals and by the Iron and Steel Institute.

Three methods of investigation, the thermal, the microscopical, and the X-ray, are of primary importance in the study of metallography. When suitably applied and combined, they are capable of revealing the principal facts concerning the equilibrium of the components. All other methods, although valuable in themselves, and sometimes indispensable, must be regarded as subsidiary to these three in the range of their applicability. These methods will therefore be discussed in detail, a shorter account being given of the investigations dealing with the physical properties, such as density, electrical conductivity, and electrolytic potential, and with the chemical behaviour of alloys. It will then be shown how the experimental results are combined with those of the X-ray method to provide a knowledge of the internal constitution of alloys and of the changes which they may undergo with temperature and with time, taking into account modern views as to the relations of atoms to

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[1] Since 1934 the principal papers have been published in advance as *Metals and Technology*.

one another in the solid state. The behaviour of alloys under mechanical stress producing deformation is another important department of metallography, with a history of its own. Lastly, short accounts of the metallography of the most important technical alloys will be given as concrete illustrations of the methods described.

It has been found impracticable, for reasons of space, to include tables of the known systems, such as were given in previous editions, but metallographic literature is well indexed, and a given system is easily traced by means of the collective indexes now issued by many scientific institutions concerned with chemistry, physics or metallurgy.

Several volumes of critical descriptions of metallic systems, with equilibrium diagrams, were published from 1909 onwards, but these compilations have been superseded by the very thorough and complete critical review of binary systems by M. Hansen, " Der Aufbau der Zweistofflegierungen " (Berlin, 1936). The alloys of iron are dealt with in a series of volumes, " Alloys of Iron Monographs " (New York, 1932 onwards).

An extensive bibliography of papers dealing with the constitution of alloys, including ternary and more complex systems as well as binary alloys, has been prepared by J. L. Haughton (Institute of Metals, 1942; Supplement, 1944).

CHAPTER II.

THE DIAGRAM OF THERMAL EQUILIBRIUM.

Of the methods of metallographic investigation enumerated in Chapter I, that which is known as thermal analysis must be regarded as the foundation of all the others. It is rarely possible to interpret correctly the results of microscopical or other investigations without some knowledge of the diagram of thermal equilibrium, which shows what phases may be expected to be present in an alloy of given composition under given conditions of cooling. In the establishment of this diagram thermal analysis usually has to be supplemented by microscopical and X-ray examination, or by dilatometric, magnetic, electrical, or other methods of study to be described later, but the fundamental importance of the thermal method demands for it the first place in a work on metallography.

The basis of the diagram of thermal equilibrium is the freezing-point curve, the co-ordinates of a point on which are the composition of the alloy and the temperature at which crystallization begins when the fused alloy is cooled. In the older metallographic investigations this was the only curve determined.[1] But the work of Roozeboom [2] showed that the complete thermal diagram comprises not only the freezing-point curve, or "liquidus," but also curves representing the composition of the solid separating from the fused alloy, and the transformations, if any, undergone by the constituents after solidification. It is in fact a graphical representation of the dependence of the number and nature of the phases possible to the system when in equilibrium, on the composition and temperature.

When a body, such as a crucible containing an alloy, is cooling by radiation without undergoing any change of state, the curve connecting its temperature with the time has a regular form, being exponential when the surroundings are at a constant temperature, and rectilinear when the temperature of the environment is progressively and regularly lowered. But this regularity disappears when the cooling involves a change of state, as in the freezing of a liquid. The continuous passage from the liquid to the glassy or amorphous state, which characterizes many silicates and also such

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[1] See for example, H. Gautier, *Bull. Soc. d'Encouragement*, 1896, [v] **1**, 1293; C. T. Heycock and F. H. Neville, *Phil. Trans.*, 1897, **189**, A, 25; *Trans. Chem. Soc.*, 1897, **71**, 383.

[2] *Z. physikal. Chem.*, 1899, **30**, 385, 413.

substances as sealing-wax, is not met with in metals, which invariably have a definite freezing-point. In all cases hitherto observed, heat is given out in freezing. The first particles of solid which separate from the solution liberate a certain quantity of heat. Any further loss of heat by radiation, instead of reducing the temperature of the mass, causes a further separation of solid, and this process continues, the temperature remaining constant, until the whole of the substance has passed from the liquid to the solid state, after which the temperature again falls in a regular manner. If we represent the fall in temperature of a substance cooling without change of state by the curve A in Fig. 1, the curve of a pure substance, freezing at constant temperature, will have the form shown at B (Fig. 2). This is an ideal curve, and owing to undercooling, to the inequality of temperature throughout the mass, and to other causes, the observed curves deviate more or less from the form represented. The nature of these deviations, and the means of deriving the ideal curve from the observations, will be discussed in Chapter XVIII. Neglecting these, and assuming ideal conditions, we have a discontinuous curve, the part *ab* representing the cooling of the fluid metal, the horizontal part *bc* the process of solidification, and the curve *cd* the cooling of the solid metal. The portion *cd* has a steeper slope than *ab*.

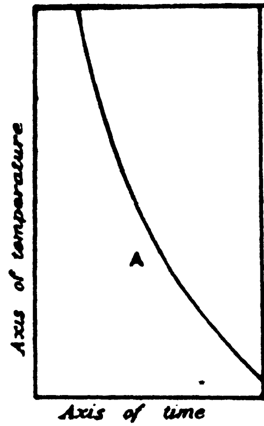

FIG. 1.—Cooling curve without change of state.

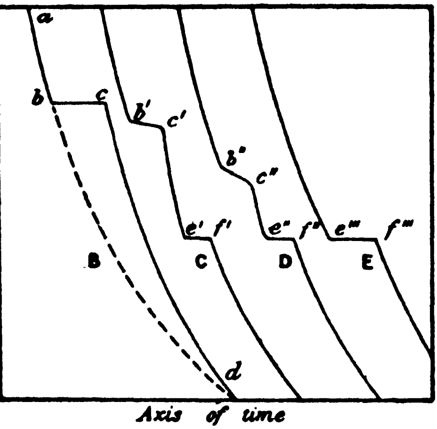

FIG. 2.—Cooling curves with change of state.

But if, instead of a pure metal, the crucible contains an alloy of two metals, the process of solidification follows a different course. We will assume, as the simplest case, that the two metals are perfectly miscible in the molten state, forming a homogeneous solution, and that each of them crystallizes in a pure state, uncontaminated by the other, and we will assume further that the quantity of the second metal, N, is small compared with that of the first, M. On cooling to a certain temperature, crystals of M separate from the solution. This temperature is not the freezing-point of the pure metal M, but a somewhat lower one, as the freezing-point of a substance under the conditions we have assumed is lowered by the addition of a second substance. We have now to see in what way this lowering proceeds, as the quantity of the second substance is progressively increased. In Fig. 3 the vertical axis is that of temperature; the horizontal axis represents the composition of successive mixtures. It is usual to express this composition as a percentage. We then represent the proportion of the second metal present by figures from 0 to 100. At the origin of the axes we have the pure metal M; so that the percentage of the metal N at that point is zero. At the right-hand limit of the diagram we have the pure metal N, which is then expressed as 100 per cent. It is often convenient, especially when dealing with the theoretical interpretation of the diagram, to express the composition of the alloy in terms of atoms or molecules. In that case the points on the axis of abscissæ represent the atomic or molecular composition; that is, the number of atoms or molecules of the second metal present in 100 atoms or molecules of the mixture. Atomic compositions will be generally employed in the sequel. The percentage of M is of course found in all cases by subtracting that of N from 100.

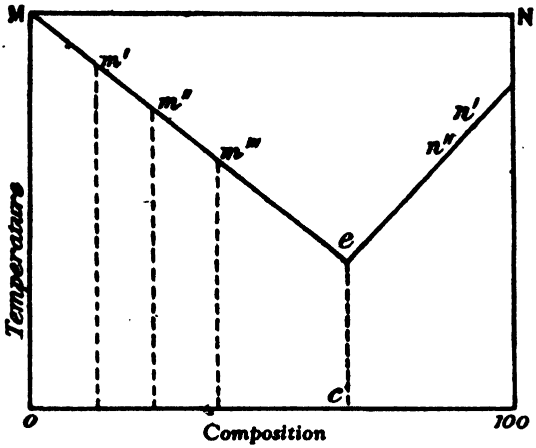

FIG. 3.—Freezing-point curve.

Neglecting for the present the rest of the cooling curve, and considering only the temperature at which crystallization begins, the effect of adding a small quantity of the metal N is to depress this temperature from *m* (the freezing-point of pure M) to *m′* (Fig. 3). Further successive small additions of N lower the initial temperature of crystallization still more, for example, to *m″* and *m‴*. In exactly the same way, if *n* be the freezing-point of the pure metal N, successive small additions of M successively lower the temperature at which solidification begins to n', n'', and n'''. If in Fig. 3, therefore, the abscissæ are taken to represent the proportions of M and N in the fluid mixtures and the ordinates the temperatures at which the first particles of solid separate on cooling, these temperatures lie on two curves (represented for the sake of simplicity as straight lines) sloping downwards from *m* and *n* respectively. A point, *e*, must consequently exist at which these two curves intersect. The alloy corresponding with the composition *c*, found by dropping a perpendicular from *e* upon the concentration axis, has the lowest initial freezing-point of the whole series. It is hence known as the *eutectic* alloy (Greek εὔτηκτος, easily-melting, from εὖ + τήκ-ειν), or simply *eutectic*, and the point *e* is called the *eutectic* point, the introduction of these convenient terms being due to Guthrie.

Returning now to the cooling curves of individual alloys, represented in Fig. 2, the point at which the curve changes its direction, owing to the development of heat on solidification, is lowered by the addition of the second metal from *b* to *b'*. The portion of the curve which represents the passage from the liquid to the solid state, however, is no longer horizontal, as *bc*; that is, the solidification of the mass no longer takes place at constant temperature. For the separation of the first crystals of the metal M alters the composition of the part remaining fluid, which is now richer in N than before. Referring to Fig. 3, it will be seen that the separation of crystals from such a mixture takes place at a temperature lower than *m'*. Consequently, as the metal M is withdrawn from the molten alloy by crystallization, the mother-liquor becomes progressively richer in N, and the temperature at which it can deposit more crystals progressively sinks. This gives to the part *b'c'* of the cooling curve C (Fig. 2) the sloping form indicated. For alloys containing more and more of the second metal N, the slope of the cooling curve becomes steeper and steeper, as in D. The change in direction at the point *b'* or *b''* being less than at *b*, the temperature of initial solidification becomes more difficult to determine as the proportion of N in the alloys increases.

In all these cases, as M is withdrawn from the molten mass, a point must be reached at which the mother-liquor has the composition and temperature represented by the eutectic point *e*. In order to determine what happens at this point, it will be convenient to consider the freezing-point curve (Fig. 3) from a somewhat different standpoint. The left-hand branch of the curve, *me*, may be considered as a solubility curve, since it represents the temperatures at which solutions of M in N become saturated with respect to M. In like manner, the right-hand branch represents the temperatures at which solutions of N in M (for in alloys either metal may be regarded in turn as solvent or as solute) become saturated with respect to N. Now, at the eutectic point *e*, being the point of intersection of the two solubility curves, the solution is simultaneously saturated with

M and N. Should crystals of M separate, it at once becomes supersaturated with respect to N, and equilibrium can only be restored by the separation of crystals of N. The metals M and N therefore crystallize together, the temperature remaining constant until the whole of the mass has solidified. This constancy of freezing-point is characteristic of eutectic mixtures.

In an alloy with the initial freezing-point *m'*, containing only a small quantity of the metal N, the greater part will have solidified before the eutectic point is reached. The amount which will solidify at the eutectic temperature is therefore very small, and will be represented by a very short horizontal portion of the cooling curve, as at *e'f'* in the curve C (Fig. 2). As alloys richer in N are examined, this horizontal portion becomes more strongly marked, as in D. Finally, an alloy having exactly the eutectic composition solidifies completely at constant temperature, so that its cooling curve has the form E. When the proportion of N in the alloys is further increased, so that the crystals which separate first are those of the metal N, the length of the eutectic horizontal again decreases, becoming less and less as the composition of the alloy approaches the pure metal N.

The time taken for the eutectic mother-liquor to solidify, that is, the length of the lower horizontal portion of the cooling curve, may be considered as proportional to the quantity of eutectic present, the conditions of cooling of all the alloys being assumed to be identical. These "eutectic times" may be plotted as ordinates against the composition of the alloys as abscissæ, as in the lower part of Fig. 4. The intersection of the two branches would, if they were straight lines, give the eutectic composition, since it indicates the maximum time of eutectic solidification. We owe this use of time-composition curves to Tammann.[1] The device gave useful service in the early days of metallography, but is now obsolete.

The exact position of the two branches of the freezing-point curve now having been determined, the remainder of the diagram may be constructed. It must be remembered that any point on this diagram represents an alloy at a definite composition and at a definite temperature given by its co-ordinates. Since the cooling curves of all mixtures of M and N show an arrest at a constant temperature, the eutectic temperature, a line may be drawn across the diagram from C to D (Fig. 4, upper part) through the eutectic point E, and parallel with the axis of composition. This line represents the solidification of the eutectic mother-liquor, and is called the *eutectic horizontal.* A vertical line from E to F separates those alloys which contain an excess of the metal M over the eutectic proportion from those which contain an excess of N.

Assuming that the alloys are not heated to so high a temperature as to produce an appreciable amount of metallic vapour, any alloy

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[1] *Z. anorg. Chem.*, 1903, **37**, 303; 1905, **45**, 24; 1905, **47**, 289.

the temperature and composition of which is represented by a point lying above the freezing-point curve AEB is in a liquid state. Points on AE or EB represent the beginning of crystallization of the metals M and N respectively. An alloy represented by a point within the triangle ACE consists of crystals of M, together with a still liquid mother-liquor. In the same way the triangle BDE encloses mixtures of N with mother-liquor. All alloys below the line CD are solid and are composed of the two solid metals. If to the left of the line EF, they consist of crystals of M together with the eutectic mixture; if to the right, of crystals of N + eutectic.

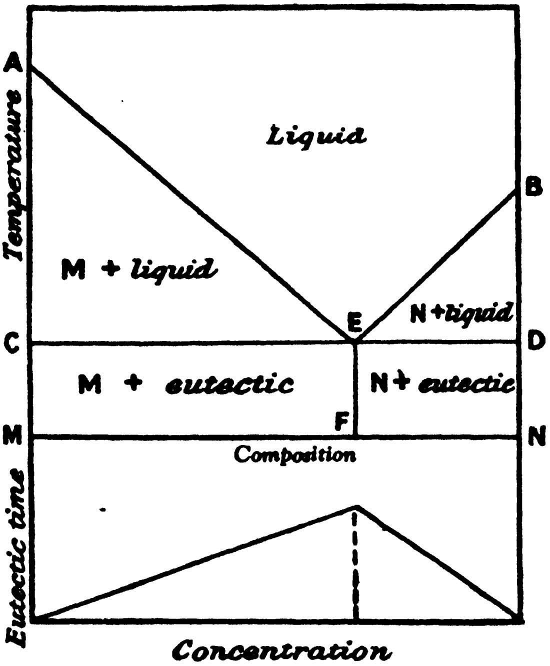

FIG. 4.—Thermal analysis, simplest case.

ATOMIC COMPOSITION.

As mentioned above, it is frequently necessary to express the composition in the form of the relative number of atoms in 100 atoms. The atomic percentage may be calculated from the percentage by weight in the following manner :—

If p and $(100 - p)$ are the percentages of the metals M and N respectively, a and b their atomic weights, and x and $(100 - x)$ the atomic percentages in the mixture, then

$$x = \frac{100p}{p + \frac{a}{b}(100 - p)},$$

and conversely

$$p = \frac{100x}{x + \frac{b}{a}(100 - x)}.$$

Since the calculation of the atomic proportions of each alloy examined is very tedious, it is usual to make the calculation for three or four percentages only, and then to plot the atomic percentages found against the percentages by weight, to draw a smooth curve through the points, and to find the composition of the remaining alloys of the series by graphical interpolation.

The error of this simple method is large when the atomic weights of the two metals differ widely, and some more accurate method is needed. The above equations may be rearranged, giving

$$\frac{x}{100 - x} = \frac{a}{b}\left(\frac{p}{100 - p}\right).$$

Tables have been constructed,[1] giving the values of $\log \frac{x}{100 - x}$ for steps of 0·1 per cent. over the whole range, allowing of interpolation to 0·01 per cent. A second table gives the values of $\log \frac{a}{b}$ for a large number of pairs of metals likely to be required, whilst the value for any other pair may be easily computed. It is only necessary to find the value of $\log \frac{x}{100 - x}$ corresponding with the percentage, either weight or atomic, which it is required to convert, and to *add* the value of $\log \frac{a}{b}$ if the conversion is from atomic to weight per cent., or to *subtract* it in the converse case. The result is the value of $\log \frac{p}{100 - p}$ [*] corresponding with the percentage required, which is then found by referring again to the first table. For percentages of the element a less that 0·3 it is better to make a direct calculation, the accuracy of the differences in the table being insufficient.

THE EUTECTIC ALLOY.

The fact that with many pairs of metals it is possible to prepare one alloy which has a freezing-point lower than that of any other member of the series has long been known, and was made use of in

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[1] C. S. Smith, *Amer. Inst. Min. Met. Eng.*, 1933, Contrib. 60.

[*] Or $\log \frac{x}{100 - x}$, as the case may be.

the preparation of the so-called "fusible metals." The production of a liquid by mixing a solid salt with solid ice in "freezing mixtures" was also well known.[1] As far back as 1864 Rüdorff[2] gave the correct explanation of the production of freezing mixtures, showing that the point of minimum temperature thus obtained was the intersection of the curve of separation of ice from salt solutions with that of the solubility of salt in water. The fact that metals showed a similar behaviour, so that on mixing two solid amalgams a liquid amalgam might be produced with considerable lowering of temperature, in complete analogy with freezing mixtures, had been observed by Döbereiner in 1824.[3]

The freezing-points of a very extensive series of salt solutions were investigated from this point of view by Guthrie.[4] Unfortunately, however, in spite of the work of Rüdorff, mentioned above, and of de Coppet,[5] the constancy of composition and freezing-point and the characteristic appearance of the mixture of minimum freezing-point led Guthrie to regard it as a combination of the salt with water, stable only below 0°, to which he gave the name of cryohydrate. In his later investigations the complete resemblance between the behaviour of cooled salt solutions, alloys, and mixtures of fused salts was shown, and the word "eutectic" was introduced.[6] The view that the cryohydrate was a chemical compound had been combated in the meantime by Pfaundler,[7] but was long popular. From the fact that cryohydrates always contain a large quantity of water in proportion to that of the salt, it is usually possible to find a formula of a hydrate to represent its composition approximately. In alloys and mixtures of fused salts in which the constituents are present in more nearly equal proportions, the deviation from a simple molecular ratio is often very marked, and the composite nature of eutectics was consequently more readily admitted. Even here the occasional approach of eutectic alloys to simple formulæ led to their being regarded as compounds. A typical case is that of the eutectic alloy of copper and silver, which was long known as Levol's alloy[8] and regarded as a compound having the formula Ag_3Cu_2.[9]

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[1] For the earlier history of freezing mixtures, see C. G. von Wirkner, "Geschichte und Theorie der Kälteerzeugung," Hamburg, 1897. The earliest quantitative measurements are those of R. A. F. de Réaumur, *Mém. Acad. Sci.*, 1734, 9.

[2] *Pogg. Ann.*, 1864, **122**, 337.

[3] *Schweigg. J.*, 1824, **42**, 182.

[4] F. Guthrie, *Phil. Mag.*, 1875, [iv], **49**, 1, 206, 266; 1876, [v], **1**, 49, 354, 446; 1876, [v], **2**, 211; 1878, [v], **6**, 35, 105.

[5] *Bull. Soc. Vaudoise Sci. Nat.*, 1871, [ii], **11**, 1.

[6] *Phil. Mag.*, 1884, [v], **17**, 462; *Proc. Phys. Soc.*, 1884-85, **6**, 124, 169.

[7] *Ber.*, 1877, **10**, 2223; see also Offer, *Sitzungsber. Wien. Akad. Sci.*, 1880, **81**, 1058.

[8] A. Levol, *J. Pharm. Chim.*, 1850, [iii], **17**, 111.

[9] Certain regularities in the composition of eutectics have been described by A. Gorboff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1241. For an examination of this and other formulæ for eutectics, see C. H. Desch, *Trans. Faraday Soc.*,

From what has been said above, in discussing the thermal diagram, it will be seen that the eutectic is really a conglomerate of the two components. From the fact that its cooling curve has the same form as that of a pure substance, namely that of Fig. 2, E, and that the crystallization of both components takes place simultaneously, so causing a very intimate mixture, the mistake of considering it as homogeneous is readily explained. It will be seen later, in treating of the microscopic and other properties of alloys, that the appearance of eutectic alloys is characteristic, and often quite unlike that of mere mechanical mixtures. The heterogeneity of cryohydrates was not definitely proved until 1895, when Ponsot[1] showed by microscopical examination that distinct crystals of ice, and of potassium permanganate, potassium dichromate, and copper sulphate, could be observed in the frozen cryohydrates of those salts. The same thing was shown for the cryohydrates of colourless salts by examination in polarized light. The term " cryohydrate " is now obsolete.

Discussion of the Phase Equilibrium.

The presentation of metallographic results in the language of the phase-doctrine is so frequent that it is desirable to discuss the simple case already examined, from this point of view. It is outside the scope of this work to set forth the principles of the phase rule, which have been fully explained in another work of this series.[2] Here it will be sufficient to take the rule itself for granted, referring elsewhere for its justification.

In all the cases to be considered in metallography, the *components* of the system are the pure metals. The *phases* are such homogeneous portions of the system as are separated from each other in space by bounding surfaces. Thus the vapour forms a single phase. There may be one or more liquid phases, for instance, a vessel containing mercury, water, and oil shows three coexistent liquid phases, separated from one another by definite bounding surfaces. Amongst alloys the system lead-zinc affords an example of two separate liquid phases. The various types of crystals which may be present in solid alloys also constitute distinct phases. The number of *degrees of freedom* of a system is " the number of the variable factors, temperature, pressure, and concentration of components, which must be arbitrarily fixed in order that the conditions of the system may be perfectly defined " (Findlay).

The phase rule now states that, if p be the number of phases,

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1910, **6**, 160 ; D. Stockdale, *J. Inst. Metals*, 1930, **43**, 193. A further attempt to establish regularities has been made by D. Stockdale, *Proc. Roy. Soc.*, 1935, **152**, A, 81.

[1] *Bull. Soc. Chim.*, 1895, [iii], **13**, 312.

[2] " The Phase Rule," by A. Findlay. In cases of doubt as to the interpretation of this rule reference should always be made to the classical work of Willard Gibbs, in which the greatest care was taken to avoid ambiguity.

n the number of components, and f the number of degrees of freedom, then

$$f = n - p + 2$$

when the system is in equilibrium. Consequently, for a system of a given number of components, the greater the number of phases present the less is the variability.

A certain simplification may be introduced into most of the cases with which we have to deal in metallography. It is commonly permissible to neglect the vapour phase when constructing the freezing-point diagram, the volatility of most metals at their melting-points being small. Systems in which the vapour phase is important form a separate class. In the same way the equilibrium may be assumed to be reached under a constant pressure, that of the atmosphere, since the vessels in which the fusion is carried out are either open to the air or communicate with vessels in which the pressure is that of the atmosphere. Pressure may therefore be omitted from the variables to be considered. The influence of pressure on freezing-point, and on the equilibrium of systems of two or more components, is of great scientific interest, but may be neglected in all but exceptional cases when dealing with metallic alloys. In the closely related subject of the formation of igneous rocks, however, this influence becomes a factor of the very highest importance.

It is usual to select, as one of the variables, the *composition* of the alloy, expressed either as grammes of one of the components in 100 grammes, or as the number of atoms of one of the components in 100 atoms of the alloy. Strictly speaking, however, the rule applies, as stated above, to the *concentration*, that is, to the weight or number of atoms of one component *in unit volume*. The substitution of composition for concentration is only justified if the system is such that no changes of volume occur unaccompanied by changes of weight.[1]

Most often, this is sufficiently near to the truth to make the error of using composition in place of concentration negligible, but neglect of this theoretical distinction has been the source of much confusion on the subject of the validity of the phase rule in certain special instances.

The effect of omitting all consideration of the vapour phase and of changes of pressure from the study of alloys is to reduce the number of variables to two, namely, temperature and composition. The conditions of equilibrium are then represented by the reduced formula

$$f' = n - p + 1,$$

and it is in this form that the phase rule is most usefully employed in the consideration of alloys.

Applying this rule to the case represented in Fig. 4, it will be seen that the whole area above the curve AEB represents mixtures of the

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[1] W. Hume-Rothery, *J. Inst. Metals*, 1926, **35**, 295.

two components containing only a single phase, the liquid, so that

$$f' = 2 - 1 + 1 = 2.$$

The system has, therefore, two degrees of freedom, or is said to be *bivariant*. This means that both temperature and composition may vary independently, without any alteration of the number of phases. Let the temperature now change so that a point on the curve AE or EB is reached. Solid begins to separate, that is, a new phase appears. There being now two phases, liquid and solid,

$$f' = 2 - 2 + 1 = 1;$$

the number of degrees of freedom is reduced to one, and the system is said to be *univariant*. In this case any change of temperature determines a corresponding change in the composition of the mother-liquor or liquid phase. Cooling the alloy causes a further deposition of the solid phase, which, being in this case the pure metal, does not vary in composition, and the part remaining liquid is correspondingly impoverished. For points on the curve AEB, therefore, to every definite temperature corresponds a definite composition, and fixing either temperature or composition immediately fixes the other variable.

At the eutectic point E, the two solid metals are simultaneously in equilibrium with the liquid. There are thus three phases present, and the number of degrees of freedom is therefore reduced to zero, or the equilibrium is only possible at a definite temperature and composition: the eutectic temperature and eutectic composition. The system is now said to be *invariant*. The two solid phases are deposited in a constant proportion, so that the composition of the mother-liquor, as well as its temperature, remains constant during the whole process of solidification.

It follows from this that the eutectic alloy is not to be regarded as a phase, but as an intimate mechanical mixture of two solid phases, in this case the two component metals. In the diagram, Fig. 4, therefore, the whole of the area CDNM represents mixtures of the two solid phases, and the line EF does not mark a boundary between distinct phases. From a micrographic point of view, however, it is necessary to make a distinction between the metal which has solidified as primary crystals along the line AE or EB, and that which has solidified, in intimate association with the second metal, at the point E. This is effected by treating the pure metals M and N and the eutectic alloy as three separate *micrographic constituents*, although the former are single phases, and the latter a conglomerate of two phases. The area CEFM then represents mixtures of primary crystals of M with the eutectic, and EDNF mixtures of primary crystals of N with the eutectic, and this distribution of phases is indicated in the diagram.

The relative proportions of the several phases present in any alloy of any given composition at a given temperature are readily determined from the diagram. In Fig. 5 the upper part of Fig. 4 is repeated. The point *g* represents an alloy of which a part is still liquid, the remainder having solidified in the form of crystals of the pure metal M. It is required to find the proportion of solid in the mixture, and the composition of the still liquid portion. A horizontal line drawn through *g* cuts the freezing-point curve AE at *r*, and the vertical axis at S. The solid phase being, by hypothesis, the pure metal, its composition is represented by S. The composition of the liquid phase is given by the point *r*, from which the percentage of the metal M in the liquid is found by dropping a perpendicular on to the composition axis at *x*. The alloy represented by the point *g* therefore consists of crystals of the metal M and a liquid portion which contains M*x* per cent. of N and N*x* per cent. of M.

If the temperature and composition of the original liquid alloy were represented at a particular moment by the point *o*, then on cooling, the curve AE is cut at the point *p*. At this temperature the composition of the liquid phase is unchanged. As crystals of M separate, however, the point representing the composition of the liquid phase moves along the line AE from *p* to *r*. A simple geometrical consideration shows that the solid and liquid phases are now respectively present in the ratio of *gr* to S*g*. Since the liquid phase must ultimately reach the eutectic composition represented by the point E, the relative proportions of solid and liquid respectively on reaching the eutectic temperature are given by the ratio *h*E : C*h*. Since the eutectic solidifies as a distinct micrographic constituent it is convenient for many purposes to express the composition of the completely solidified alloy in terms of the percentage of crystals of the free metal M or N and of the eutectic. For this purpose a simple graphical method introduced by Sauveur[1] is very convenient. The

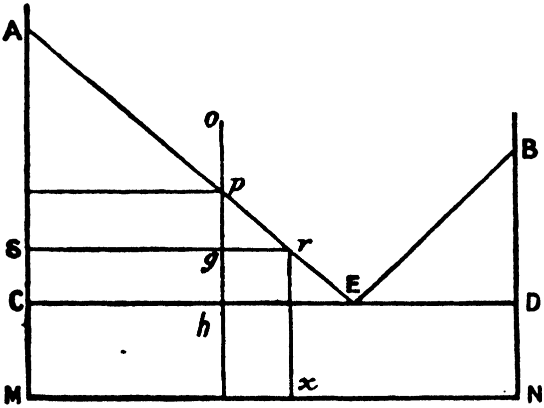

FIG. 5.—Ratios of solid and liquid phases.

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[1] *Metallographist*, 1898, 1, 27.

vertical axis (Fig. 6) is divided into 100 parts, and the horizontal axis represents the percentage of the two metals in the alloy. The eutectic composition being, as before, E, straight lines are drawn from M to E and from E to N. An alloy of the composition *x*, that is, containing M*x* per cent. of the metal N and N*x* per cent. of M, will in the solid state be made up of *xy* per cent. of eutectic and *yz* per cent. of crystals of M.

When using binary thermal diagrams in metallography it is only rarely necessary to refer to the phase rule. In the study of equilibria in ternary and more complex systems, however, the relations between the phases are often complicated, and it is useful to check the diagram by examining whether the several boundary lines and points of intersection are compatible with the phase rule. Any incompatibility indicates that the diagram has been incorrectly constructed. The relation of the phase rule to practical metallography is something like that of formal logic to scientific discovery. No new scientific fact is ever likely to be discovered by the aid of formal logic, but it is sometimes useful to state a process of scientific reasoning in syllogistic form as a means of detecting fallacies. In a similar way, fallacies in the expression of equilibria in complex systems may be detected by applying the strict logic of the phase rule.

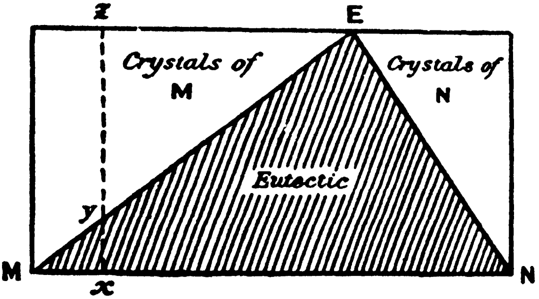

FIG. 6.—Micrographic constituents of a simple binary system.

The limitations of the rule must always be borne in mind. It is based on thermodynamical principles, and applies only to conditions of equilibrium. The metallographer has constantly to deal with systems which are not in equilibrium, and to study the processes which occur in the course of departure from or approach to equilibrium. Moreover, the rule takes no account of the arrangement of atoms within a phase, whilst succeeding chapters will contain many examples of changes of great theoretical and practical importance, occurring within a phase without altering its mean composition. Even when, as in the process of age-hardening, a new constituent makes its appearance in a state of minute subdivision, sometimes even in the form of minute two-dimensional nuclei, it is impossible to regard these as a separate phase, separated from neighbouring phases by a definite boundary. The conception of a phase breaks down under such conditions, and instead of attempting to devise a nomenclature which will cover such special cases it is better to regard them as lying outside the scope of the phase rule. Similar difficulties arise when masses of small dimensions are considered. The vapour pressure of a liquid or solid varies with the radius of curvature, an effect which is naturally only perceptible in very small masses, whilst the ratio of the numbers of two kinds of atoms in a solid phase changes when the crystal becomes so small that the surface is large in proportion to the number of atoms. The phase rule is inapplicable under such conditions, but no practical difficulty arises, as such problems are readily dealt with on atomic principles.

THE MELTING-POINT.

We may now consider what happens when a solid alloy of this type is heated. If the alloy has exactly the eutectic composition, the whole of it will liquefy at the eutectic temperature, although this is much below the melting-point of either of the component metals. If, on the other hand, it consists of a mixture of crystals of one of the metals with the eutectic, only the eutectic portion will liquefy at this temperature. The temperature will then rise, the now fluid eutectic acting as a solvent for the solid crystals, and the composition of the liquid changing in a way which may be represented by a point travelling upwards along the solubility curve, until the last crystals are dissolved at a temperature which is the same as that at which crystallization first began on cooling. The course of events on melting is in fact the reverse of that on freezing, and the heating curve is the reverse of the cooling curve, if we suppose the rate of influx of heat to be sufficient to maintain equilibrium throughout the process. In practice, however, it is more difficult to ensure equilibrium during melting than during freezing.

Since the eutectic alloy is only a conglomerate of two phases, it would seem that a sufficiently intimate mixture of the two metals should melt at the eutectic temperature, and such is found to be the case. With mixtures of coarse particles, such as filings, the contact is not sufficiently intimate, and melting does not take place to an appreciable extent until a somewhat higher temperature has been reached. This point has been investigated experimentally for mixtures of lead and tin.[1] The eutectic alloy of this series melts at 180°, and a mixture of the finely powdered metals, the particles of which did not exceed 0·15 mm. in diameter, melted exactly at that temperature when slowly and regularly heated. When, however, the particles varied in diameter from 0·15 to 0·52 mm., the melting-point rose to 183°, and coarser particles required a still higher temperature to produce fusion. A similar phenomenon, of some practical importance,

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[1] C. Benedicks and R. Arpi, *Metallurgie*, 1907, 4, 416.

has been stated to occur in grey cast iron.[1] The graphite, which is one of the constituents of the eutectic, collects together during solidification in the form of comparatively coarse plates. These plates are only slowly dissolved on heating by the metal in immediate contact with them, with the result that the melting-point may be as much as 70° higher than the freezing-point Another explanation is, however, possible.

Compression of the particles will evidently increase the intimacy of contact, and a compressed mixture of metals is therefore more likely to melt at the eutectic temperature than one mixed by stirring or shaking only. The fact that fusible metals, such as Wood's and Rose's alloys, which melt in hot water, can be formed by subjecting their components to a pressure of 7500 atm.,[2] does not prove, as was at first supposed, that a reaction occurs between the metals in the solid state, as the result may be explained as being due to the bringing of the particles into such close contact by pressure that equilibrium is readily attained on heating to the eutectic temperature.

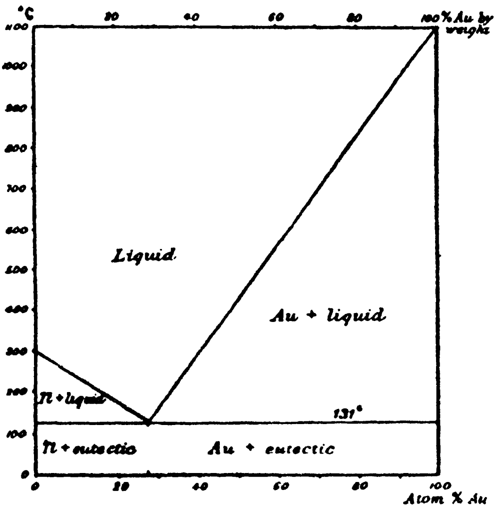

FIG. 7.—Thallium and gold.

Two typical diagrams for eutectiferous series of alloys are shown in Figs. 7 and 8. Fig. 7 represents the alloys of gold and thallium,[3] which approach very closely the ideal condition of complete immiscibility in the solid state. The two branches of the curve are very nearly straight lines, indicating a very simple constitution of the solution.

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[1] P. Goerens, *Metallurgie*, 1907, 4, 137.
[2] W. Spring, *Ber.*, 1882, 15, 595.
[3] M. Levin, *Z. anorg. Chem.*, 1905, 45, 31.

The second example is that of the alloys of silver and lead, the equilibrium diagram of which is represented in Fig. 8.[1] The form of the freezing-point curve in this case is of great practical importance, since on it depends the well-known Pattinson process for the desilverization of lead. The eutectic point lies, as will be seen from the diagram, very near to the lead end of the curve, the eutectic alloy containing only 4 atomic per cent. of silver, or 2·25 per cent. by weight. The silver branch of the curve is far from being straight, and has a point of inflection; the appearance is therefore different from that of the gold-thallium diagram, but the arrangement of the fields of phase-equilibrium is nevertheless the same. It is not certain whether the eutectic horizontal reaches exactly to the limits of the diagram, as assumed, but microscopical examination and the study of the cooling curves indicate that this must be very nearly true.

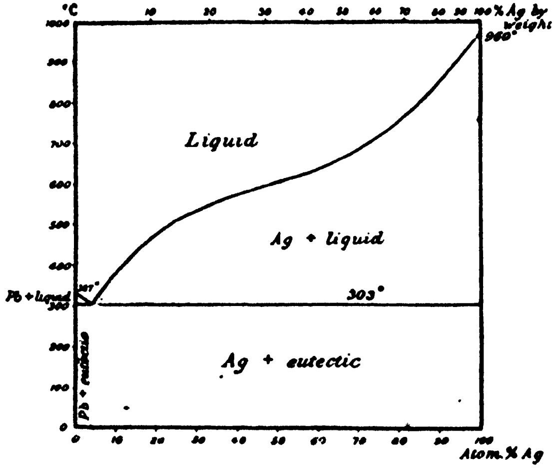

FIG. 8.—Lead and silver.

The object of the Pattinson process is the fractional crystallization of an extremely dilute solution of silver in molten lead. The lead, containing 0·009 per cent. of silver or more, is cooled until a certain proportion—for instance, seven-eighths—has crystallized, and the crystals are removed by means of a perforated ladle. The portion remaining liquid is then nearer to the eutectic composition than the original alloy, that is to say, it is richer in silver. The crystals collected are those separating on the left-hand branch of the curve in Fig. 8, and consist of practically pure lead. Since, however, a portion

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[1] The upper branches of the curve were determined accurately by Heycock and Neville (*Phil. Trans.*, 1897, **189**, A, 25). The complete diagram is drawn from the observations of K. Friedrich (*Metallurgie*, 1906, **3**, 396) and G. J. Petrenko (*Z. anorg. Chem.*, 1907, **53**, 200). All three sets of figures are in good agreement.

of the mother-liquor is always retained mechanically, it is necessary to remelt the crystals and to repeat the process. The liquid portions are also again partly frozen, until the final products are almost pure lead, containing at most 0·001 per cent. Ag, and an alloy of the eutectic composition (2·25 per cent. Ag by weight, or 4 atomic per cent.). Since this alloy solidifies at constant temperature, it is evident that the process of fractionation cannot be carried any further.

SOLID SOLUTIONS.

The component metals have so far been assumed to crystallize from the molten alloy in a pure state. More frequently the mutual solubility of the components which is evident in the liquid state also persists, although usually to a smaller extent, in the solid state. That is to say, the crystals of M which separate on cooling usually contain a greater or less quantity of N, and this not mechanically retained, but in a state of true solution. We may speak of true solution in solids whenever we find homogeneous crystals of two or more components, the composition of which may be varied continuously within certain limits. A " solid solution " (the term is due to van't Hoff) is therefore a single phase. Certain pairs of metals are isomorphous, that is, they crystallize together in all proportions to form homogeneous crystals, the properties of which vary continuously from one end of the series to the other. Others, although crystallizing in different forms, are each capable of crystallizing with a small quantity of the second metal, which is thus constrained to take up a crystalline form foreign to it. Roozeboom introduced the word " Mischkrystall " for a solid solution, both components of which are crystalline, and this term is now very generally used in German. The English rendering " mixed crystals " is not equivalent and is inappropriate, since it suggests to the mind rather a conglomerate than a single phase. For this reason the older term " solid solution " will alone be used in the present work.

It is probable that all metals should be regarded theoretically as mutually soluble, in however slight a degree, in the solid state, the complete insolubility considered in the preceding chapter being regarded as an ideal limiting case. The quantity held in solution is, however, frequently very small, although of great practical and theoretical importance (Chap. XIX.). When the solubility is too small to be recognized by thermal methods, microscopical and physical methods have to be used.

The different types of equilibrium in which solid solutions can co-exist with liquid alloys have been worked out by Roozeboom[1] and by Bruni.[2] Whereas Bruni used the temperature-concentration diagram, Roozeboom based his exhaustive study of the subject on the highly abstract principle of the thermodynamical potential.

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[1] H. W. Bakhuis Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 385.

[2] G. Bruni, *Rend. R. Accad. Lincei*, 1898, [v], **7**, ii, 138, 347.

Both authors arrived at very similar results. For the practical purposes of metallography, the method of the temperature-concentration diagram is more convenient and will be used exclusively.

The two component metals may be isomorphous, only one series of solid solutions being formed, their properties varying continuously from one end of the series to the other. It is easy to show that the freezing-point curve of such a series must be continuous. The points at which the direction of a freezing-point curve changes suddenly in direction, so that two intersecting tangents to the curve may be drawn at the same point, are *invariant* points, at which the number of co-existing phases, vapour being excluded, exceeds the number of components by one. A series of solid solutions, however, constitutes but a single phase, and since the only other phase present is the liquid alloy, the number of co-existing phases never exceeds two. By our simplified formula

$$f_1 = n - p + 1 = 2 - 2 + 1 = 1,$$

that is, the system always has a degree of freedom, and the freezing-point curve must be continuous.

Systems of this kind have been grouped by Roozeboom in three different classes, according as the freezing-point curve lies wholly between the freezing-points of the two components (Type I), or presents either a maximum (Type II) or a minimum (Type III). The first and third of these types are met with in alloys.

Type I.—The freezing-points of alloys of isomorphous metals frequently lie entirely between the freezing-points of the pure metals. There is then no alloy in the series which on freezing deposits crystals having the same composition as the liquid with which they are in contact. The liquid phase is always proportionately richer than the solid phase in that component, the addition of which lowers the freezing-point.

In Fig. 9 the two isomorphous metals melting at A and B respectively form a continuous series of solid solutions. We will assume that the freezing-point curve is concave to the concentration axis, as A*m*B. An alloy containing M*x* per cent. of the metal N and N*x* per cent. of the metal M will, on cooling from the molten state, be represented by a point travelling down *lm*. At the point *m* crystallization sets in. But in accordance with what has been said above, the crystals contain comparatively less of the metal M than does the liquid—they have a composition represented, let us suppose, by *n*. As freezing continues, the composition of the liquid is expressed by a point travelling down *m*A towards A, the solid phase being successively represented by points on a second curve, *np*A, which lies throughout its length to the right of A*m*B. Roozeboom has called the curve which represents the composition of the liquid phase the "liquidus," and that which represents the composition of the solid phase the "solidus." The solidus lies entirely below the liquidus, and since the two coincide at A and B, where both liquid and solid phases consist of the pure metal, the solidus must always be less concave or more convex towards the concentration axis than the liquidus.

When the temperature has fallen to *q*, the last of the alloy solidifies, and *mq* is called the "crystallization interval." But it will be seen that the last portions of the liquid had the composition *r*, and could not therefore deposit crystals of the composition *q*. It follows that the solid phase is only represented by *q* as regards its *average* composition, unless some further change occurs beyond those described above. The further change, in conditions of complete equilibrium, is one of diffusion in the solid phase. For example, the crystals deposited when the composition of the liquid phase has changed by an infinitesimal amount, say from *m* to *m′*, will have a composition represented by a point lying somewhat to the left of *n′*. But the first crystals deposited had the composition *n*, so that the solid phase can only become homogeneous, a condition necessary for equilibrium, by diffusion, the final result of which is the production of entirely homogeneous crystals of the composition *n′*. This readjustment by diffusion must take place at each stage in order that the solid phase may remain homogeneous. As diffusion in a solid is very slow in comparison with crystallization from a liquid, complete equilibrium is only reached if the cooling of the alloy through the solidifying range of temperature is extremely slow. This condition is rarely completely fulfilled in practice, and the crystals deposited from the molten alloy therefore fall short of complete uniformity of composition. It is possible, by heating the alloy for a long time at a temperature somewhat below the melting-point, to cause diffusion to take place, and such an "annealing" process is generally necessary to destroy the heterogeneous structure of solid solutions.

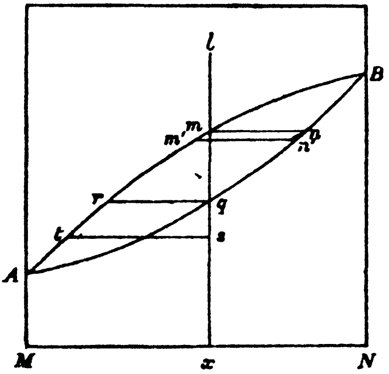

FIG. 9.—Solid solutions, Type I.

If we suppose that no diffusion whatever takes place in the solid state, the crystals will be composed of concentric layers of progressively changing composition. The first layer of crystalline matter deposited will have the composition *n* as before, but when the liquid of composition *m′* is solidifying there will be no diffusion to restore equilibrium, so that the composition of the new solid layer will lie slightly to the right of *n′*. The composition of successive layers of solid will then lie on a curve somewhat below the true solidus. Supposing that no diffusion whatever takes place, the condition that the last drop of liquid must have the same composition as the solid formed by its freezing can only be satisfied by a part of the alloy remaining liquid until the pure metal A is reached, this being the only point at which the liquidus and solidus curves touch. Should a limited amount of diffusion occur, the end of the solidification may be considered to be at some such point as *t*. The effect of imperfect equilibrium is to lengthen the range of temperature during which the alloy is solidifying, the interval in the case described being from *m* to *s* instead of from *m* to *q*. The effect is to exaggerate the distance between the liquidus and the solidus. In practice, the crystals obtained are heterogeneous, but less so than in the hypothetical case of entire absence of diffusion. The effect of such imperfect equilibrium on structure will be discussed in connection with the microscopical study of alloys.

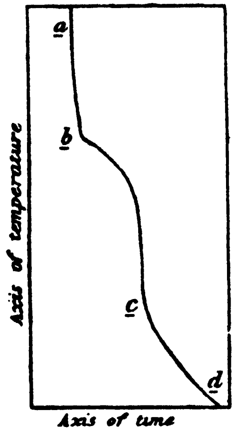

FIG. 10.—Direct cooling curve of solid solution.

Since the process of crystallization of a solid solution is a gradual one, extending over an interval of temperature, the cooling curve of such an alloy cannot have the same form as that of an alloy belonging to a eutectiferous series, such as those described above. The characteristic form is that shown in Fig. 10. The portion *ab* represents the cooling of the liquid alloy. The first separation of crystals at *b* is well marked, but the curve then assumes a rounded form, and the final solidification of the remaining mother-liquor, instead of producing a horizontal arrest-line as in the case of eutectiferous alloys, is only indicated by a slight change of direction at *c*, where the curve of solidification, *bc*, joins the cooling curve of the solid alloy, *cd*. This change of direction is difficult to observe, the two portions of the curve appearing to pass smoothly into one another. An improved method of plotting increases the distinctness of the break, but under the ordinary conditions of working, the determination of the solidus curve and of the interval of solidification is less accurate than the cther determinations needed in constructing a thermal diagram, and it is usually necessary to resort to quenching methods. The point is better marked on a heating curve.

Examples of complete isomorphism are most abundant among the metals of high melting-point, such as the platinum and iron groups, and gold, silver, and copper. The diagram of the alloys of copper and nickel (Fig. 11) is typical of such isomorphous pairs of metals. If the liquidus and solidus curves were to approach one another still more closely, they might be imagined to coincide, in which case the solid and liquid phase in equilibrium with one another at any temperature would be identical in composition. It is very improbable that this case ever occurs in alloys, and there are theoretical reasons for supposing it to be impossible.[1]

Type II, in which the freezing-point curve presents a maximum, has only been observed so far in organic optical isomerides, and not in alloys, although it may occur as a part of a more complex curve in metallic systems. The nature of the diagram will be readily understood from a comparison with Type III. The liquidus and solidus curves coincide at the maximum.

Type III.—The metals form a continuous series of solid solutions, the freezing-point curve passing through a minimum.

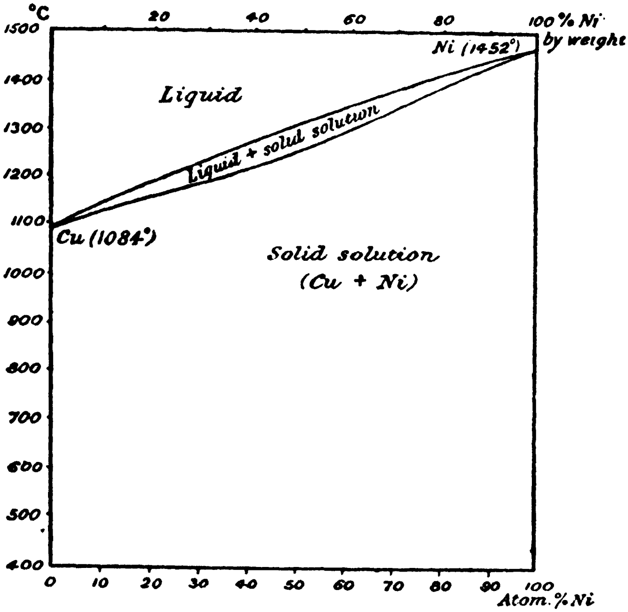

FIG. 11.—Copper and nickel.

This type may be illustrated at once by a concrete example, the alloys of copper and gold (Fig. 12). The freezing-point of each component is lowered by addition of the other, but there is no eutectic point, the liquidus curve being continuous throughout. Where it passes through a minimum the solidus and liquidus curves coincide, so that at that point the solid and liquid phases have the same composition. At all intermediate points on the curve the composition of the solid phase differs from that of the liquid with which it is in contact, the relation between the two being found by the method described on page 20. The remarks there made as to the effect of imperfect equilibrium apply in this case also.

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[1] J. J. van Laar, *Z. physikal. Chem.*, 1906, **55**, 435.

Since the alloy of minimum freezing-point solidifies at constant temperature, its cooling curve has a horizontal portion like that characteristic of a pure metal or a eutectic alloy. A mere determination of the liquidus would in fact suggest that the series was eutectiferous, the trough-like form of the curve near the minimum not being readily distinguishable from the intersection of two lines. A determination of the solidus curve, however, enables the two conditions to be distinguished with certainty. The eutectic horizontal is absent, the solidus taking the form of a continuous curve, convex throughout to the axis of concentration. As the accurate determination of the solidus is a matter of considerable difficulty, this is essentially a case in which the thermal and microscopical investigation should go hand in hand, since the absence of the characteristic eutectic structure, and the presence of homogeneous crystals of the solid solution at the minimum point, should be readily detected by the latter method. The determination of the electrical conductivity is also a most valuable aid in doubtful cases.

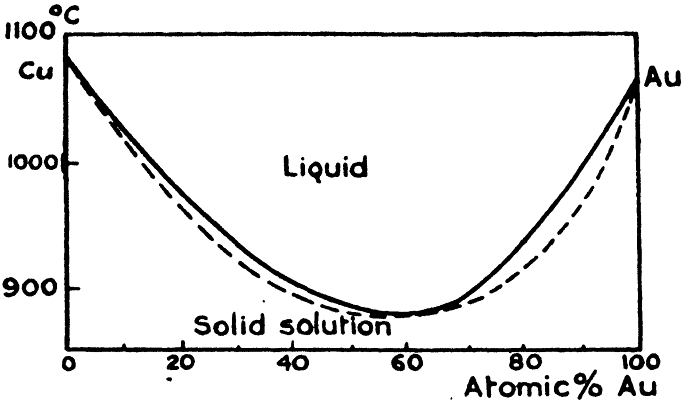

FIG. 12.—Copper and gold.

How necessary such a control may be is well seen in the instance of the alloys of copper and gold. The liquidus curve was determined by W. Roberts-Austen and T. K. Rose,[1] who regarded it as being composed of two branches meeting in a shallow eutectic trough, a conclusion which seemed to accord with micrographic evidence. They were unable, however, to observe any eutectic arrests on the cooling curves, or to determine any points on the solidus. A determination of both liquidus and solidus led to the conclusion that the curve is of the type just discussed, a continuous series of solid solutions being formed. Later investigations have shown that the solid solution undergoes remarkable changes at lower temperatures, which affect the microstructure of the alloys. These changes are discussed in Chapter XX.

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[1] *Proc. Roy. Soc.*, 1900, 67, 105.

The next case to be considered is that in which the two metals have only a limited reciprocal solubility in the solid state. If we compare a pair of isomorphous metals with two completely miscible liquids, such as alcohol and water, the alloys of the present type are comparable with a pair of liquids such as water and ether, of which each can dissolve a certain limited proportion of the other, so that all mixtures richer than the limiting value separate into two layers, consisting of saturated solutions of water in ether, and of ether in water respectively. In the same way certain pairs of metals may form two series of solid solutions, and any alloys falling between the limits of saturation must consist of a complex of two phases, each of which is a saturated solid solution.

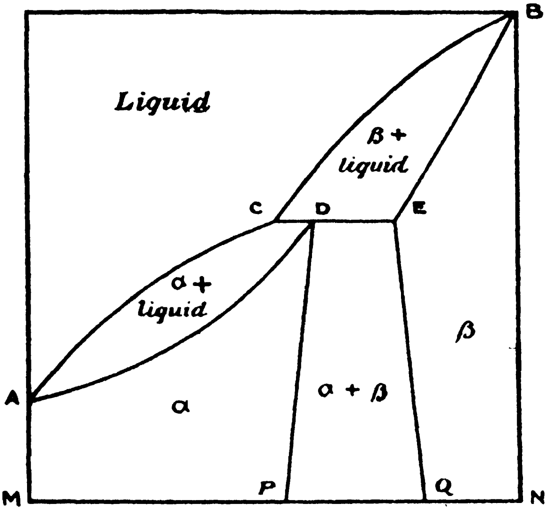

Fig. 13.—Solid solutions, Type IV.

In the first case (Roozeboom's Type IV) the two series of solid solutions meet at a transition point, as indicated in Fig. 13. The two branches of the freezing-point curve, AC and CB, have each a corresponding solidus, AD and EB respectively. At the temperature of the transition point C, there are two solid phases in simultaneous equilibrium with the liquid; C is therefore an invariant point, and the transition from one series of crystals to the other, indicated by the line CE, must take place at constant temperature, that is, CE must be horizontal. Such a transformation is called a peritectic transformation. Its mechanism is discussed on page 37. The arrangement of fields will be seen from the diagram. All alloys lying to the left of C solidify as crystals of the solid solution α, as in Type I. Similarly, alloys to the right of E form only crystals of the solid solution β. Alloys between C and D at first deposit crystals of β, but on cooling past the transition temperature these are converted into the stable form α. All alloys between D and E form, when solid, a complex of saturated α and β crystals, having the compositions D and E respectively. Such a complex is the exact analogue of a mixture of water and ether which has separated into two layers. Varying the composition of the alloy between the two limits D and E changes only the relative proportions of the two phases, without altering their concentration.

The lines DP and EQ have been drawn with a slight inclination from the vertical, since the solubility of one solid metal in another, like that of liquids, usually decreases with falling temperature, so that, sufficient time being given to establish equilibrium, the composition of the two saturated solid solutions, α and β, will change to a certain extent with the temperature. These changes will be discussed fully later. The simple case represented in Fig. 13 has an excellent representative in the series cadmium-mercury. The cadmium amalgams form two series of solid solutions, and the ordinates of the points of intersection are :

A	Pure Hg, — 38°
C	65 atom. per cent. Cd, + 190°
D	75 ,, ,, ,,
E	77 ,, ,, ,,
B	Pure Cd, + 322°.

The lines DP and EQ diverge at lower temperatures, the limits of the two solid solutions being at 25°, for instance, 65 and 79 atom. per cent. Cd respectively. It was only found possible to determine the liquidus curve by measurements with the thermometer, the thermal changes indicated by the other lines of the diagram being so small as to escape observation, hence it was found necessary to complete the investigation by studying other physical properties of the amalgams. The position of the solidus was in fact determined from measurements of volume in the dilatometer, and that of the lines DP and EQ from measurements of electrolytic potential.[1]

Liquidus and solidus curves of this type, although not often found representing a complete series, such as that of the cadmium amalgams, are of frequent occurrence when compounds are present, when they form only a part of the equilibrium diagram.

The next case (Roozeboom's Type V) occurs very frequently. Two limited series of solid solutions are now formed, between the limits of which a eutectiferous series of alloys occur (Fig. 14). The lettering corresponds with that of Fig. 13. The two branches of the liquidus now intersect at a eutectic point, C, at which the two

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[1] H. Bijl, *Z. physikal. Chem.*, 1902, **41**, 641. See also N. A. Pushin, *Z. anorg. Chem.*, 1903, **36**, 201 ; R. F. Mehl, *J. Amer. Chem. Soc.*, 1928, **50**, 381.

saturated solid solutions are at once in equilibrium with the liquid phase. The eutectic horizontal, DE, does not reach the limits of the diagram, as in the example considered on page 13, but stops short at the limits of saturation of the two series of solid solutions.

We will now consider what happens during the solidification of alloys of this series. A liquid alloy represented by the point *p* will, on cooling, deposit crystals of the solid solution α, and its cooling curve will be of the form shown in Fig. 10. A liquid alloy represented by *p′*, however, at first deposits crystals of α, and the composition of these crystals changes from *q* to D as the temperature falls. At the point D the α crystals are saturated, that is, they are incapable of taking up any further quantity of the second metal. The point C is then a eutectic point, at which the two phases D and E (saturated α and β crystals respectively) separate simultaneously. The cooling curve therefore differs from Fig. 10 in that the part *bc* is separated from *cd* by a horizontal portion corresponding with the solidification of the eutectic.

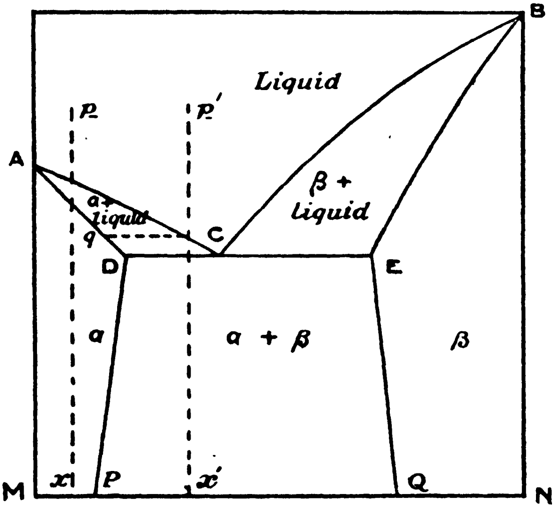

FIG. 14.—Solid solutions, Type V.

A good example of this type is furnished by the alloys of silver and copper. The freezing-point curve was accurately determined by Heycock and Neville,[1] who, however, did not fix the limits of the eutectic horizontal. The complete diagram is shown in Fig. 15.[2]

In the examples so far considered the only solid phases have been the pure metals or solid solutions in which one of the components

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[1] *Phil. Trans.*, 1897, **189**, A, 25.

[2] N. Ageew and G. Sachs, *Z. Physik.*, 1930, **63**, 293 ; N. Ageew, M. Hansen and G. Sachs, *ibid.*, 1930, **66**, 350 ; D. Stockdale, *J. Inst. Metals*, 1931, **45**, 127.

may be regarded as a solvent. It most often happens, however, that one or more intermediate solid phases are formed, so that the liquidus curve consists of more than two branches. This is sometimes due to the formation of a definite compound between the two metals, and such "intermetallic compounds" have been the object of much study.[1] They early attracted the attention of metallurgists and of physical chemists from their apparent disregard of the rules of valency, the formulæ of some of the most stable of them appearing arbitrary. Instances of doubtful interpretation will be excluded from the present simple treatment, and the nature of such compounds will be discussed later (Chap. XIX.).

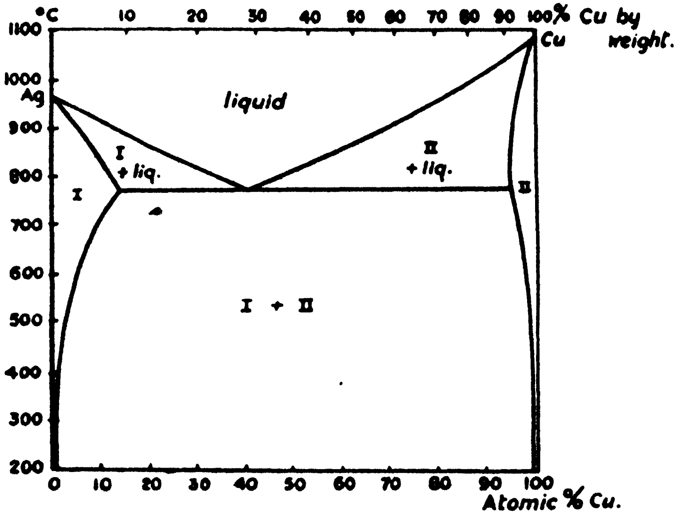

FIG. 15.—Silver and copper.

The simplest condition is that in which the intermetallic compound separates from the liquid in a pure state, without the formation of solid solutions. This is, again, only an ideal limiting condition. The equilibrium diagram may take one of two forms.

A. THE FREEZING-POINT CURVE SHOWS A MAXIMUM.

When the compound formed by the union of the two metals is so stable that it may be heated to its melting-point without decom-

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[1] The subject was reviewed by the writer in "Intermetallic Compounds" (London, 1914), but since that date the new knowledge of the arrangement of atoms and of electrons in alloys has led to new conceptions of the constitution of solid metallic phases, and it has become more difficult to define exactly an intermetallic compound. For the purposes of the present chapter the older conceptions will suffice.

position, it behaves similarly to a pure metal, and its freezing-point is depressed by the addition of either of the components. The freezing-point curve therefore shows a maximum corresponding with the composition of the compound. If the affinity of the one metal for the other be so great that the compound is formed with a large development of heat, this maximum may lie considerably above the freezing-point of either of the component metals. A conspicuous example of this is found in the amalgams of the alkali metals with mercury. Whilst the freezing-points of mercury, sodium, and potassium are respectively 38·8°, 97·6°, and 62·5°, the compounds $NaHg_2$ and KHg_2 solidify at 346° and 279° respectively.[1]

A compound such as $NaHg_2$, occupying a maximum on the freezing-point curve, melts to a liquid of the same composition as the solid. Fusion and solidification therefore take place at a constant temperature, and the cooling curve of the compound is in every respect like that of a pure metal. This being so, alloys containing as solid phases only the compound MN and one of its component metals, for instance M, may be considered as a binary system of the same type as those already discussed, consisting, that is to say, of two branches intersecting in a eutectic point. A second binary system is made up of alloys containing MN and N as solid phases. Two diagrams similar to Fig. 4 might be placed beside one another, the second descending branch starting from the point B. This would, however, give a sharp point to the summit representing the compound, and this is incompatible with equilibrium, the conditions of which demand that the tangent to the curve at such a point shall be horizontal. The flattening of the curve at the summit indicates that the compound is dissociated to some extent into its components in the liquid phase, the flatness of the curve increasing with increasing dissociation.

The form of curve which presents itself in practice is best illustrated by a concrete example. Fig. 16 has been constructed from the results obtained by three different observers for the alloys of magnesium and tin.[2] The curve rises to a very pronounced maximum at 66·7 atomic per cent. Mg, indicating the formation of a stable compound Mg_2Sn, melting at 783·4°, that is, considerably above the melting-point of either of the component metals. Two eutectic points occur, the solid phases Sn and Mg_2Sn being in equilibrium with the liquid phase at 210°, and the phases Mg_2Sn and Mg similarly at 565°. The middle branch of the curve is considerably rounded at the summit, indicating that in the fused compound a certain

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[1] A. Schüller, *Z. anorg. Chem.*, 1904, 40, 385 ; N. S. Kurnakow, *ibid.*, 1900, 23, 439 ; E. Jänecke, *Z. physikal. Chem.*, 1907, 58, 245.

[2] G. Grube, *Z. anorg. Chem.*, 1905, 46, 76; N. S. Kurnakow and N. J. Stepanow, *ibid.*, 177; W. Hume-Rothery, *J. Inst. Met.*, 1926, 35, 336. From the work of G. Grube and H. Vosskühler, *Z. Elektrochem*, 1934, 40, 566, it appears that solid solutions are formed at the magnesium end of the diagram, but this does not affect the present discussion.

amount of dissociation takes place, represented by the equation

$$Mg_2Sn \rightleftharpoons 2\ Mg + Sn.$$

It will be seen that at all temperatures between 565° and 783° there exist two liquid alloys with which solid Mg_2Sn can be in equilibrium, the one containing an excess of tin, the other an excess of magnesium. The constituents present in solidified alloys of this series are represented in Fig. 17. On account of the great difference in atomic weight between the two metals, the atomic percentages used in plotting differ greatly from the percentages by weight, which are added for comparison, above Fig. 16.

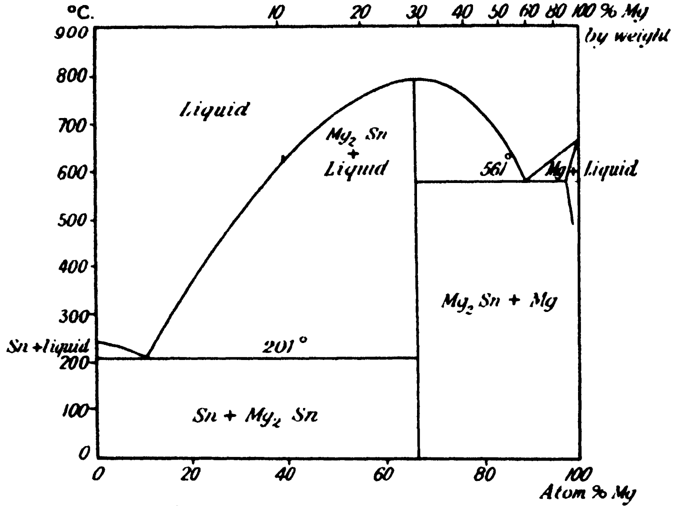

FIG. 16.—Tin and magnesium.

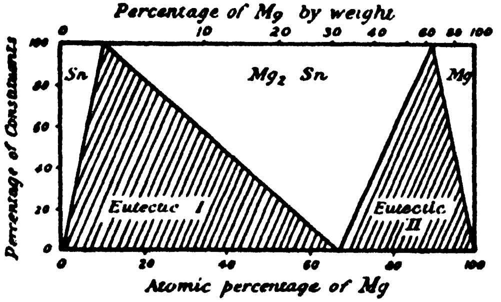

FIG. 17.

B. THE FREEZING-POINT CURVE SHOWS A BREAK, BUT NO MAXIMUM.

Many intermediate phases break up below their melting-point into a liquid alloy and crystals of another phase. This case is comparable with that of many hydrated salts, which dissociate on heating into an aqueous solution and a hydrate containing less water. The conditions are represented in Fig. 18. The pure metal M separates along the branch AE, the eutectic point being reached at E. The ascending branch EF corresponds with the crystallization of a compound of the two metals M and N, but instead of reaching a maximum and again falling to a second eutectic point, as in the alloys of magnesium and tin, the freezing-point curve changes in direction at the point F, and ascends to the temperature of solidification of the pure metal N at B. The branch BF then corresponds with the crystallization of N from the molten alloys. The break at F is to be interpreted as follows. On heating, the solid phase dissociates at the point F, partly melting to a liquid, and giving up the whole of the metal M contained in it to the liquid, leaving crystals of N. At the temperature represented by F, then, there is equilibrium between two solid and one liquid phase:

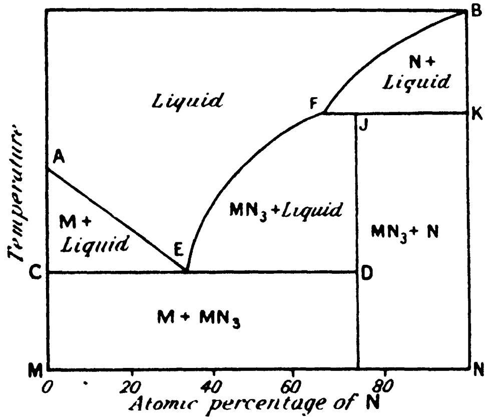

FIG. 18.—Peritectic system.

$$M_xN_y \rightleftharpoons N + \text{(solution of N in M)}. \qquad (1)$$

Such a reaction is called a *peritectic* reaction; F is a peritectic point; and FK is a peritectic horizontal. Neglecting the vapour phase, we have three phases and two components, or, since $f_1 = n - p + 1$, we have $f_1 = 0$, or the system is invariant, and can only exist at a definite temperature and concentration of the liquid phase.

The amount of each constituent present in the solidified alloys can be determined from Fig. 19. This is, however, an ideal case which presupposes slow cooling, so that complete equilibrium is attained. The reaction at the point F takes place between two solid phases and a solution saturated with respect to both of them:

$$MN_3 \rightleftharpoons N + (\text{solution of N in M}).$$

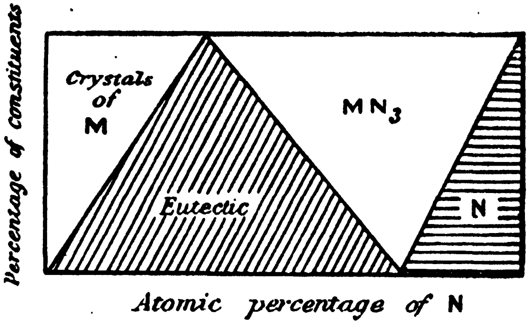

FIG. 19.

It is therefore likely to remain incomplete on cooling, owing to the compound being deposited as an insoluble layer coating the crystals

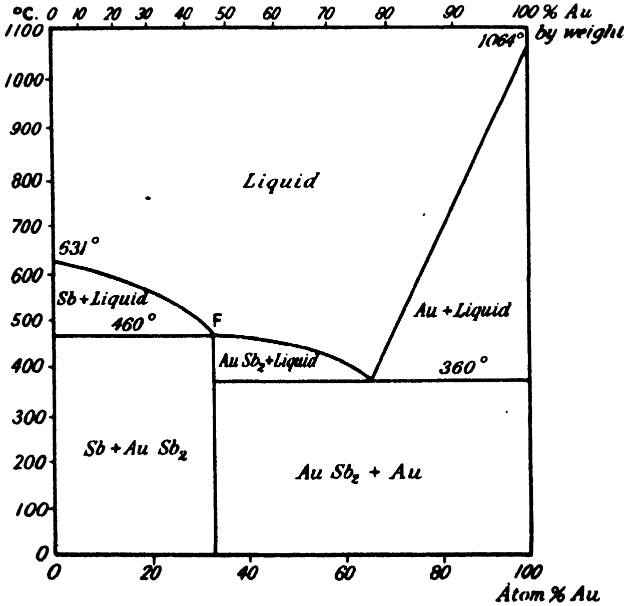

FIG. 20.—Antimony and gold.

of N and hindering further action. The methods of detecting and allowing for such a condition of incomplete equilibrium will be discussed later; for the present it is sufficient to say that the error is reduced to a minimum by very slow cooling.

In the diagram of the antimony-gold alloys (Fig. 20)[1] the break in the curve coincides with the composition $AuSb_2$, and this is therefore an exceptional case. On cooling liquid alloys containing less than 33·3 atomic per cent. Au, crystals of antimony separate, but on reaching 460° a portion of these reacts with the mother-liquor to form crystals of the compound $AuSb_2$. From alloys containing from 33·3 to 65 atomic per cent. Au, this compound constitutes the primary crystallization, and from alloys richer in gold, crystals of gold are

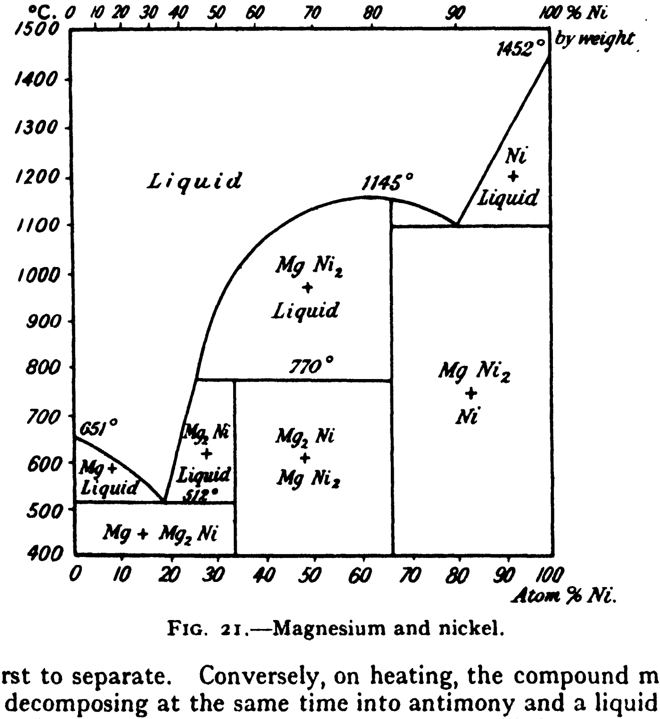

FIG. 21.—Magnesium and nickel.

the first to separate. Conversely, on heating, the compound melts at 460°, decomposing at the same time into antimony and a liquid alloy, so that F is an invariant point, at which the equilibrium

$$AuSb_2 \rightleftharpoons Sb + \text{(liquid alloy of Au and Sb)}$$

occurs.

More complicated conditions are very frequent. The freezing-point curve may present several maxima, or several breaks, or both maxima and breaks may occur on the same curve. Examples of this are afforded by the alloys of magnesium and nickel,[2] and of

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[1] R. Vogel, *Z. anorg. Chem.*, 1906, **50**, 145.; A. T. Grigoriev, *ibid.*, 1932, **209**, 289.

[2] G. Voss, *ibid.*, 1908, **57**, 34; J. L. Haughton and R. J. M. Payne, *J. Inst. Metals*, 1934, **54**, 275.

potassium and mercury,[1] represented in Figs. 21 and 22 respectively. The former system has a well-marked maximum, corresponding with the compound $MgNi_2$, and a break at 770°. Since the transformation at 770° has a maximum duration at 33·3 atomic per cent. Ni, and the eutectic arrest at 512° vanishes at the same concentration, the existence of a compound Mg_2Ni is clearly indicated. The arrangement of phases is obvious from an inspection of the figure.

The system potassium-mercury (Fig. 22) is considerably more complicated. There is only one maximum, that corresponding with the remarkably stable compound Hg_2K, melting 216° higher than the less fusible of its two components. The breaks in the curve, however, indicate no less than four other compounds, undergoing decomposition below their freezing-points, namely, HgK, Hg_3K, Hg_9K_2, and Kg_9K.

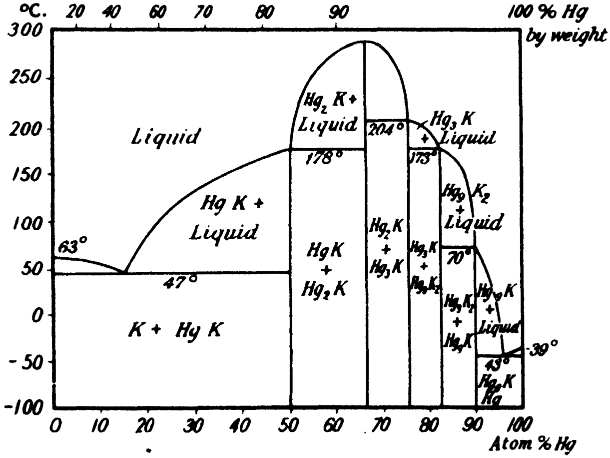

FIG. 22.—Potassium and mercury.

CHANGES IN SOLID SOLUTIONS.

The changes which may take place in an alloy during cooling are not at an end when the mass has solidified. Crystallization from solution, change from one solid phase to another of different crystalline form, even chemical reactions between the constituents, are possible in the solid state without the presence of a liquid solvent, although the velocity of such changes is in general less than when a liquid is present. The first case to be considered is that of a metal or inter-metallic compound which exists in more than one crystalline

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[1] E. Jänecke, *Z. physikal. Chem.*, 1907, **58**, 245. A revision by the same author, *Z. Metallk.*, 1928, **20**, 113, suggested some modifications, but the details of the diagram are still uncertain.

form, having different temperature ranges of stability. Such a substance is said to be *polymorphic;* when heated or cooled it shows a change of properties at a definite temperature, the *transition temperature*, and the change is generally accompanied by a development or absorption of heat, making itself known as a further arrest in the cooling curve. Such heat-changes are often comparatively slight, and are not readily detected on the ordinary temperature-time curve; special differential and other methods have therefore been devised for their recognition, and will be described in the chapter on practical thermal measurements.

The number of polymorphic metals and inter-metallic compounds is very great, and the equilibrium diagrams of alloys owe a large part of their complexity to this cause. When the polymorphic metal or compound occurs in a eutectiferous series, it undergoes the same change whether present as primary crystals or as a constituent of the eutectic, and the transformation takes place at the same temperature in both cases. The polymorphic change is therefore represented by a horizontal line extending over the same limits as the eutectic. When, on the other hand, the polymorphic metal forms solid solutions, the transition temperature varies with the composition. Moreover, it has been shown by Roozeboom,[1] that the transformation of a solid solution, like its solidification, must take place over a certain interval of temperature, so that we have two curves, representing the beginning and the end of the polymorphic change, and corresponding very closely with the liquidus and solidus curves already studied. This will be understood by reference to

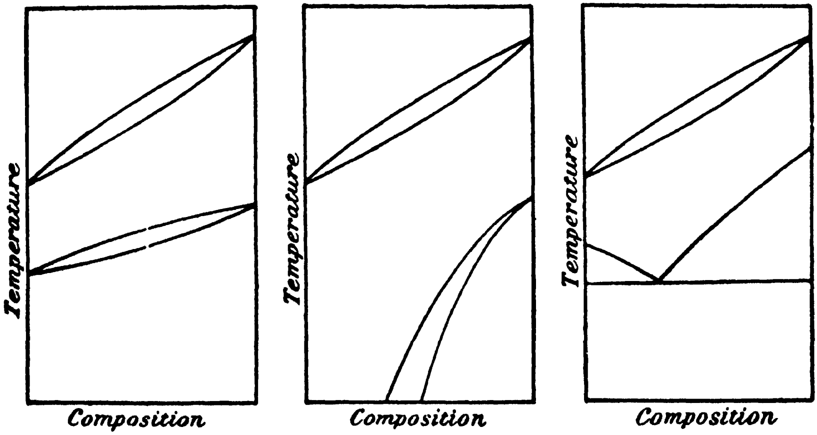

FIG. 23. FIG. 24. FIG. 25.

Polymorphic changes in solid solutions.

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[1] *Z. physikal. Chem.*, 1899, **30**, 385.

Figs. 23 and 24. In the former of these, both the low and the high temperature modifications of the two metals are completely isomorphous. In the second figure, only one of the components of the isomorphous series undergoes a change on cooling.

One of the components may crystallize from the solid solution along a solubility curve, as in Fig. 15, or the homogeneous phase may be resolved into two new constituents, when the diagram assumes the form shown in Fig. 25. The temperature at which each component crystallizes from the solid solution is lowered by addition of the other, and we consequently obtain a solubility curve with two branches. The resemblance of this curve to the freezing-point curve of a eutectiferous series is at once apparent, and the analogy is a real one. Primary separation of the components takes place along the two branches, and when the temperature of intersection is reached the remaining solid solution splits up into a conglomerate of the two components. From the resemblance of this alloy in its physical properties as well as in its mode of formation to a eutectic, it is called a *eutectoid.*[1] Fig. 26 is a small part of the complete diagram of the iron-carbon alloys. The homogeneous solid solution of carbon in γ-iron breaks up on cooling, setting free pure iron in the α-form and iron carbide, Fe_3C. Pure iron separates along the left-hand branch, whilst from alloys richer in carbon, the carbide crystallizes along the right-hand branch, intersecting the other at the eutectoid point, at which the remaining solid solution splits up into a finely laminated conglomerate of iron and carbide, known as *pearlite.* All alloys comprised within the limits of the diagram show an arrest on their cooling curves at 690°, corresponding with the formation of pearlite. The heat-development reaches a maximum at the eutectoid composition, that is, at 0·81 per cent. of carbon (see p. 349).

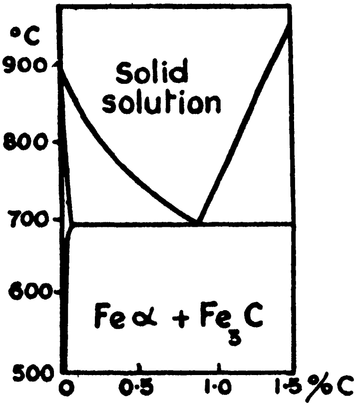

FIG. 26.—Iron and carbon.

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[1] H. M. Howe, *Metallographist*, 1903, 6, 249. The word " æolic " had been previously used, but not generally adopted.

CHAPTER III.

THE DIAGRAM OF THERMAL EQUILIBRIUM—*Continued.*

TERNARY AND MORE COMPLEX ALLOYS.

THE methods of investigating alloys of three or more metals are the same in principle as when the simpler alloys of two metals are dealt with, but the experimental difficulties, and the complexity of the conditions which may present themselves, are naturally much greater. For this reason, in spite of the number of alloys of technical importance containing three metals, few ternary systems have been completely investigated, and still fewer quaternary or more complex systems. A large number of individual alloys must be examined and all sources of error met with in binary systems recur in an aggravated form, the consequence being that the construction of the diagram of thermal equilibrium of a ternary system is an undertaking of considerable magnitude.

The thermal equilibrium of a ternary system can only be represented graphically by a model in three dimensions or by phase projections of such a model. The method employed in metallography is that due, in the first place, to Willard Gibbs,[1] but more generally associated with Stokes, who independently devised the same scheme,[2] basing it on the method employed by Clerk Maxwell for the composition of colours.

The percentage compositions of the alloys are represented by an equilateral triangle, the height of which is 100 (Fig. 27). The three points A, B and C there represent the pure metals, a point on the line AB represents a binary alloy of A and B, and so on for the pairs AC and BC, whilst any point within the triangle corresponds with an alloy of the three metals.

In practice, the very similar arrangement due to Roozeboom[3] is usually preferred. The vertices representing the pure metals as before, the sides of the triangle are each divided into 100 parts, and the co-ordinates of a point representing a ternary alloy are measured in directions parallel with the sides. The sum of these distances is always 100. Paper ruled with such triangular co-ordinates is now obtainable in various sizes, so that the plotting

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[1] *Trans. Connecticut Acad.*, 1876, **3**, 176.

[2] *Proc. Roy. Soc.*, 1891, **49**, 174.

[3] H. W. B. Roozeboom, *Z. physikal. Chem.*, 1894, **15**, 147.

of a diagram is greatly simplified. Only the lines at 10 per cent. intervals are shown in Fig. 27. A point such as M thus represents an alloy of 25 per cent. of the metal A, 15 per cent. of B, and 60 per cent. of C. Since the sum of the percentages is always 100, it is sufficient to determine two of them to fix the composition.

For a complete representation of the system, the ordinates of temperature must now be erected as perpendiculars to the plane of the triangle, and their summits joined to form a surface or a system of surfaces, so that the space-model finally obtained is a vertical triangular prism (as, for example, Fig. 32). Such models, showing the form of the liquidus surface, are often constructed in plaster, but in order to exhibit the solidus and any transformations in the solid state some other plan must be adopted. For most purposes, the system is represented by a series of horizontal projections or of vertical sections through the model, constructed as described below, and by drawing them in suitably coloured lines on glass or celluloid and setting them up with the appropriate spacing, a comprehensive view may be obtained.[1] A more convenient construction uses a wire model.[2] The ordinates, boundary curves, and contour lines are made of wires, soldered together where they meet, and coloured on such a plan as to make the model easy to interpret. Models of this kind are useful for demonstration and for teaching, but the practical metallographer makes little use of them, preferring plane diagrams.

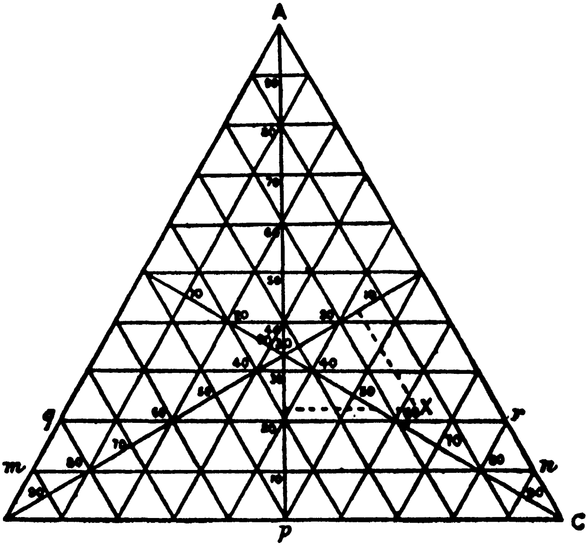

FIG. 27.—Graphical representation of a ternary system.

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[1] P. Goerens, *Metallurgie*, 1909, 6, 531.
[2] W. Rosenhain, *J. Inst. Metals*, 1920, 23, 247.

In the actual investigation of a ternary system, the alloys subjected to thermal analysis are usually taken in such on order as to provide a series of vertical sections through the space model, each of which is represented as a diagram in two dimensions. These sections

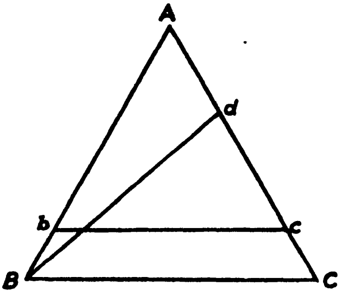

FIG. 28.

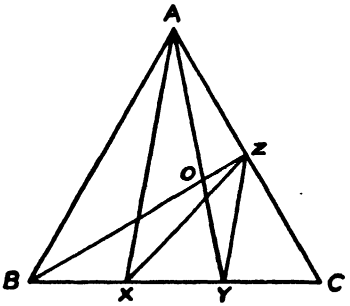

FIG. 29.

may be chosen in either of two ways. In the first (*bc* in Fig. 28) a series of alloys is examined, all of which contain the same proportion of one of the component metals, say A. The compositions of these are represented by points lying on a line parallel with BC. The second method (B*d* in Fig. 28) selects points on a line drawn from one of the vertices,

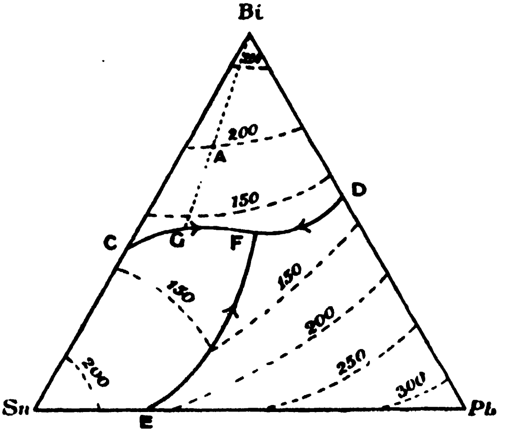

FIG. 30.—Bismuth, tin, and lead.

say B, to the opposite side. All alloys represented by points on this line contain the metals A and C in the same ratio. The first method is to be preferred in the investigation of a previously unknown system, but the second has advantages which will appear later, especially when the line is drawn to the composition of an intermetallic compound or intermediate phase of definite composition, which forms a

" pseudo-binary " system with the third metal. Such a condition is common, and its occurrence simplifies the construction of the complete ternary diagram, and when more than one pseudo-binary section is possible, as in Fig. 29, a study of a single alloy, such as O, will save time in determining the constitution of the system, as indicated in Chap. XVIII.

It is sometimes preferred to draw horizontal rather than vertical sections through a space-model. Each such section represents an isothermal diagram, and is different in type from such a triangular diagram as Fig. 30, which is a projection of the liquidus surfaces on to a horizontal plane, and is therefore not isothermal. These horizontal sections show the phases which are in equilibrium with one another at a determined temperature. For most purposes in metallography vertical sections are to be preferred, as indicating the course of crystallization in any given alloy, although when a system has been determined, horizontal sections give a more convenient view. The use of sections is discussed later (Chap. XVIII.).[1]

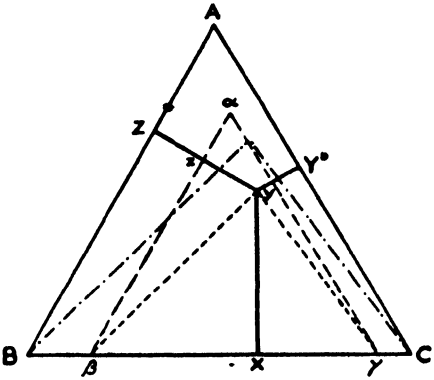

FIG. 31.—Conversion of weight to atomic composition.

The conversion of percentages by weight into atomic percentages in ternary systems is much more troublesome than in binary systems, and has the disadvantage that it is not easy to detect errors in arithmetic, as the result cannot be checked by the simple plotting of a curve. Graphical methods of conversion have therefore been devised. The atomic weights of the three component metals being a, b, and c, their percentages by weight in the alloy p, q, and r, and their atomic percentages x, y, and z, the atomic ratios become

$$p; \quad q \times \frac{a}{b} = B; \quad r \times \frac{a}{c} = C,$$

and when the ratios $\frac{a}{b}$ and $\frac{a}{c}$ have been found they may be used throughout the series of alloys. The following geometrical construction may then be used.[2] It is advisable to arrange the three metals so that these two ratios are less than unity, so that the new lines which

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[1] More detailed accounts are given in " Die Heterogenen Gleichgewichte," by H. W. Bakhuis Roozeboom, Brunswick, 1901-18, especially in Vol. II; also by G. Masing, " Ternäre Systeme," Leipzig, 1933; and A. Portevin, " Introduction à la chimie des alliages métalliques," Paris, 1934.

[2] W. Hume-Rothery, *J. Inst. Metals*, 1933, 52, 131.

have to be drawn are within the triangle. In Fig. 31 the point P represents a ternary alloy in a position corresponding with its composition by weight. y is found by multiplying the length PY by the ratio $\frac{a}{b}$, using a slide rule. z is found in the same way from PZ. Lines parallel with AB and AC are then drawn through y and z, giving a new equilateral triangle, $\alpha\beta\gamma$, in which the point P now represents the atomic composition of the alloy. Further calculation may be avoided by drawing lines parallel with βP and γP from B and C, meeting in a new point Q. The atomic composition corresponding with this point is read off on the triangular co-ordinates of the original triangle ABC. The same procedure is followed for each alloy examined, without making further calculations. A slight simplification is possible if two pairs of proportional compasses are available.[1]

Several typical kinds of equilibrium in ternary systems may now be considered.

(*a*) *The metals form solid solutions in all proportions.*

The simplest form of ternary system is one in which all three metals are isomorphous, so that they can form a complete series of solid solutions throughout the whole range of composition. Under conditions of equilibrium both the liquidus and the solidus surfaces are continuous. A maximum or a minimum is possible, on the condition, as in binary solid solutions, that at such a point liquidus and solidus must coincide and have a common horizontal tangent. If the process of diffusion keeps pace with that of freezing, the alloy solidifies homogeneously, over a range of temperature represented by the difference between the liquidus and the solidus. An example is the ternary system gold-silver-copper, in which two of the pairs have liquidus curves passing through a minimum, so that the surface of the prism has a transverse trough.[2]

In the absence of diffusion, when the alloy solidifies in the form of a large number of successive layers of progressively changing composition, the distance between the observed liquidus and solidus is increased as in a binary system (see p. 27) and the contour lines of the liquidus are curved towards the metal of lowest freezing-point.

(*b*) *The three metals crystallize in a pure state.*

If we assume that the only solid phases which separate on cooling are the pure metals, neither compounds nor solid solutions being formed, the three binary systems obtained by taking the metals in pairs will each be of the form shown in Fig. 4, page 14, and the space-model will therefore be a triangular prism, of which the three vertical

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[1] Other graphical methods are given by F. Hoffmann, *Metallurgie*, 1912, 9, 133, and by W. Schischokin, *Metallurg* (Russian), 1933, No. 1.

[2] P. de Cesaris, *Gazzetta*, 1914, 44, i, 27.

faces are bounded at the top by V-shaped curves. The freezing-point surfaces which start from the angles of the prism intersect along three lines, forming three valleys. The eutectic temperature of a binary system may be regarded as the simultaneous freezing-point of the two component metals, and the addition of a third metal lowers this freezing-point, just as the addition of a second substance lowers the freezing-point of a pure metal.

The curves of intersection, or the bottoms of the valleys, therefore slope downwards from the outer faces to the interior of the prism. They finally intersect at a point, the *ternary eutectic point*, which necessarily represents a lower temperature than any of the binary eutectics. It is on the existence of such a ternary eutectic that the possibility of preparing the so-called "fusible metals," melting below 100°, depends, a mixture of three metals in the eutectic proportion in such a case melting more readily than any possible mixture of the same metals taken two at a time.

The well-known ternary system, lead-tin-bismuth, is usually referred to this type.[1] Strictly speaking, the condition that the solid phases separating shall be the pure metals is not fulfilled here, since solid solutions are formed,[2] and other changes occur in the solid alloys, but this fact does not affect the form of the freezing-point surface, which alone falls to be considered here. A projection of the surface on the basal plane of the prism gives the result shown in Fig. 30, in which the positions of the binary two-phase lines and of the ternary eutectic point are clearly seen.[3] The dotted curves are isothermals, drawn at equal intervals of temperature.

The process of crystallization of an alloy belonging to this system may now be followed in detail. If we consider a liquid alloy, the composition of which is represented by the point A, the cooling of such an alloy will be represented by a point travelling down the perpendicular erected on the triangular base at the point A. This perpendicular cuts the freezing-point surface BiCFD, that is, the surface corresponding with the crystallization of bismuth. The position of the isothermal indicates that the separation of bismuth begins at 200°. The passage of a part of the bismuth from the liquid to the solid state does not alter the relative proportions of lead and tin in the portion remaining liquid, and the change of composition of the liquid alloy with falling temperature is therefore represented by a point travelling along the line BiAG from A towards G. When G is reached, this line intersects the line CF, which represents a system in which solid bismuth and solid tin are simultaneously in equilibrium

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[1] G. Charpy, *Compt. rend.*, 1898, **126**, 1569; *Bull. Soc. d'Encouragement*, 1898, [v], **3**, 670.

[2] W. Rosenhain and P. A. Tucker, *Phil. Trans.*, 1908, **209**, A, 89; K. Honda and H. Abé, *Sci. Rep. Tôhoku Univ.*, 1930, **19**, 315.

[3] The diagram is taken from Charpy, corrected by the later results of E. S. Shepherd, *J. Physical Chem.*, 1902, **6**, 519, and recalculated into atomic percentages.

with the liquid mother-liquor. A two-phase alloy of bismuth and tin therefore separates.[1] The relative proportion of the two solid phases changes somewhat as the temperature falls, as is indicated by the line CF, which is not straight, but slightly curved. When the point F is reached, the whole of the remaining alloy solidifies at constant temperature. The ternary point F corresponds with the simultaneous equilibrium of one liquid and three solid phases, namely, the three pure component metals.

Examination shows that the process described accords with the indications of the phase doctrine. We are now dealing with a system of three components. When solid bismuth separates, there are two phases present, namely, the crystals of the solid metal, and the still liquid alloy. Since

$$f' = n - p + 1 \text{ (p. 17)}$$

$f' = 2$, or the system is bivariant, and temperature and composition may be varied independently. When the first two-phase boundary is cut, a new phase appears, namely, solid tin. The number of phases being now three, the system is only univariant, so that, the temperature being given, the composition is also determined. At the ternary eutectic point F, four phases are in equilibrium, namely, the three solid metals and the liquid ternary eutectic, so that

$$f' = 3 - 4 + 1 = 0.$$

The system is invariant, and can exist only at one definite temperature, the temperature indicated by F. It will be noticed that, on the space-model, bivariant systems are represented by surfaces, univariant systems by lines, and invariant systems, of which only one is possible in the case considered, by points. A three-dimensional region, such as that existing above the freezing-point surface, represents a tervariant system, since the concentration of two components, and the temperature, may be varied independently. Below the ternary eutectic temperature, three solid phases co-exist, and any further changes which may occur proceed in the solid state. For the purpose of the present discussion they have been ignored.

A good example of a ternary series in which solid solutions are formed to a limited extent, no compounds being formed, is furnished by the amalgams of cadmium and lead.[2] The three binary systems are of a simple type, and it is not necessary to reproduce the corresponding diagrams separately. Cadmium and lead form a eutectiferous series, the eutectic point lying at 249° and 33 atom. per cent. Cd. Each of these metals is capable of retaining small quantities of the other in solid solution, lead holding up to 4 atom. per cent. cadmium, and cadmium holding a very small percentage of lead.

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[1] Such an alloy is frequently called a binary eutectic. Since, however, it has not a constant freezing-point, this term should be avoided.

[2] E. Jänecke, *Z. physikal. Chem.*, 1907, **60**, 399; 1910, **73**, 328.

In the lead-mercury series, the eutectic point lies so near to the mercury end of the curve as to be indistinguishable from it, and solid solutions

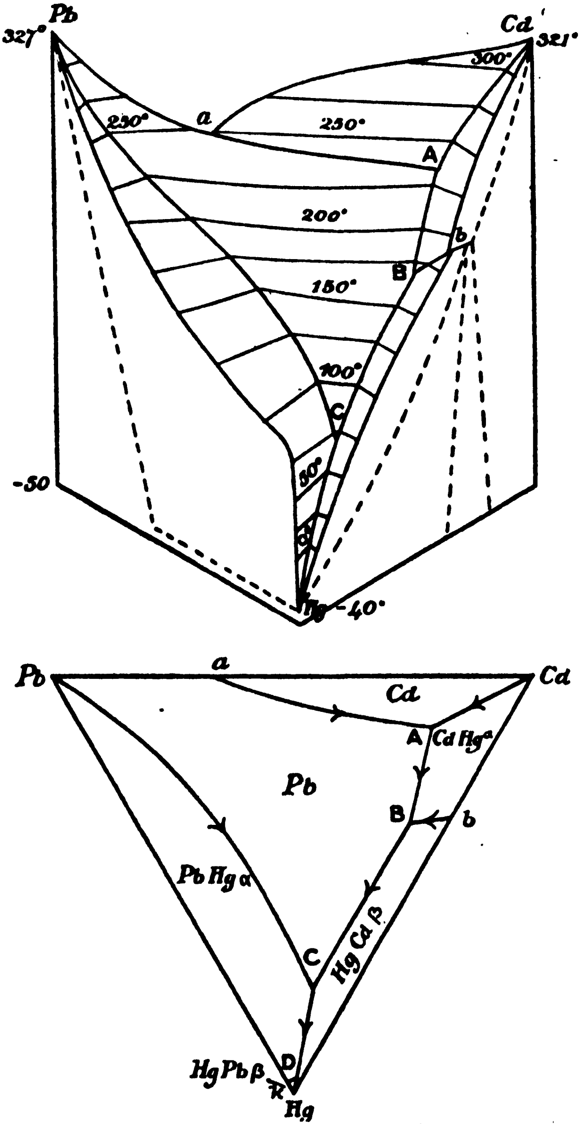

FIG. 32.—Lead, cadmium, and mercury.

are also formed up to a concentration of about 40 atom. per cent. Hg. The cadmium-mercury diagram has been described in a previous chapter. Fig. 32 shows, above, an elevation of the space-model, and, below, the projection of the same on the base. The latter is divided into six fields, each of which corresponds with the primary separation of a distinct crystalline constituent from the molten alloy. The lines separating these fields, and the points at which these lines intersect, indicate the temperatures and concentrations at which different phases are in equilibrium. There is no ternary eutectic point, and only a single binary eutectic curve, *a*A, namely, that separating the regions of crystallization of lead and cadmium. The points *k* and D are not to be distinguished from the freezing-point of mercury, the second solution in the lead-mercury system being practically pure mercury, but for the sake of completeness their distance from the angle Hg of the triangle is exaggerated. The meaning of the points of intersection of the eutectic and transformation curves is shown in the following table :—

Point.	Character.	Phases in Equilibrium with Liquid.	Temp. °C.
a	Eutectic .	Pb, Cd	249
b	Transformation.	CdHgα, HgCdβ	188
k	,,	PbHgα, HgPbβ	− 40
A	,,	Pb, Cd, CdHgα	235
B	,,	Pb, Cd, HgCdβ	169
C	,,	Pb, PbHgα, HgCdβ	50
D	,,	PbHgα, HgPbβ, HgCdβ	− 40

The general behaviour of the alloys during solidification will be seen from a comparison of the upper and lower diagrams in Fig. 32. Consider an alloy represented by a point within the area *a*ACd. As the temperature falls it will deposit crystals of cadmium. Its composition then changes in the manner described in connection with the alloys of lead, tin, and bismuth (p. 48); the point representing it travels down the freezing-point surface until it reaches the line *a*A. The two-phase alloy of lead and cadmium then separates, and the temperature continues to fall until the point A is reached. This is not a ternary eutectic point, but represents a reaction between the crystals and the mother-liquor, in accordance with the equation

$$\mathrm{Cd} + \text{a solution of composition A} \rightleftharpoons \mathrm{Pb} + \mathrm{CdHg}\alpha.$$

The temperature remains constant at 235° so long as this reaction continues. If the cadmium is in excess, the mother-liquor solidifies completely at this temperature; but if the cadmium is used up in the reaction, and some liquid of composition A remains, this will fall in temperature, depositing simultaneously crystals of Pb and CdHg*a* along the line AB. The other lines on the diagram are explained in the same way.

(*c*) *Intermediate phases are formed.*

As an example of a system containing an intermediate phase we may take the alloys of magnesium, lead, and tin.[1] One of the three binary systems has been described already (p. 35). The systems Mg-Pb and Mg-Sn resemble one another very closely, each containing a binary compound of the same type, solid solutions not being formed to on appreciable extent. As regards the system Pb-Sn, Vegesack, working with somewhat rapid cooling, did not detect the formation of the solid solution which undoubtedly exists; but this error does not noticeably alter the form of the liquidus surface.

The results are shown in Fig. 33, the upper diagram in which represents in elevation the space-model, and the lower the projection of the liquidus on the basal plane. The two compounds Mg_2Sn and Mg_2Pb form solid solutions with one another, the solutions forming two series with a small gap, that is, belonging to the Type IV (p. 31). A vertical section along the line *ab* therefore represents a binary system of precisely the same type as the cadmium amalgams (p. 32). The width of the gap between the two solid solutions is, however, increased by the addition of lead or tin to the alloy, so that, near the eutectic line *hfe* the α crystals may be regarded without serious error as pure Mg_2Sn, and the β crystals as pure Mg_2Pb. A section on the line *a*Pb will then show a freezing-point curve corresponding with a simple eutectiferous series, the two components of which are Mg_2Sn and Pb.[2] Fig. 34 represents the sections on *ab* and *a*Pb respectively, with the arrest time-concentration curves dotted. In the second diagram the atomic percentages of lead only are indicated on the line of abscissæ. Since the starting-point on the left-hand side is the point *a*, representing the compound Mg_2Sn, the tin and magnesium are in the constant atomic ratio 1 : 2 throughout, and may be calculated with ease.[3]

At the ternary eutectic point *h* (Fig. 33), three solid phases, Sn, Pb, and α crystals (practically pure Mg_2Sn), are in equilibrium with the liquid. There should be two other invariant points in the ternary system, corresponding with the equilibrium of Mg, α and β, and with that of α, β, and Pb respectively. These points are, however, found to coincide with the binary eutectic points *d* and *e* respectively, thus introducing a certain simplification into the diagram. Only one ternary eutectic mixture is therefore formed.

It will be sufficient to examine the process of solidification in two cases. Consider first a point lying somewhat to the left of the line *a*Pb in the triangular projection (Fig. 33). An alloy of this composition will, on cooling, deposit crystals of the α solution, which will continually adjust their composition to maintain equilibrium with the liquid,

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[1] A. von Vegesack, *Z. anorg. Chem.*, 1907, **54**, 367.

[2] Such a section then represents a "pseudo-binary" system.

[3] In the second diagram, the dotted curve is somewhat idealized. Owing to the rapid rate of cooling, Vegesack did not obtain complete equilibrium, and his eutectic arrest vanished before reaching the limit of the diagram.

until, when the line *hf* is approached, they consist, as mentioned above, of practically pure Mg_2Sn. When a point on *hf* is reached, crystals

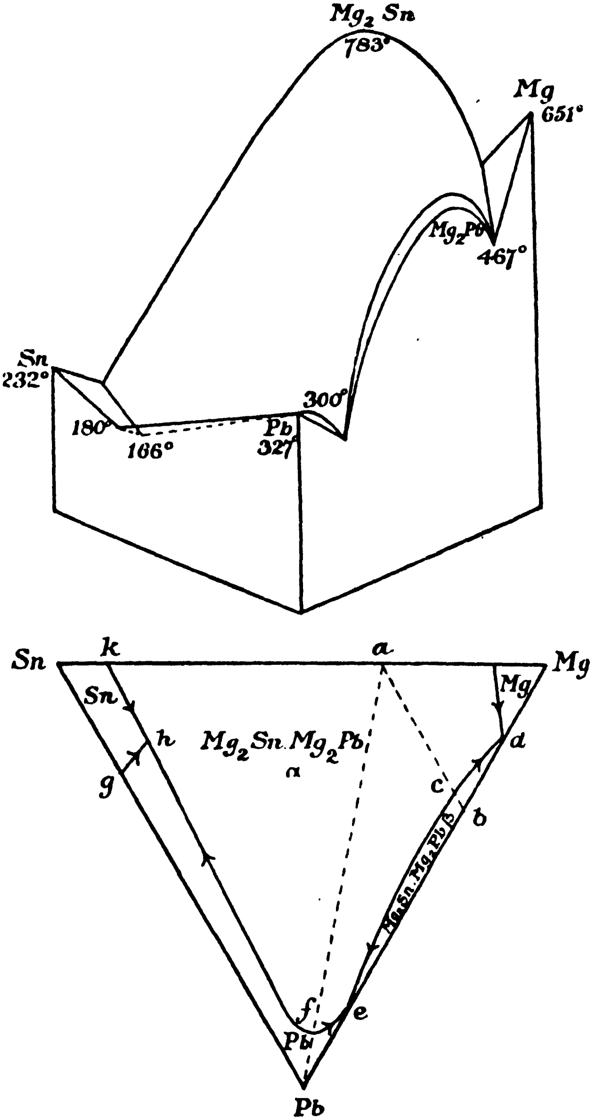

FIG. 33.—Tin, magnesium, and lead.

of lead begin to separate, a two-phase alloy of lead and Mg_2Sn being thus formed. The temperature continues to fall, as indicated by the arrow-head, until the point *h* is reached, when the whole of the mother-liquid solidifies at constant temperature as the ternary eutectic.

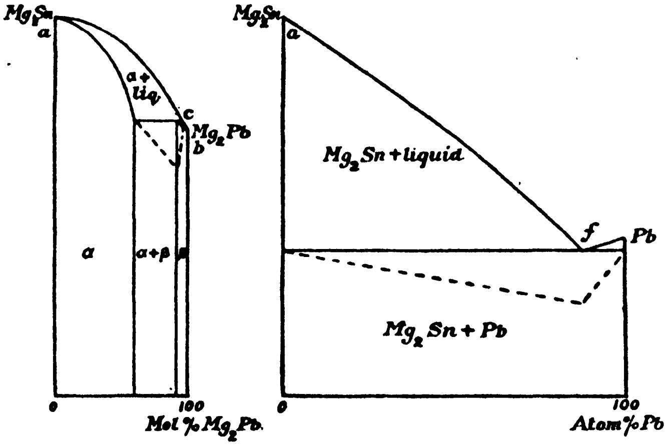

FIG. 34.—Sections through the model (Fig. 33).

If, on the other hand, the point representing the composition of the alloy lies between the lines *ab* and *a*Pb, the first crystals deposited are, as before, the α solution; but the line *dce*, when intersected, is one of transformation. When it is reached, the α crystals react with the mother-liquor, according to the equation

$$\alpha + \text{liquid} \rightleftharpoons \beta.$$

With the progressive formation of β crystals, the temperature falls towards *e*, at which a third solid phase appears, namely lead, and the remaining liquid solidifies at constant temperature. The behaviour of any other alloy of the series may be predicted by similar reasoning.

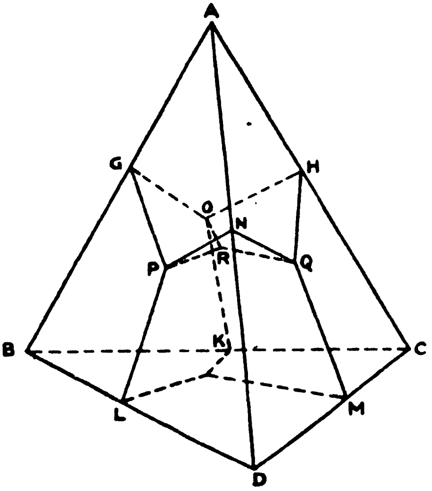

FIG. 35.—Simple quaternary system.

When the number of components is greater than three, the representation becomes much more difficult. With four components the equilibrium may be represented graphically by using a regular tetrahedron, the angles of which are occupied by the pure metals, whilst binary alloys appear as points on the edges, the four ternary combinations of the components form the faces, and points in the interior represent quaternary alloys.[1] It is not possible to plot another variable, such as temperature, in this already three-dimensional model, but important points, such as eutectic or transformation points, may be indicated, and the corresponding temperatures written against them. When the four metals form between themselves only simple eutectiferous systems, a quaternary eutectic may be formed, and this simple condition is indicated in Fig. 35. The alloys of lead, tin, bismuth and cadmium conform approximately to this type.[2]

An alternative method has been devised,[3] according to which any required part of the quaternary system may be represented on a plane. The composition of a quaternary alloy is given by a point inside a right-angled isosceles triangle, and it is not difficult to transfer critical points to a plane diagram with a vertical scale of temperature and a horizontal scale which gives the composition.

THERMAL EQUILIBRIUM OF METALS WHICH ARE INCOMPLETELY MISCIBLE IN THE LIQUID STATE.

All the alloys hitherto considered have been assumed to melt to a homogeneous liquid. This is, however, by no means a universal condition. Whilst many pairs of liquid metals resemble alcohol and water, mixing in all proportions to form a single liquid phase, others behave like water and ether, the mixtures, within certain limits of concentration and temperature, separating into two immiscible liquid phases. All degrees of miscibility, from the almost complete mutual insolubility of water and mercury to complete miscibility, are observed. Amongst metals, certain pairs, such as lead and aluminium, behave, at temperatures only slightly above their melting-points, like mercury and water, separating into two layers, each of which consists of one of the metals in an almost pure state. More often each metal has a certain limited power of dissolving the other, so that the two liquid layers consist of dilute solutions of A in B, and of B in A respectively. Complete immiscibility cannot be said strictly to occur.

This last statement will be understood after a consideration of the effect of temperature on the equilibrium of incompletely miscible liquid phases. The reciprocal solubility of two liquids may either increase or decrease with rise of temperature ; both cases have been observed in alloys, but the former is the more usual. As the temperature rises, then the liquid layer in which A is in excess becomes increasingly richer in B, and the layer in which B is in excess becomes

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[1] N. Parravano and G. Sirovich, *Atti. R. Accad. Lincei*, 1911, [v], **20**, ii, 206, 331, 412 ; J. M. Bell, *J. Physical Chem.*, 1911, **15**, 580.

[2] N. Parravano and G. Sirovich, *Gazzetta*, 1912, **42**, i, 630 ; J. G. Thompson, *U.S. Bur. Stand. J. Res.*, 1930, **5**, 1085.

[3] W. Hommel, *Z. Metallk.*, 1921, **13**, 511.

increasingly richer in A, that is, the compositions of the two layers become more nearly equal. This points to the existence of an upper limit of temperature, at which the two liquid phases would become identical in composition, resulting in the formation of a single homogeneous liquid. Such a *critical solution temperature* probably exists in all cases of partial miscibility, although its experimental realization is usually difficult, owing partly to the fact that many of the metals forming alloys of this type are volatile, so that the boiling-point is reached below the critical temperature, and partly to the difficulty of observing the formation of layers directly, owing to the absence of transparency.

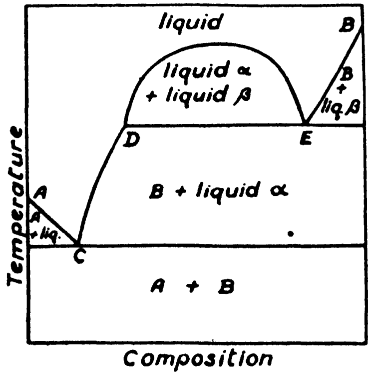

FIG. 36.—Partial miscibility.

If we consider two metals, the miscibility of which at a temperature slightly above the melting-point of the less fusible metal is so small as to escape observation, the process of freezing of any mixture of the two will be a very simple one. The freezing-point of each metal will be entirely unaffected by the presence of the other, and will thus be the same, whatever be the composition of the mixture taken. The whole of the less fusible metal thus crystallizes at its normal freezing-point, after which the temperature falls to the freezing-point of the second metal. The thermal diagram in the limiting case consists then of two horizontal lines drawn through the respective freezing-points of the two metals. Such complete immiscibility, however, never occurs, and the diagram therefore takes the form shown in Fig. 36. The freezing-point of A is depressed by the addition of small quantities of B; and conversely, that of B is depressed by the addition of A. The eutectic temperature will probably lie near to the freezing-point of the more fusible metal, as at C; and in fact, usually lies so near to the end of the series as to be practically indistinguishable from the freezing-point of the pure metal. Thus, in the alloys of copper and lead (Fig. 37) the freezing-point of lead is only lowered to the extent of 1·17°, the eutectic mixture containing only 0·06 per cent. of copper.[1]

From Fig. 36, in which the assumption is made that both metals crystallize in a pure state, neither compounds nor solid solutions being formed, it will be seen that liquid alloys rich in B will first deposit crystals of B, the temperature falling as indicated by the curve BE. This continues until the liquid reaches the temperature

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[1] C. T. Heycock and F. H. Neville, *Trans. Chem. Soc.*, 1892, **61**, 905.

and concentration represented by the point E, at which the freezing-point curve intersects the miscibility curve, shown as a dotted line. At this point the mother-liquor, if it continued to deposit crystals of B, would attain a composition represented by a point lying somewhere between D and E. The diagram shows, however, that all such points lie within the region of immiscibility, and the result of the crystallization must therefore be the formation of a second liquid phase having the composition of the alloy D. There are thus three phases in contact with one another, namely, the solid metal B and the two liquid phases α and β. The system is consequently invariant, and the further crystallization must take place at constant temperature. This is the meaning of the horizontal line DE. As crystallization proceeds, the mean composition of the part of alloy remaining liquid is represented by a point travelling along this line from E to D, until D is reached, and the liquid alloy E disappears. There are now only two phases present, and any further withdrawal of heat has the effect of lowering the temperature, the metal B now crystallizing from a homogeneous liquid along the branch DC until the eutectic point C is reached, after which the process continues in a perfectly normal fashion. On the individual cooling curves of alloys of this system, the formation of the second liquid phase is marked by a horizontal portion, exactly resembling the arrest due to the solidification of a eutectic. Microscopical examination, however, generally suffices to distinguish the two cases.

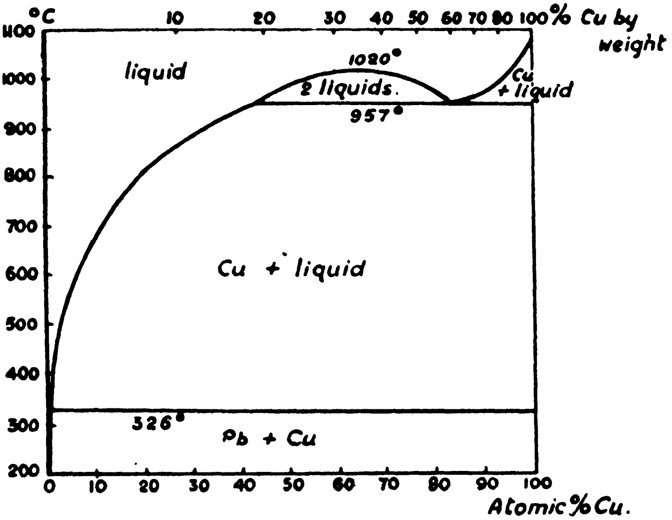

FIG. 37.—Copper and lead.

If the liquid alloy has originally a composition between D and E, the separation into two layers takes place before the crystallization of solid metal begins. As crystals of B separate from the liquid alloy E, a larger quantity of the conjugate alloy D is formed, and this process continues until the whole of E has disappeared.

The thermal arrests due to the separation of the homogeneous liquid into two layers are so small as to be undetectable, and other methods have to be used to determine the liquid solubility curve. In the study of the alloys of copper and lead the critical solution temperature lies so low (1000°) that it is practicable to heat each alloy until it is homogeneous, and after stirring well to allow it to cool to the required temperature, at which it is allowed to remain long enough to ensure the complete separation into two layers. The composition of the alloy as a whole being known, it is only necessary to remove a small quantity of the upper layer by means of an iron spoon and to make a chemical analysis, to obtain a point on the copper side of the solubility curve. This has been done for a series of alloys.[1] To obtain points on the other side, an analysis of the lower liquid layer is needed, and as this involves using a pipette passing through the upper layer, the measurement is less likely to be accurate, and the figures obtained agree less well with the thermal results for the end of the horizontal line.[2] The fact that these alloys become homogeneous on heating is made use of in the production of " lead bronzes " for bearing metals.

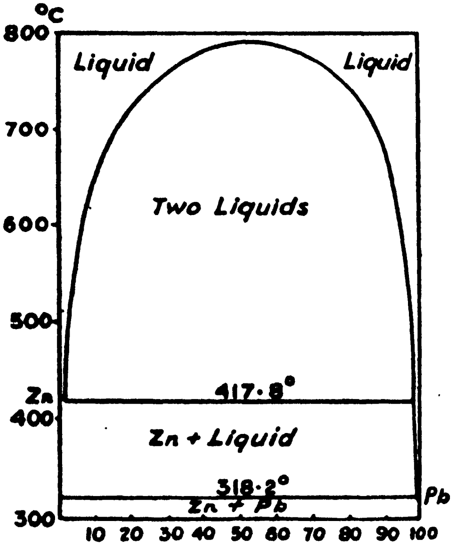

FIG. 38.—Zinc and lead.

In the alloys of lead and zinc the horizontal and the eutectic point are very near to the melting-points of the pure metals, and the temperature of complete miscibility is much higher. The complete curve has been traced, using four different methods.[3] The two liquid layers were brought to saturation by prolonged stirring, followed by a period of rest to allow any emulsion to separate, a sample of the

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[1] S. Briesemeister, *Z. Metallk.*, 1931, **23**, 225.

[2] K. Friedrich and M. Waehlert, *Metall. u. Erz.*, 1913, [ii], **10**, 574. The freezing-points were determined accurately by C. T. Heycock and F. H. Neville, *Phil. Trans.*, 1897, **189**, A, 25.

[3] R. K. Waring, E. A. Anderson, R. D. Springer, and R. L. Wilcox, *Trans. Amer. Inst. Min. Met. Eng.*, 1934, **111**, 254. There are several earlier determinations, but all probably failed to reach equilibrium.

upper layer being taken for analysis. In a further series, samples were also taken from the lower layer with, however, some risk of contamination. The temperature was found at which both samples had the same composition. In a third series, an H-shaped glass vessel was used, in which the two metals were contained in opposite arms and allowed to mix by diffusion, samples being obtained from both layers by breaking the tube. Lastly, a single alloy was examined by taking advantage of the greater opacity of lead to X-rays, the temperature being found at which the metal became homogeneous. The four methods gave concordant results, which are represented in Fig. 38.

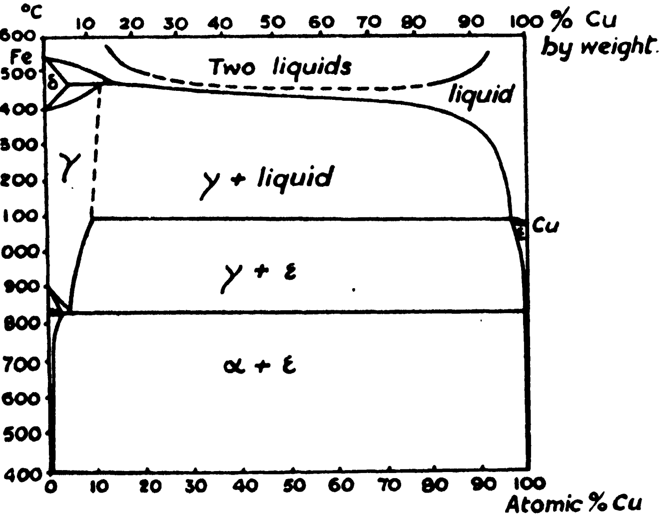

FIG. 39.—Iron and Copper.

The converse condition, of a homogeneous liquid which separates into two phases on further heating, is less common. It is known among organic liquids, and has been found in the alloys of copper and iron. The early studies of this system gave contradictory results, some observers describing the alloys as homogeneous, whilst others found a separation into two layers. When equal weights of the pure metals are melted together and cooled rapidly from different temperatures, it is found[1] that the mixture is homogeneous at temperatures between the freezing-point and 1520°, but separates into two well-defined layers above that temperature. The form of the curve of liquid solubility has not been determined, but the minimum is probably very flat (Fig. 39).[2] Small additions of foreign

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[1] A. Müller, *Mitt. K. W. Inst. Eisenforsch.*, 1927, 9, 173.

[2] Taken from J. L. Gregg and B. N. Daniloff, "The Alloys of Iron and Copper," New York, 1934, in which the evidence is fully reviewed. The changes indicated in the solid state are without influence on the conditions described in the present chapter.

elements such as carbon lower this minimum until the curve intersects the liquidus, so that a region of immiscibility appears. This accounts for the earlier discrepancies, many of the alloys examined having contained carbon. When in an equilibrium diagram a very flat shoulder is found on the liquidus curve, it may be suspected that a region of liquid immiscibility is not far removed. Another example probably presents itself in the alloys of beryllium and silver,[1] where, also, the liquidus is very flat in its middle region, and although the alloys are homogeneous, the effect of adding copper is to cause separation into two immiscible liquids.

It is not necessary to enter minutely into the nature of the modifications which it is necessary to make in such a diagram in order to embrace the cases in which either solid solutions or intermetallic compounds are formed. A comparison of the diagrams already discussed will render the construction of such a complex diagram for any particular case an easy matter.

TERNARY SYSTEMS IN WHICH A REGION OF PARTIAL MISCIBILITY OCCURS.

The formation of immiscible liquid phases is of importance in systems composed of three metals.

When, to a mixture of two metals, such as molten lead and zinc, a small quantity of a third metal is added, the mutual solubility of the two original metals is changed. For instance, if the added metal is tin, the solubility of lead in zinc, and of zinc in lead, will be increased by the addition and at the same time both liquid layers will be found to contain tin. The result is that the two layers approach more nearly to equality of composition as the quantity of tin is increased, until finally a point is reached at which the two liquid alloys become identical, and a single homogeneous liquid phase is formed. If we now construct a triangular diagram showing the composition of the liquid phases at some given temperature, we obtain a result such as that shown in Fig. 40,[2] which represents the results obtained with mixtures of lead, zinc, and tin at 650°. A mixture, the original composition of which is expressed by a point falling within the curved boundary, as at P, separates into two liquid layers, the composition of which at 650° is represented by Q and R respectively. The alloys Q and R are then *conjugate* alloys. The line joining them must pass through P, and was called by Stokes a *tie-line* or *tie*. As the proportion of tin is increased, the ties become shorter, finally vanishing at the point L. At this point the two liquid phases become identical in composition, and the mixture becomes homogeneous. Thus all points in the triangle lying outside the curve HQLRK represent homogeneous liquid alloys; whilst points within this curve

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[1] H. A. Sloman, *J. Inst. Metals*, 1934, **54**, 161,

[2] C. R. Alder Wright, C. Thompson, and J. T. Leon, *Proc. Roy. Soc.*, 1891, **49**, 174.

represent alloys which, at the given temperature, can only exist in the form of two liquid phases. The curve separating the two regions is the *critical curve*, and points falling within it represent what are termed by Alder Wright *ideal* alloys.

The diagram in Fig. 40 is an isothermal diagram, that is, it represents the state of things at a certain constant temperature, in this case 650°. If we construct similar triangular diagrams for a number of different temperatures, the area enclosed by the critical curve diminishes with increase of temperature, in accordance with the increase of mutual solubility of the two liquid phases when heated. At a sufficiently high temperature it would vanish entirely, and all mixtures of the three metals, whatever their relative proportions, would form a homogeneous liquid. In the space-model of the ternary system, the *critical surface* will thus be closed above, and the highest point of the surface will evidently be the critical point of the binary system which yields immiscible liquid phases, in this case lead-zinc (see p. 58).

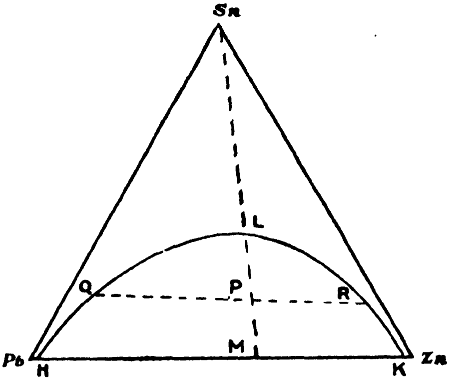

FIG. 40.—Isothermal of tin, lead, and zinc at 650°.

In accordance with the doctrine of phases, the composition of two conjugate alloys should be independent of their relative quantity. If a further quantity of tin be added to the alloy P, consisting of two liquid phases having the compositions Q and R, the composition of the mixture must move along a line SM, the ratio of lead to zinc remaining constant. The summit L must lie on this line. The tie-lines, such as QR, are not in general parallel with the base of the triangle, and the curve is then unsymmetrical.

An equilibrium of this kind may be looked at from another point of view. We may require to consider, instead of the influence of a third metal in altering the mutual solubilities of two others, the proportion in which the third metal is distributed between the two others. In the example already mentioned, tin dissolves in both the lead layer and the zinc layer. The ratio of the concentrations of tin in the upper and the lower layers may be called the *partition-coefficient* of tin between lead and zinc. The concentration of tin in the two liquid phases is not usually the same, and the tie-lines are therefore not, in general, parallel to the base of the triangle; the critical curve is consequently more or less asymmetrical. The experimental data at present available are very scanty, and are quite insufficient to allow us to calculate the partition-coefficient with any approach to accuracy.[1] The coefficient will be affected by the formation of compounds between the added metal and either of the original, partly miscible metals.

A ternary system in which a gap in the liquid miscibility occurs is that of silver, lead and copper.[2] The space-model is illustrated in elevation in Fig. 41, the divisions of which represent atomic percentages. The diagrams of the three binary systems have been given previously (silver-lead, Fig. 8; silver-copper, Fig. 15; copper-lead, Fig. 37). The freezing-point surface of the ternary system is made up of three surfaces, one of which, however, representing the separation of pure lead, is of very small area compared with the two others. The crystals separating on the surface Cu consist of a solid solution of silver in copper, and those separating on surface Ag of a solid solution of copper in silver. The region of immiscibility in the liquid state diminishes with the addition of silver, but the boundaries of the region have not been determined accurately, and they have therefore been shown in dotted lines. The surface falls towards the interior of the model. There is a ternary eutectic point E, the co-ordinates of which are

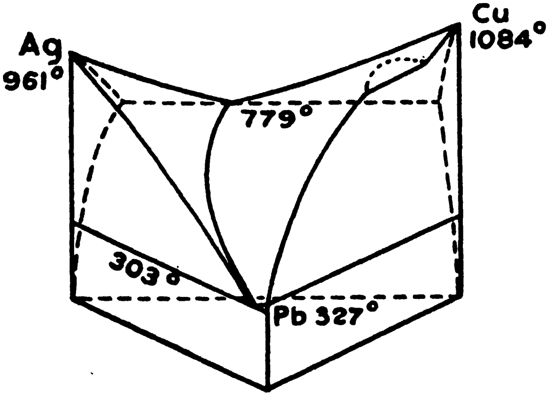

FIG. 41.—Silver-copper-lead alloys.

$$\left.\begin{array}{ll}\text{Ag} & 3{\cdot}8\\ \text{Cu} & 1{\cdot}6\\ \text{Pb} & 94{\cdot}6\end{array}\right\}\text{atomic per cent.}\quad \text{Temp.} = 302{\cdot}5^\circ.$$

The form of the diagram therefore resembles that of the lead-tin-bismuth series in having three sloping valleys meeting at a ternary eutectic point, only in this example the point of intersection lies very near to the angle of the triangle.

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[1] This aspect becomes very important in the study of metallurgical processes, as in the equilibrium between molten metals and slags in smelting operations.

[2] K. Friedrich and A. Leroux, *Metallurgie*, 1907, 4, 293.

CHAPTER IV.

PRACTICAL THERMAL ANALYSIS.

The practical work of metallography calls for means of (*a*) melting metals and alloys under such conditions as to avoid contamination; (*b*) heating or cooling specimens at known rates; (*c*) maintaining a constant temperature for long periods; (*d*) measuring temperatures with any required degree of accuracy. It is frequently necessary to exclude air or other chemically active gases, either by maintaining a high vacuum or by using an atmosphere of an inert gas, and the principal change in metallographic practice at high temperatures in recent years has been the increased use of high vacuum technique. The difficulties increase rapidly with rise of temperature above 1000°, and progress in this direction has depended largely on advances in the production of refractory materials, resistant to the action of molten and gaseous metals and their oxides, and with greatly reduced porosity.

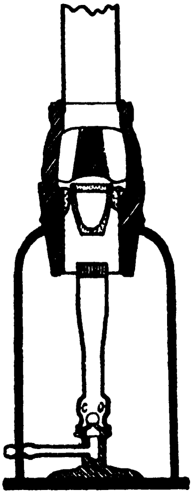

Fig. 42. — Méker crucible furnace.

For melting alloys and for the determination of freezing-points a simple gas furnace is sometimes sufficient. The Méker crucible furnace, shown in Fig. 42, has large holes for the admission of air, and firing back is prevented by a deep nickel grid. Copper can be melted in a short time. For the taking of freezing-point curves, loss of heat by radiation must be lessened by screening by two concentric cylinders of asbestos card or metal, having the space between them filled with magnesia. A lid, made of several thicknesses of asbestos card, has a central hole for the passage of the thermocouple.

Usually, however, electric furnaces are to be preferred. These are of several kinds: (*a*) resistance furnaces wound with wire or ribbon, and supplied with current at or near the standard voltage; (*b*) resistance furnaces using rods or bars of a refractory resisting material; (*c*) resistance furnaces packed with a granular material; (*d*) resistance furnaces using rings or helices of graphite or carbon—the last two types requiring heavy currents at low voltages; and (*e*) high-frequency induction furnaces. Arc furnaces and low-frequency induction furnaces may be left out of consideration, and the cathode-ray type has only a limited use.

The most generally used laboratory furnaces are of the first type. When platinum is used, a ribbon of thin platinum foil is to be preferred to wire. The temperature of the foil is never greatly different from that of the tube, and local overheating is avoided. The helix should be wound so closely that adjacent turns are separated by the shortest possible distance.

A furnace of this type, which has answered well in practice, is shown in Fig. 43. The ribbon is wound on a tube of alundum, and is enclosed in an outer alundum tube. A third concentric tube, of fireclay material, is shown, but in the simpler types the refractory insulating material immediately surrounds the second tube. A temperature of 1650° may be reached, and the furnace may be safely used at 1400° for considerable periods. The resistance when cold is 1 ohm. For temperatures up to 1200° nichrome wire or ribbon, wound on an alundum or fireclay tube, is perfectly satisfactory, and has the advantage of a very low temperature coefficient, so that the current carried remains fairly constant. It is convenient to allow the ends of the inner tube to project beyond the furnace, so that they may be closed by rubber stoppers and waxed to make a tight joint, glass tubes passing through the stoppers serving to lead gases in and out of the tube, to allow of exhaustion by a vacuum pump, or to hold the thermo-couples. At the higher temperatures, these projecting ends may be cooled by winding several turns of " compo " pipe round them, and passing a current of water. Tubes of vitreous silica are very useful for this purpose, but the wire should not be wound on to them directly. For moderate temperatures a wrapping of asbestos is used, or the silica tube may be placed inside an alundum tube which carries the winding. Helically grooved tubes of alundum are obtainable, and serve to keep the winding in place. Several other resistance alloys are available for windings, but nichrome (or one of its varieties) is in most general use.

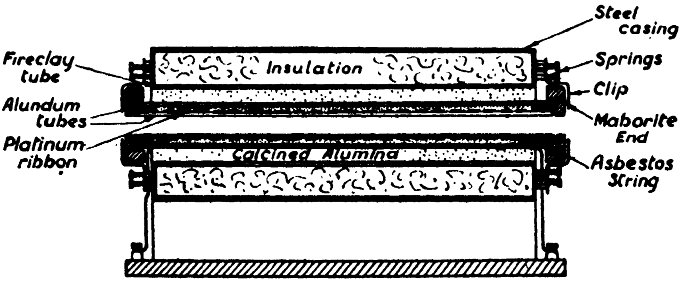

FIG. 43.—Platinum resistance furnace.

As there is a steep temperature gradient from the middle to the ends in a wire-wound furnace, it is necessary to make the heated part of the tube long in proportion to the object to be heated. Even with this precaution, however, only a short length will have a reasonably uniform temperature unless some compensating device be used. The winding may be spaced more closely towards the ends to balance the greater cooling there, or, when circumstances permit, one or more concentric cylinders of copper or other metal with good thermal conductivity may be placed inside the inner tube, being kept apart by small spacing pieces. This device gives great uniformity of temperature.

When a furnace is merely required to heat a glass or silica containing vessel, the tube may itself be made of iron, covered with asbestos paper and wound with nichrome wire, which is again covered with asbestos and enclosed in a container packed with insulating material. Such a furnace, with a pipe 37 cm. long and 10 cm. diameter, used vertically, gave a good distribution of temperature at 1000°.[1]

For work on the alloys of iron, when temperatures of 1500°-1700° are required, the use of platinum is impracticable. Molybdenum wire or ribbon gives excellent service, but being readily attacked by oxygen or water vapour when hot, it must be protected by means of a reducing atmosphere. For this purpose a mixture of nitrogen and hydrogen, prepared by "cracking" ammonia, is convenient.[2] In a typical furnace of this class [3] two concentric tubes of alundum were used, with internal diameters of 12·5 and 7·5 cm. respectively, the height of the inner tube being 60 cm. and of the outer 50 cm. The winding is on the inner tube, and is protected by the outer from contact with the refractory material used for heat insulation, in this instance crushed sillimanite. It is not practicable to make a gas-tight joint between these tubes and the casing, so steel tubes, a little larger than the refractory tubes, are made to project from the casing and closed by caps, which are provided with sighting windows, thermocouple tubes, etc. When starting the furnace, all moisture must be driven out before the winding reaches redness, otherwise the molybdenum is soon destroyed. The whole is enclosed in a steel casing with flanged ends, provided with tubes for the entrance and exit of the gas. This is prepared from ammonia gas, taken from a cylinder or generated by heating concentrated (sp. gr. 0·880) ammonia solution over a small flame, and then passed through several cracking tubes (refractory tubes packed with iron turnings) in series, heated to 600° in a nichrome furnace, in which they are placed side by side. The gas passes through a washing vessel in which any undecomposed ammonia is removed by water, and then through a drying train.

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[1] E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc.*, 1926, **112**, A, 542.

[2] W. Fehse, *Z. tech. Phys.*, 1927, **8**, 119; J. H. Andrew and D. Binnie, *J. Iron Steel Inst.*, 1929, i, 309.

[3] C. H. Desch and B. S. Smith, *ibid.*, 358.

The mixture of nitrogen and hydrogen circulates through the whole of the interior of the steel enclosing vessel, and is so regulated that a small jet escapes and is burned, the flame indicating the rate of flow. When the furnace is used in a vertical position, the gas should enter at the top and escape below.

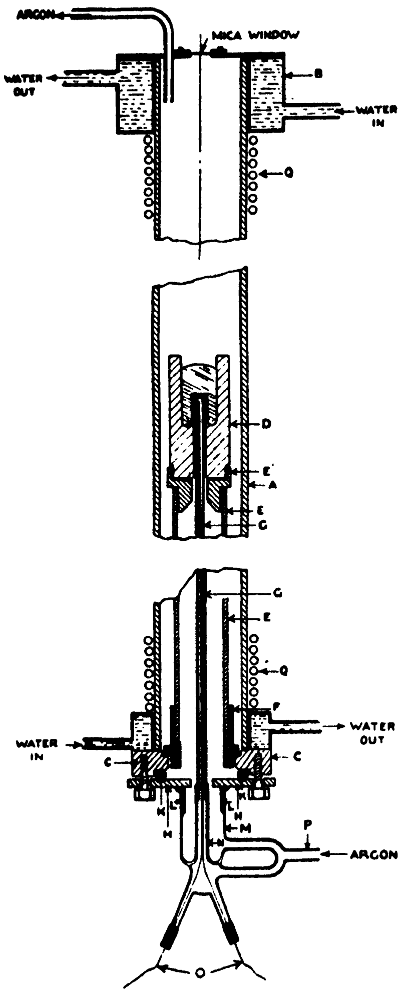

FIG. 44.—Furnace heated by silit rods. (Gayler.)

For work in vacuum or in hydrogen at high temperatures tungsten may be used, preferably wound on a tube of pure, highly fired alumina. The metal is fragile after heating, but can be used for a long time if undisturbed. A temperature of 2200° has been reached with a furnace in which a tungsten wire, 0·8 mm. diameter, is wound on an aluminium collapsible former, crushed zirconia, previously fired at 2000°, being packed around it, so that when the former is removed the wire remains embedded in the inside of a coherent refractory mass. An atmosphere of cracked ammonia is used, and the metal casing is water cooled.[1]

An alternative method of obtaining high temperatures is by the use of non-metallic resistance rods. For a simple tubular furnace, the general construction is similar to that with a wire winding, two concentric tubes of alundum or similar material being enclosed in an insulating packing, whilst rods of "silit" (silicon carbide mixture) are arranged, with their length parallel with that of the furnace, in the annular space between the tubes.[2] The resistance rods are fitted with ends of low resistance to keep down the temperature where they leave

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[1] W. Fehse, *loc. cit.*

[2] C. H. M. Jenkins, H. J. Tapsell, C. R. Austin and W. P. Rees, *J. Iron Steel Inst.*, 1930, i, 237.

the furnace, and they are conveniently grouped in series to suit the voltage of the supply of current. Such furnaces are suitable for use between 800° and 1400°. A modified form, designed for use with an atmosphere of inert gas and also, when slightly modified, for rapid quenching, is illustrated in Fig. 44.[1] The tube A is of " Pythagoras " material, 80 cm. long. It is sealed with wax into the water-cooled ends B and C, and further cooling is obtained by winding metallic tubing in a coil at E and F, to guard against softening of the wax. Heating is, as in the furnace just described, by silit rods, and by blowing nitrogen round them the working temperature may be taken as high as 1600°. The metal is placed in a crucible of hard alumina of the shape shown in Fig. 45, and is supported by a refractory tube G, the lower end of which is fixed in a brass fitting which can be made gas-tight. The thermo-couple is enclosed in a Pythagoras tube inserted into the mass of the crucible from below. Purified argon is circulated through the interior to prevent oxidation. This apparatus was used successfully in the study of the alloys of iron and manganese, which present special difficulties from their corrosive action, both when molten and in the form of vapour, on refractory material. When required for quenching, a gas-tight top is fitted, through which the thermo-couple passes, as well as wires forming a loop from which the specimens to be quenched are suspended. Argon is circulated through the apparatus. At the required moment, the suspending wire is fused by an electric current, immediately after removing the plate which closes the lower end, allowing the specimens to fall into a vessel of water. Other devices for quenching, allowing of very high rates of cooling, are described later.

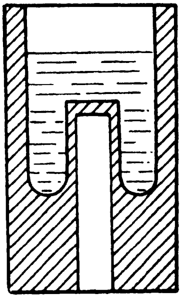

FIG. 45.—Crucible with inverted tube.

Furnaces with granulated carbon resistances are extensively used on the Continent, but have not found favour in England for metallurgical work, although they are used as a convenient means of reaching high temperatures in work on refractory materials. Granulated carbon, usually crushed electrode material, is sifted and graded, and packed into a space surrounded by refractory material, contact being made by means of carbon blocks (Fig. 46).[2] Owing to uneven packing, it is difficult to avoid local hot spots caused by arcing, and in the course of use the granules tend to pack more closely, so that the resistance, and therefore the attainable temperature, falls.

Rings of graphite, machined to shape and laid flat on one another so as to build up a tubular resistance, also require a heavy current at low voltage.[3] Temperatures of well over 2000° may be reached, and

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[1] M. L. V. Gayler, *J. Iron Steel Inst.*, 1933, ii, 293.

[2] H. Harkort, *Metallurgie*, 1907, 4, 617; K. Friedrich, *ibid.*, 778. This type of furnace has been much used by Tammann and his students.

[3] W. Rosenhain and E. A. Coad-Pryor, *Trans. Faraday Soc.*, 1919, 14, 264.

this type of furnace is useful for firing refractory materials, although it has been superseded for metallographic work. A current of nitrogen should be kept passing through the furnace, but on account of the high gas content of graphite, some contamination by carbon is unavoidable. The resistance may be varied within limits by altering the pressure on the rings.

A carbon helix is often used as the heating element for operations conducted in a good vacuum. In one such type, illustrated in Fig. 47,[1] the helix is made by cutting a helical slot in a tube of hard carbon, 30 cm. long and 4 cm. inside diameter, the thickness of the tube being 6·5 mm. It is insulated from the enclosing carbon tube by porcelain collars. The brass vessel, which can be evacuated, has glass connections above and below and is enclosed in a water jacket.

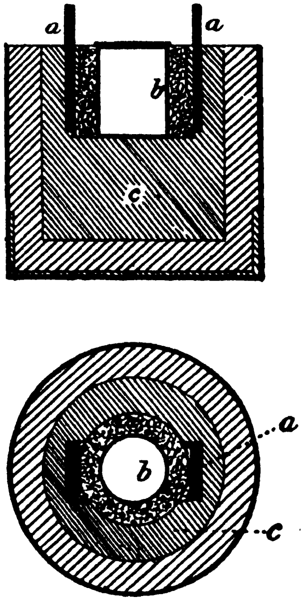

FIG. 46.—Granular carbon furnace.

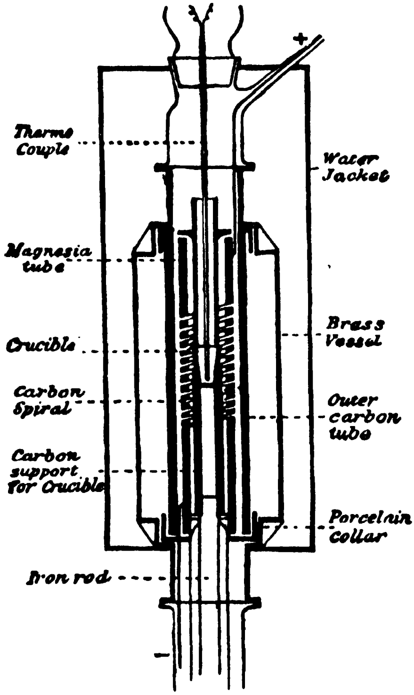

FIG. 47.—Carbon spiral vacuum furnace.

The resistance unit may take the form of a metallic tube, through which the heating current is short-circuited. For very rapid heating to 1600° an iridium tube has been used with success in the study of

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[1] A. Müller, *Metallurgie*, 1909, 6, 145.

silicates,[1] but the volatility of iridium is against its use for metals. A thin cylinder of molybdenum is more convenient, the ends being cut into strips, bent over, and clamped to water-cooled rings, which are connected by water-cooled tubes to heavy terminals. The metal case which contains the furnace is itself water-cooled and gas-tight, and the use of refractories is avoided by inserting a number of concentric radiation screens of molybdenum sheet. A high vacuum is employed, and very rapid heating to 2000° is practicable, although the power consumption is high. Such a furnace is not suitable for work with metals having an appreciable vapour pressure.[2] Much larger furnaces may be constructed by using parallel strips of molybdenum in place of a single tube, and an inner tube of refractory material may then be inserted to prevent the access of vapours from the crucible to the heating elements.[3]

It is sometimes convenient to heat the metallic specimen directly by the passage of an electric current through it, without the interposition of a separate heating element. This plan is often adopted in X-ray work at high temperatures (see Chap. X.) and finds other applications. The specimen is suspended in a vertical vessel, which can be evacuated or filled with an inert gas, the suspending wire or rod serving to carry the heating current, whilst the connection at the lower end, in order to allow for expansion, is made by a wire or rod dipping into mercury. Furnaces of this type are used technically in the sintering of such materials as tungsten. On the laboratory scale they may be constructed very simply, and their use avoids many complications.[4]

When a resistance furnace is being used for the taking of cooling curves, it is usual to cut off the current and to allow the furnace to cool by radiation, the rate of cooling then depending mainly on the efficiency of the thermal insulation. To obtain a more regular rate of cooling, the heating current may be reduced continuously by means of a wire resistance wound on a porcelain cylinder and slowly rotated by a motor.[5] Control by a liquid resistance has been used for the same purpose.[6]

The gradient furnace, which provides a more efficient means of attaining the same end, consists of a vertical tube furnace, the upper part of which only is wound with a heating coil, which is maintained at a constant temperature. With a tube 60 cm. long, wound only for a length of 12 cm. at the upper end, the whole being enclosed in a porous magnesia covering, a regular temperature gradient is found to exist in the tube, when the conditions have become constant.

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[1] A. L. Day, E. S. Shepherd and F. E. Wright, *Amer. J. Sci.*, 1906, [iv], **22**, 265; K. Friedrich, *Metallurgie*, 1908, **5**, 703.

[2] N. R. Davis and C. Sykes, *J. Soc. Chem. Ind.*, 1931, **50**, 506.

[3] G. Burrows and F. L. Clark, *J. Sci. Instruments*, 1933, **10**, 248.

[4] Davis and Sykes, *loc. cit.*; P. P. Cioffi, *J. Franklin Inst.*, 1931, **212**, 601.

[5] W. Plato, *Z. physikal. Chem.*, 1906, **55**, 721.

[6] A. Portevin, *Rev. Métall.*, 1908, **5**, 295.

Instead, therefore, of allowing the furnace to cool down, as in the usual way of working, the specimen is lowered at a uniform rate through the furnace. This is done by suspending the metal, if a solid, or the crucible if a molten metal is being examined, from a fine wire which is lowered by a governed gramophone or electric motor or by a heavy plunger descending in an oil cylinder. The thermo-couple must be attached to the specimen and move with it. The rate of cooling is readily varied within wide limits by simply varying the speed of descent of the specimen.[1] The cooling curve of a substance which does not undergo any transformations within the range of the experiment is nearly a straight line in such a furnace, provided that the range of temperature is below 1000°. The smoothness of the gradient is improved by placing inside the winding a heavy copper or nickel sleeve.

The gradient furnace is not suitable for the most refined work, as a vertical temperature gradient is necessarily set up in the specimen itself, so lessening the sharpness of the arrests, especially when small.

An improvement on Plato's method, which gives a strictly linear fall of temperature with time, makes use of control by a photo-electric cell.[2] The E.M.F. generated by a thermo-junction near the heating element of the furnace is opposed to the E.M.F. from a potential divider in a circuit which includes a mirror galvanometer. The beam of light reflected by the galvanometer mirror falls on a photo-electric cell, which controls a thyratron, and through it the resistance included in the furnace heating circuit. When the beam falls on to the cell, the conditions being such that the E.M.F. from the furnace thermo-couple exceeds that from the potential divider, an additional negative bias is applied to the grid of the thyratron, and the anode current is suppressed, thus stopping the small electric motor by means of which resistance is removed from the heating circuit. Meanwhile the E.M.F. supplied by the potential divider is increasing and soon exceeds that from the thermo-couple. The galvanometer is now deflected in the opposite direction, and the beam leaves the cell, so that the original grid bias of the thyratron is restored. Anode current again flows, and the motor actuated by it removes resistance from the supply circuit until the cycle of operations is completed. The speed of rotation of the cylinder carrying a helix of wire which forms the potential divider is regulated to give the required rate of change of temperature with time. Provided that the thermo-couples used for furnace control and for the thermal analysis of the specimen are of the same materials, the thermal curves in the absence of thermal changes are linear even if the relation between E.M.F. and temperature of the couple is not linear.

Induction furnaces of the older type, with an iron core, are no longer used, but the high-frequency or coreless type is finding increasing uses, in the laboratory as well as in industry. Heating is brought

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[1] W. Rosenhain, *J. Inst. Metals*, 1915, **13**, 160.

[2] F. Adcock, *J. Sci. Instruments*, 1935, **12**, 285.

about by eddy currents generated in the metal to be melted, by induction from a coil which surrounds the crucible and its contents, and carries an alternating current of such frequency as to produce an appreciable " skin effect." The actual frequency may vary within wide limits. Three types of high-frequency induction furnaces are in use in metallographic laboratories, the alternating current being supplied from (*a*) a spark gap, (*b*) a motor-driven generator, or (*c*) a power valve such as is used in radio work.

(*a*) The Ajax-Northrup furnace was introduced for industrial purposes, but has been replaced by larger units, and many of the earlier industrial furnaces have now been set up in laboratories, where their size is found convenient for melting metals to form alloys, or for refining metals in a vacuum. The high-frequency current is produced by supplying an alternating current of high voltage from a transformer to a pair of water-cooled copper electrodes supported so that their lower ends are just above a bath of mercury, contained in a vessel which is also water-cooled. The electrodes pass downwards through stuffing boxes in insulating sleeves of silica, and the vessel is kept full of hydrogen or of alcohol vapour during the working of the generator. In the original form [1] the power was varied by raising or lowering the electrodes by an external gear, but as this involves the difficulty of keeping the stuffing boxes tight, and the electrodes are apt to get out of alignment, an improved arrangement has fixed electrodes, the length of the spark being varied by altering the level of the mercury in the bath.[2] This is done by connecting the spark-gap vessel with another iron vessel in which an iron armature can be rotated in such a way as to displace mercury, so giving smoother working.

The generator requires a bank of condensers, the circuit being arranged as shown diagrammatically in Fig. 48. The high frequency current is supplied to a primary coil, consisting of flattened tubing of high-conductivity copper, wound as closely as is consistent with proper insulation. This surrounds the crucible, and the secondary circuit is formed by the charge itself, if of conducting material, or by the crucible in such operations as the melting of a silicate slag in a graphite container.

For the larger furnaces, the spark gap has been superseded by the motor-driven rotary generator, giving a frequency of 8000-10,000 cycles a second, and this pattern is now made in sizes small enough for laboratory purposes.[3]

Very high frequencies are most easily obtained by the use of radio

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[1] E. F. Northrup, *Trans. Faraday Soc.*, 1917, **13**, 212 ; *Trans. Amer. Electrochem. Soc.*, 1919, **35**, 69. Another type of generator, using a rotating spark-gap in place of the quenched spark in mercury, was devised by G. Ribaud, *Techn. Mod.*, 1923, **15**, 225, but is much less convenient.

[2] W. Rosenhain and F. Adcock, *Electrician*, 1928, **101**, 395.

[3] F. Wever and W. Fischer, *Mitt. K.W. Inst. Eisenforsch.*, 1926, **8**, 149 ; and for a convenient application of this type, H. A. Sloman, *Iron Steel Inst., 6th Rep. Com. Heterogeneity of Steel Ingots*, 1935, 71.

valves, and furnaces on this principle are convenient, especially for vacuum melting. A simple furnace, which has given constant good service over a number of years,[1] makes use of a single thermionic valve oscillating at 10^6 cycles/second, delivering 2 to 3 kw. to the inductor coil, which consists of 7 to 10 turns of water-cooled copper tubing wound round a silica tube 6 cm. in diameter. This tube is closed at the upper end by a steel flange and a glass window, whilst at the lower end it makes a tight flanged joint with a mercury vapour pump. Charges of 20 to 30 grams of metal are brought up to the melting-point in a few minutes, provided that the metal has not a high vapour pressure. The presence of metallic vapour allows an electrodeless discharge to occur, and the efficiency of heating falls at once. When it is impracticable to prevent this by maintaining an atmosphere of an inert gas, the vapour may be confined to a small part of the cross-section by placing a narrow silica chimney on the top of the crucible.

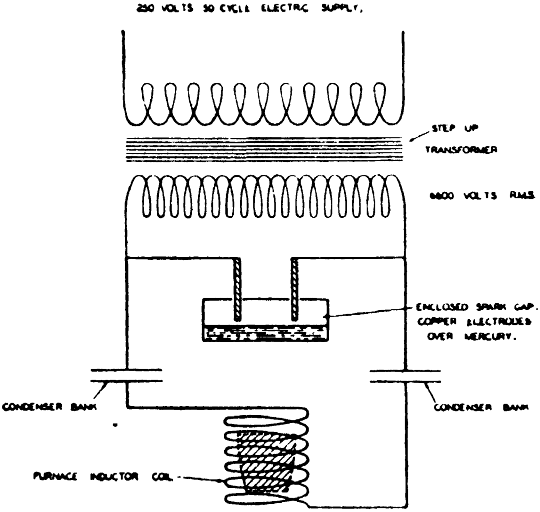

FIG. 48.—Circuit for spark-gap induction furnace.

Details of the electrical arrangements of another furnace, which has been used in a great variety of researches, are given in a paper by Adcock.[2] Two silica valves are arranged on the " push-pull " principle, and the installation is provided with a number of safety devices intended to guard against damage by accidental overload. The general construction of the furnace itself is illustrated in Fig. 49, and in this form the apparatus has been used for the exact determina-

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[1] T. E. Allibone and C. Sykes, *J. Inst. Metals*, 1928, **39**, 173 ; T. E. Allibone and N. R. Davis, *Metropolitan-Vickers Gaz.*, 1925, **9**, 119.

[2] F. Adcock, *Trans. Faraday Soc.*, 1930, **26**, 544.

tion of melting-points and of transformations in the solid state at high temperatures.

The high-frequency furnace finds its chief application in experiments which involve either a high vacuum or the maintenance of a special atmosphere. For such purposes the crucible must be enclosed in an outer vessel which can be exhausted. This may be of pyrex glass, or of vitreous (translucent) or transparent silica. Ground joints are to be preferred, and it is often necessary to provide external cooling by water, which may be arranged without detriment to the heating. The main vessel is conveniently of vitreous silica, but where a head is required for connection to vacuum pumps, glass or transparent silica is preferable. It is advisable to keep down the quantity of refractory material in the heated zone as far as possible, as these porous solids retain gas very persistently, and long pumping is required before a good vacuum can be obtained. Concentric cylinders of bright molybdenum, or of silver for lower temperatures, serve as radiation screens and may often replace refractory material for heat insulation.

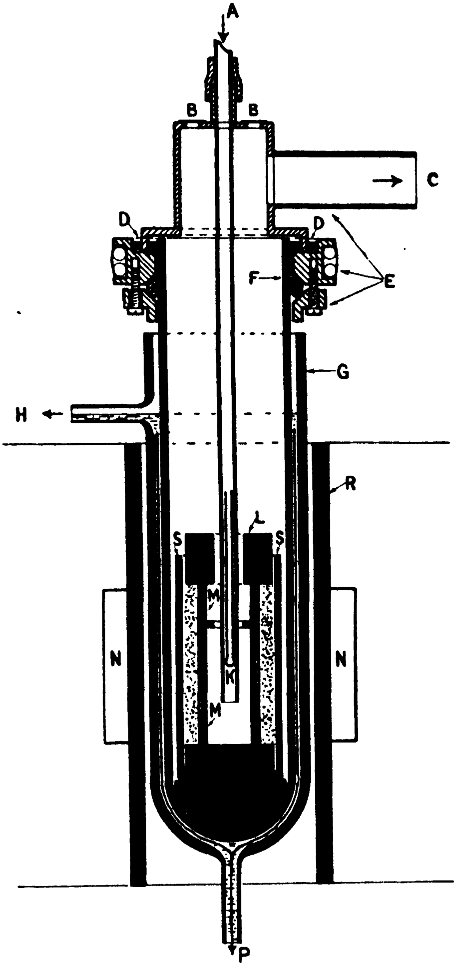

FIG. 49.—Valve induction furnace (Adcock). A refractory tube, B window, C connection to pump, D wax seals, E brass water-cooled head, F silica furnace tube, G outer jacket of silica, containing earthed screen, H water outlet, K thermo-couple, L alumina radiation screen, M liner of pure alumina, enclosed in molybdenum heating sleeve, N inductor coil, P water inlet, enclosing earthing lead for screen.

Rubber connections should be avoided wherever possible. When they are unavoidable in vacuum experiments they should be coated with wax. Ground joints are made tight by a very small quantity of "Apiezon" grease, whilst flanges, bungs, etc., should be coated on the outside with sealing wax or, as being less brittle, with one of the specially made vacuum waxes.

REFRACTORY MATERIALS.

The proper choice of refractory materials for crucibles, tubes, vacuum vessels, boats, and other purposes is of great importance in metallographic research, and the more so the higher the temperature. It may even be said that at and above the melting-point of iron the principal limitation to new research is set by the need of suitable refractory vessels. Not only mechanical strength at high temperatures is required, but also resistance to chemical action and, in a very important field, impermeability to gases. Materials which are satisfactory in one or two of these respects may fail in the third, and the progress of investigation at high temperatures is intimately linked with the progress in the production of what are sometimes called "super-refractories," for use above the range of temperature for which materials are commercially readily obtainable.

For crucibles, fireclay or plumbago, the latter containing graphite and clay, may be used for general melting purposes when the temperature is not too high. At quite low temperatures, as in the examination of amalgams, pyrex glass may be used. Metals having a strong reducing action, however, absorb silicon when melted in vessels containing silica. For metals which do not react with carbon, crucibles turned from a block of Acheson graphite are satisfactory even for the highest temperatures, and are sometimes the only possible, but metals of the iron group are readily carburized, and unless the furnace can be kept free from traces of oxygen, carbon monoxide will be formed, which is absorbed by many metals. The attack of slags on fireclay or plumbago may be prevented by "brasquing," that is, by lining either with a paste of graphite or alumina with syrup or tar, or with fused and ground magnesia, mixed with a little magnesium chloride.

Furnace tubes are obtainable in several materials. Alundum, a slightly impure form of alumina with good heat-resisting properties, is one of the most generally useful. The same material, in the form of a powder mixed with a silicate, can be made into a paste and used as a cement for covering metallic windings and for making joints. "Pythagoras" mass is used in the making of furnace and thermocouple tubes which are impervious to gases up to about 1450°, and find wide application in metallographic research. Vitreous and transparent silica are invaluable, but they become porous to gases at comparatively low temperatures, being permeable to hydrogen at 1000°, and to helium even at atmospheric temperatures, although to a minute extent.

For work with pure metals at high temperatures, as in the study of the alloys of iron at their melting-points, special refractory materials are essential and are not readily obtainable. In the course of many years, the National Physical Laboratory has found it necessary to prepare vessels and objects designed for specific purposes, from the purest possible materials and with precautions against contamination. A description of the principal materials and methods has been published.[1] When the presence of silica is not a disadvantage, mixtures of pure alumina and china-clay make strong and convenient crucibles. The alumina is previously fired at 1550°, and is mixed with three times its weight of pure china-clay. The mixture is "slip-cast," that is, it is suspended in water with a small addition of sodium carbonate and sodium silicate, and poured into a mould of plaster of Paris. After a short interval, the slip is poured out again, leaving a shell on the inside of the mould. As the plaster withdraws further water from it, the shell shrinks, and may be removed and dried. After firing at 1550°, such crucibles may be safely used up to 1600°. A denser material, for muffles, is obtained by using four times as much clay as alumina.

A mixture of 60 per cent. of Carborundum (silicon carbide) and 40 per cent. of china-clay, fired at 1480°, is readily slip-cast, and is useful for outer sleeves (see below), for supporting blocks, and for recuperator tubes.

Of materials free from silica, pure alumina has been found the most generally useful. It is very refractory, chemically very inert, and capable of being fired until hard and translucent. It is strong enough to bear machining on a lathe with carbide tools, a property which is useful when exact dimensions are necessary in complicated apparatus. Being non-plastic, it must be moulded with care, small quantities at a time being rammed into a metal mould with a wooden rod. The core is removed by a screwing motion. Turner describes a mould of aluminium in three sections for large crucibles (30 cm. high), a paper lining being inserted to hold the moulded mass while the sections are separated. The metal core is held in place by being screwed into the sections when assembled.

For the most refined work, alumina of high purity, obtained in the form of a powder passing a sieve of 120 meshes to the inch, is treated with dilute hydrochloric acid,[2] which roughens the grains and gives greater strength to the mass during firing. Moulded as described, these crucibles are fired at 1560°, standing on a layer of loose alumina powder. For thin-walled vessels, which cannot be made in a mould, the powder is made plastic by grinding until very fine in an iron mill and heating to 90° in hydrochloric acid. Iron is thus removed, and the particles are roughened. The acid is removed by decantation, and the suspension is slip-cast. The mass does not shrink easily from the plaster mould, but is made to do so

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[1] D. Turner, *Trans. Faraday Soc.*, 1931, **27**, 112; amplified in *N.P.L. Coll. Researches*, 1935, **25**, 409.

[2] O. Ruff and W. Goebel, *Z. anorg. Chem.*, 1924, **133**, 220.

by heating with a Bunsen flame. The shrinkage at 1560° is only about 4 per cent., but when a highly impermeable vessel is required firing is carried to 1900° or 2000°, when the mass becomes very hard and translucent, with a shrinkage of 20 to 25 per cent. Not only crucibles, but boats, and objects of special form, such as the container for use in optical pyrometry with molten metals (p. 67), may be made from this material. Where crucibles of pure alumina are not available, fire-clay crucibles may be lined with a mixture of powdered alumina with 7 per cent. of calcium fluoride and a strong solution of gum. After drying in air, the crucibles are heated very slowly to 800°, and then to 1300°. Such linings resist molten alloys of iron or manganese with aluminium.[1, 2]

Pure thoria is even more refractory and inert than alumina, and is handled in the same way. It is too costly for general use, but alumina crucibles may be lined with thoria by mixing the oxide with gum and water, and pouring the slip several times into and out of the crucible. Pure beryllia has been used for research on beryllium,[3] the oxide being moulded as above. Magnesia has been found less useful, and zirconia, although very refractory, is difficult to purify and is highly reactive at high temperatures. Above 2000°, however, the use of magnesia, thoria, or zirconia is almost unavoidable.

Thin-walled, flat-bottomed pots of pure alumina are useful for melting operations in the high-frequency induction furnace. They may be made up to 35 cm. high and 15 cm. diameter, but as severe temperature gradients may occur, they are liable to crack. To guard against damage, they are enclosed in sleeves made of slip-cast Carborundum mixture, the space between being packed with powdered alumina, previously fired at 1550°. Even should the pot crack, the molten metal does not escape.

Thermo-couple and other tubes have to be sufficiently impervious to protect the couple against attack by either molten metal or vapour. For many purposes Pythagoras tubes answer well, but for pure iron and its alloys tubes of pure alumina are necessary. An extrusion press, capable of making tubing from fine capillary to 25 mm. diameter, is described by Turner (*loc. cit.*). The powder must be made plastic by mixing with a little cellulose acetate solution ("aeroplane dope") and is flexible after extrusion, and hard after firing. Such tubes are not quite impervious, but some success has been obtained in glazing them externally with an oxy-hydrogen flame, after first firing at 1800-1900°.[4] A glazing process was also employed[5] for shallow crucibles of magnesia, required to contain

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[1] A. H. Jay, *J. Iron Steel Inst.*, 1932, i, 427.

[2] Crucibles and tubes of sintered alumina are now supplied by the Thermal Syndicate and, under the name of "Sinterkorund," by the Deutsche Gold- und Silber-Scheideanstalt.

[3] A. C. Vivian, *Trans. Faraday Soc.*, 1926, **22**, 211.

[4] F. Adcock and D. Turner, *J. Sci. Instruments*, 1930, **7**, 327.

[5] F. S. Tritton, *Proc. Roy. Soc.*, 1925, **107**, A, 287.

ferrous oxide, which attacks all refractory materials. The crucibles were rotated under an electric arc, so as to cover the surface with an impermeable glaze.

PREPARATION OF ALLOYS.

Alloys are generally prepared by fusing together their components. When these are readily fusible, the operation presents no difficulty, as it is sufficient to introduce the weighed metals into a crucible and to heat until molten, when the mass is thoroughly stirred to ensure complete admixture. It is not possible to alloy metals of very different melting-points in this way. If zinc and copper are heated together the zinc is mostly lost by volatilization and oxidation before the melting-point of the copper is reached. The copper should, therefore, be melted first, and the zinc added to it. The zinc should be in coarse pieces, and should be immediately pushed under the surface of the copper, the mass being stirred with a fireclay or carbon rod after each addition. As the first fragments of zinc are added, the high temperature of the molten copper causes some volatilization of zinc, and a white flame is produced, white flakes of zinc oxide being formed. As the temperature of the alloy is lowered by successive additions of zinc, the " flaring " becomes less marked. The loss of zinc, amounting to about 2 per cent. when making up an alloy of 60 per cent. Cu and 40 per cent. Zn on a small scale, must be allowed for in weighing out the quantities of metal to be used.

Aluminium should be added in the same way as zinc, as if melted alone it becomes covered with a thin, but very tenacious layer of aluminium oxide, which coats any solid metal on its introduction and thus prevents alloying. When aluminium is added to molten copper a great rise in temperature is observed, owing to reaction with dissolved copper oxide, the alloy often becoming white-hot, in spite of the cooling due to the introduction of the cold metal.

Special difficulties are presented by highly reactive metals, such as sodium, and by metals which have a high vapour pressure at the temperature of operation. Alloys with arsenic are troublesome to prepare, on account of the great volatility of this element, but by using an electric furnace with carbon tube resistance, and heating very rapidly to a high temperature, alloys with platinum containing from 2·7 to 28·3 per cent. of arsenic have been prepared.[1] It is generally preferable to make a rich alloy of the metal in question with arsenic, and to dilute this by melting with successive larger quantities of the second component. Alloys containing arsenic, selenium, or tellurium are conveniently prepared in porcelain tubes provided with a constricted neck, which may be sealed in the oxyhydrogen flame. A tube is sealed in to receive the thermo-couple.[2] In the study of the

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[1] K. Friedrich and A. Leroux, *Metallurgie*, 1908, **5**, 148.

[2] W. Heike, *Intern. Z. Metallogr.*, 1913, **4**, 143; Q. U. Mansuri, *Trans. Chem. Soc.*, 1923, **123**, 214.

phosphides of tin it has been found a satisfactory plan to enclose the components in a sealed glass tube and to seal the couple, enclosed in a very thin glass sheath, to the wall of the tube. Small quantities of oxidizable metals or of metals which dissolve with difficulty on account of their high melting-point, are added in the form of a rich alloy with the solvent metal previously prepared.

With high-frequency furnace melting it is usually necessary to allow the ingot after fusion to solidify in the crucible, but with metals of moderate melting-point, using external heating, it is often practicable to construct an apparatus for casting the alloy in a chill mould without exposure to the air. Such an apparatus, used for alloys of sodium with tin and similar materials, is illustrated in Fig. 50.[1] The alloy is melted in the tube A, which may be of resistance glass or other refractory material, which is packed round with asbestos. By tilting through a right angle, the liquid is caused to flow into the thick-walled split copper mould, which causes rapid solidification, giving a homogeneous ingot.

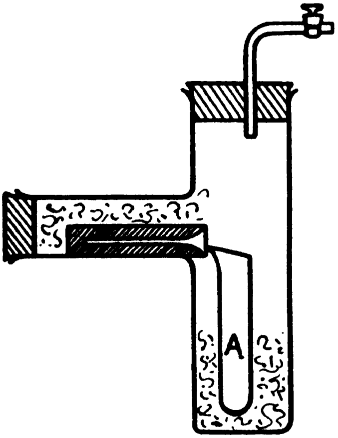

FIG. 50.—Tube for volatile alloys.

When the conditions are such that the metal may be exposed to the air during pouring, it is often sufficient to cover the surface with powdered charcoal or with a flux, and to hold this back at the moment of pouring into the mould. A jet of coal gas is a further precaution against oxidation. In casting magnesium and its alloys, powdered sulphur is sprinkled on the surface of the mould, the atmosphere of sulphur dioxide which is formed being the best means of preventing oxidation.

Moulds for chill-casting are conveniently made of cast iron, divided lengthwise and held together by a clamp. The inner surfaces should be rubbed with graphite and the mould dried by warming before use. For more rapid cooling the moulds are best made of massive copper, or of thin sheet copper immersed in water.

Simple sand moulds are easily prepared, a smooth wooden rod being used as the pattern around which the moulding sand is rammed. A sufficient head of metal must be allowed, so that gas bubbles, etc., will collect in the upper part of the rod, which is cut off and rejected. A short length at the lower end should also be rejected, as it is liable to contain sand swept down by the first rush of metal into the mould.

To guard against errors due to segregation in the ingot, a small piece should be cut from the upper and also from the lower end of the rod for microscopical examination and chemical analysis. Oxi-

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[1] W. Hume-Rothery, *J. Inst. Metals*, 1928, **40**, 65.

dizable alloys of low melting-point may be cast into rods by drawing into glass tubes previously warmed and coated with carbon from a smoky flame. A filter pump is used for suction. At higher temperatures silica tubes may be used.

Alloys in which the specific gravity of the crystals which separate first differs widely from that of the liquid present difficulties in the taking of cooling curves from the liquid state on account of segregation. To overcome these difficulties stirring is necessary. A simple arrangement of a propeller-shaped stirrer of silica, which can be lifted out when the eutectic point is approached, was used for the alloys of lead, tin, and antimony, in which the liability to segregation is strongly marked.[1] For reactive metals, such as the alloys of magnesium, a more elaborate apparatus has proved useful, in which the crucible, in this instance of iron, and closed with a cap, is mounted with its axis horizontal, and the thermo-couple tube, which fits into a steel tube screwed into the bottom of the crucible, rotates with it. The whole is mounted on a horizontal shaft, through the axis of which the thermo-couple tube passes, which is rotated by means of a worm-drive from a motor. The thermo-couple leads make contact through copper rings which rotate in mercury cups.[2]

In furnaces used either for melting or for annealing it is frequently necessary to exclude air or oxygen. Nitrogen is often used as an inert gas, but the nitrogen supplied in cylinders always contains a little oxygen, which is difficult to remove, and is sufficient in quantity to spoil an experiment in which its absence is important. Passing over copper gauze heated to 600° and then over iron gauze heated to 800° will remove oxygen if the iron gauze be rendered active beforehand by oxidizing and then reducing in hydrogen. The water formed is absorbed in drying towers containing calcium chloride, the last traces being removed by passing through a tube immersed in a freezing mixture of solid carbon dioxide and acetone. Nitrogen must not be used for metals which combine with it, such as chromium or the reactive metals of the alkaline earth group, and where hydrogen is for any reason inadmissible resort must be had to one of the rare gases, usually argon. This is purified in the same way as nitrogen, but as it usually contains some nitrogen, this must be removed by passing over metallic calcium at 450° or magnesium at 600°.[3]

The circulation of a limited quantity of gas through a system is of advantage when a costly gas, such as argon, is used, and is also advisable when a gas is being employed to remove some impurity, and contamination must be avoided, as in the treatment of solid electrolytic chromium with hydrogen for the removal of oxide. Any trace of residual gas in the hydrogen is rendered of less effect by the use of the same gas over and over again, the system including absorbing vessels to retain the water formed. The circulating pump

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[1] F. D. Weaver, *J. Inst. Metals*, 1935, **56**, 209.

[2] R. J. M. Payne, *J. Sci. Instruments*, 1934, **11**, 90.

[3] F. Soddy, *Proc. Roy. Soc.*, 1906, **78**, A, 429.

is operated electro-magnetically, and the arrangement lends itself well to use with a high frequency induction furnace.[1]

Heating in a high vacuum finds even wider application in metallography than the use of inert atmospheres, and the most striking change in the appearance of metallographic research laboratories in recent years has been the increase in the number of pumps for the production of high vacua, attached to apparatus for performing a great variety of operations. The older, slow-working Sprengel and Töpler pumps have been largely superseded by vapour pumps employing mercury or organic liquids, with their very high speed of exhaustion. However, it must not be supposed that such costly equipment is always essential. For much of the work of metallography, even of high precision, a Töpler pump is quite satisfactory, provided that the experimenter has the patience to repeat the lifting and lowering of the mercury reservoir often enough.

If advantage is to be taken of the high speed of modern pumps, all connections must be of wide bore, as the efficiency of exhaustion falls off rapidly with diminution of the diameter of the connecting tubes. This also involves the use of large taps. Wherever possible, joints should be made by sealing glass or silica, or by ground joints, which are now procurable of standard taper. Rubber connections must be used as sparingly as possible, and as the soundness of even thick pressure tubing leaves much to be desired, rubber connecting pieces should be fitted tightly and then completely waxed over. Metal flanges, lapped together and fitted with a mere trace of " Apiezon " grease, having a negligible vapour pressure, make an excellent joint, and may be secured by covering on the outside with vacuum wax.

Mercury vapour pumps are most generally used for the production of high vacua. They must be supplemented by rotary backing pumps in order to exhaust down to the stage at which a vapour pump becomes operative. For details of pumping methods and of gauges for measuring low pressures, reference must be made to special works.[2] The presence of mercury vapour, even at a very low pressure, is often objectionable, and it is then necessary to interpose a liquid air trap or other device between the pump and the vessel being exhausted. Mercury may be dispensed with by using in its place a specially purified oil of negligible vapour pressure at ordinary temperatures,[3] or butyl phthalate.[4] With these organic liquids, great care must be taken to ensure that the backing pressure is sufficiently reduced before beginning to heat the vapour pump, or the temperature

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[1] F. Adcock, *J. Iron. Steel Inst.*, 1927, i, 369.

[2] See S. Dushman, *J. Franklin Inst.*, 1931, **211**, 689, with list of works of reference; W. Kerris, *Arch. Techn. Messen*, 1936, Z. 69. Very full details are given in W. Espe and M. Knoll, "Werkstoffkunde der Hochvakuumtechnik," Berlin, 1936.

[3] C. R. Burch, *Proc. Roy. Soc.*, 1929, **123**, A, 271.

[4] K. C. D. Hickman and C. R. Sandford, *Rev. Sci. Instr.*, 1930, **1**, 140.

will increase sufficiently to cause a break-down of the organic molecules, producing uncondensable gas.

In concluding this section, it may be well to add a few general remarks on the preparation of alloys for thermal examination. It is of the highest importance that the metals selected should be of the highest purity. An amount of impurity which has only a small effect on the freezing-point may have a greater influence on transformations in the solid state, especially when these consist in changes in solubility with temperature, producing marked changes in physical and mechanical properties, as in the age-hardening alloys. Moreover, it is important that the properties of alloys should be determined with accuracy on the purest available materials. Chemical and metallurgical literature is unfortunately overburdened with data respecting physical properties of alloys determined, often with great labour, from materials taken from a laboratory stock without special chemical investigation. This fact is largely responsible for the wide discrepancies between data in the standard tables of constants.

In beginning an investigation of a system of alloys, trouble should always be taken to secure supplies of pure materials for their preparation. Researches at the National Physical Laboratory have called for elaborate studies of methods of purification before determining any portion of the equilibrium diagram, as in the instances of chromium,[1] manganese,[2] silicon,[3] magnesium,[4] and iron.[5] Certain metals may be obtained commercially in a state of purity which cannot be surpassed by laboratory methods, such as gold and silver, which lend themselves to very careful purification, whilst zinc has been manufactured with a purity of 99·996 per cent.,[6] and aluminium of 99·997 per cent.[7] Deoxidized copper may reach a purity of 99·996 per cent.[8] and lead over 99·99 per cent.[9] In important work, the metals used should always be analysed before use, quantitative spectrographic analysis being called for when the quantities of impurities are very small.[10] As a rule, alloys should be analysed after determining their transformation points, etc., to ensure that no change in composition has occurred in the course of the experiment. This is essential when one of the components is volatile, as zinc or

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[1] Spectroscopically pure. F. Adcock, *J. Iron Steel Inst.*, 1927, i, 369.

[2] 99·99 per cent. M. L. V. Gayler, *ibid.*, 1927, i, 393.

[3] 99·94 per cent. N. P. Tucker, *ibid.*, 1927, i, 412.

[4] 99·97 per cent. J. L. Haughton and R. J. M. Payne, *J. Inst. Metals*, 1934, **54**, 275.

[5] 99·987 per cent. F. Adcock and C. A. Bristow, *Proc. Roy. Soc.*, 1935, **153**, A, 172.

[6] J. R. Freeman, F. Sillers, and P. Brandt, *U.S. Bur. Stand. Sci. Paper*, 1926, **20**, 661.

[7] G. G. Gautier, *J. Inst. Met.*, 1936, **59**, 129.

[8] W. R. Webster, J. L. Christie, and R. S. Pratt, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **104**, 166,

[9] R. S. Russell, *Proc. Astral. Inst. Min. Met.*, 1934, **95**, 125.

[10] See D. M. Smith, " Metallurgical Analysis by the Spectrograph," London, 1933.

arsenic, or easily oxidized, as manganese. It is also important to be on guard against contamination during melting or annealing, as by the taking up of silicon by reduction of refractory materials containing silica, or the converse process of loss of a component by oxidation, as in the removal of carbon from steel.

Before analysing an alloy which has been melted, the mass removed from the crucible should, if possible, be sawn through vertically. Any lack of uniformity in composition may generally be detected in this way. Should the alloy have separated into two liquid phases, these will be recognized as two layers in the solidified mixture, or if stirring has been so vigorous that separation has not taken place so completely, the one constituent may be seen distributed in the form of globules through the mass, as in alloys of copper and lead. When the crystals which separate at the initial freezing-point are of lower specific gravity than the mass of the alloy, they float up to the surface, and cause a corresponding concentration of that constituent in the upper part of the ingot. Thus, in ternary alloys of lead, tin, and antimony, the cubical crystals approximating to the composition SbSn float to the surface, and are seen on sawing through the ingot and filing to a flat surface, without the necessity of polishing or examining under the microscope. Should such a lack of homogeneity be recognized, it is advisable to re-melt the alloy, and to cool rapidly with constant stirring. It is not enough to trust to making analyses of the upper and lower portions of the ingot separately and averaging the results.

THERMOSTATS.

In order to bring alloys into a condition of equilibrium, means must be provided for maintaining a constant temperature over long periods, and for accurate work the variation of temperature must be kept within narrow limits. Electrical resistance furnaces are commonly used, and means have to be found by which the current through the windings is automatically varied when any change of temperature occurs in the heating chamber. One way of accomplishing this is by making the winding of the furnace itself serve as a resistance thermometer. When the winding is of platinum, its resistance at a given temperature will remain constant over long periods. The coil forms one arm of a Wheatstone bridge, the resistances in the other arm being of metals with a low temperature-coefficient. They are so adjusted that the bridge is balanced when the furnace is at the desired temperature. A rather complicated arrangement of a triode valve and a galvanometer, the pointer of which can make contacts on each side of its zero position, allows the resistance of the winding to oscillate through a small interval on each side of equilibrium, with a period of a few seconds. The temperature of the wire thus varies to the extent of several degrees, but, on account of lag, the temperature inside the furnace remains closely constant (even to the extent of 0·1° at 1200°).[1]

A separate platinum thermometer may be used in a Wheatstone bridge, and a simple combination of a triode with suitable relays gives convenient control.[2] Several modifications of this plan have been used.

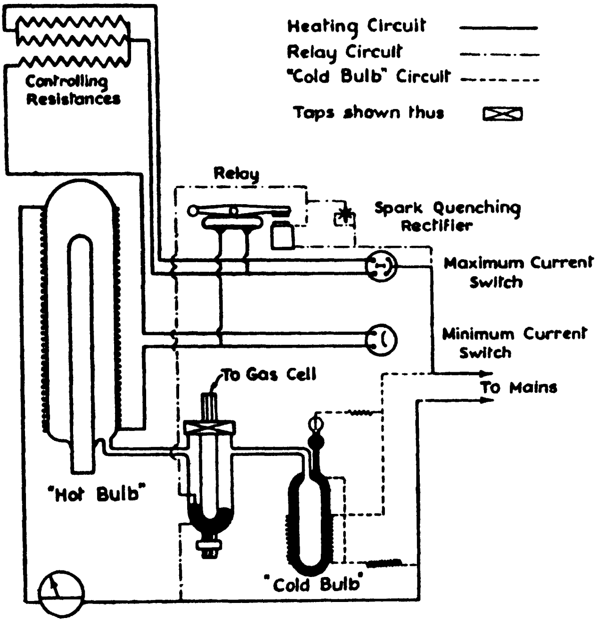

FIG. 51.—Diagram of Haughton-Hanson thermostat.

Advantage may be taken of the heat capacity of a large mass of metal as a means of avoiding fluctuations of temperature, provided that the annealing process is a continuous one, not requiring the opening of the furnace during the operation. In technical annealing, at temperatures not above 450°, it is convenient to have hollow blocks of aluminium, inside which the specimens are placed, the blocks in turn being placed inside a furnace, provided with one of the automatic temperature controllers supplied by manufacturing firms.[3]

On the laboratory scale a furnace which was used for the determination of vapour pressures could be adapted for annealing. The specimens are inserted into a heavy copper block, having two windings. The current through the larger winding produces nearly the required temperature, whilst the smaller is only in use when a relay

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[1] W. P. White and L. H. Adams, *Phys. Rev.*, 1919, [ii], **14**, 44; H. S. Roberts, *J. Opt. Soc. Amer.*, 1925, **11**, 171.

[2] E. A. Cooke and J. C. Swallow, *J. Sci. Instruments*, 1929, **6**, 287.

[3] Cambridge Scientific Instrument Co., and Messrs. Leeds and Northrup Co.

makes contact. A resistance thermometer actuates a bifilar galvanometer, and the spot of light reflected from the mirror falls on to a photo-electric cell, which in turn, by means of a sensitive relay, operates the relay in the heating circuit.[1] This arrangement gives great constancy of temperature.

By making the chamber of the furnace in the form of a double-walled silica cylinder, the annular space may be used as a gas thermometer, the change of volume of the enclosed gas being utilized to control the supply of current to the winding. This is the principle of the thermostat used in the National Physical Laboratory for annealing experiments.[2] The gas space communicates with another bulb, kept at a constant temperature, through a U-tube containing mercury. Fluctuations of temperature in the hot space cause changes of volume which produce small displacements of the mercury, and these, by making and breaking a circuit containing a relay, alter the current flowing through the furnace. Arrangements are provided for enabling slow cooling or slow heating to be carried out, and the apparatus can be arranged to control one or more supplementary furnaces. The general construction is shown in Fig. 51.

Such devices have become less necessary since the development of commercially produced controllers, which owe their origin to the demands of industry for furnaces which can be kept constant in temperature within a narrow range. Several of these are equally suitable for laboratory use, and are supplied by makers of potentiometer recorders. A temperature having been determined on, a pointer is set, and any rise above that temperature leads either to a reduction of the heating current (in the case of an electric furnace) or to its complete cutting off; and conversely. The same principle is applied to gas-heated furnaces.

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[1] A. C. Egerton, *Proc. Roy. Soc.*, 1923, **103**, A, 469.

[2] J. L. Haughton and D. Hanson, *J. Inst. Metals*, 1915, **14**, 145; 1917, **18**, 173; J. L. Haughton, *J. Sci. Instruments*, 1932, **9**, 310.

CHAPTER V.

PYROMETRY AND DILATOMETRY.

PYROMETERS.

Of the many types of instrument employed for the measurement of temperature, very few are suitable for the accurate determination of freezing and transformation-points in metallography. Mercurial thermometers are only available for those amalgams which are liquid at or near the ordinary temperature, and for experiments on fusible alloys melting at or near 100°. Thermometers of special glass having the stem above the mercury column filled with nitrogen or carbon dioxide under pressure, are obtainable with graduations up to 450°; their employment at such temperatures, however, is unsatisfactory for accurate work, owing to the uncertain character of the permanent deformations and creep produced in the glass bulb.

The available types of pyrometer, excluding the mercury thermometer, are three in number, namely, the thermo-electric couple, the electrical resistance pyrometer, and the optical pyrometer. Of these, the first is by far the most generally used. It depends on the measurement of the thermo-electric difference of potential produced when a junction of two dissimilar metal wires is heated or cooled, the other junctions being maintained at some constant temperature. In practice, the two wires forming the couple are welded together to form the hot junction, the cold junctions being the points at which the ends of the couple wires are joined to the galvanometer leads.

For measurements at high temperatures it is necessary that the metals forming the couple should be highly infusible, and should also be unaffected by hot air. In both the couples in general use one wire is of pure platinum, the other being an alloy of 88 per cent. platinum and 12 per cent. rhodium. An alloy of platinum and iridium gives a higher E.M.F. at a given temperature, but iridium is volatile, and above 1000° the vapour causes contamination of the second wire. Both wires should be thoroughly annealed before any measurements are taken, and re-annealing by passing such a current as to heat to redness is also necessary when a couple has been long in use, as the pure platinum wire readily absorbs gases.

Of base-metal couples, suitable for use at moderate temperatures, the most useful are copper-constantan, silver-constantan, and a couple composed of one wire of an alloy of 90 per cent. nickel and 10 per cent. chromium, and one of 98 per cent. nickel and 2 per cent. aluminium (the chromel-alumel couple).

The E.M.F. of a thermo-couple is not proportional to the temperature. Accurate comparisons of couples with the gas thermometer have been made,[1] and it has been found that the relation over a limited range is most conveniently given in the form

$$E = a + b\theta + c\theta^2,$$

in which E is the E.M.F. in microvolts, θ is the temperature, and a, b, and c are constants. A logarithmic formula, of the form

$$\log E = a \log \theta + b$$

is applicable over a somewhat wider range.

In practice, however, the temperature is best found from the E.M.F. by a graphical construction from determinations of the freezing-points of pure metals. The fixed datum-marks thus obtained are used for the construction of a curve, from which the temperature corresponding with a given reading is obtained with ease. It must be remembered that extrapolation beyond the highest point actually determined is attended with great uncertainty, and the equations expressing the relation between E and θ become less and less trustworthy as the temperature increases.

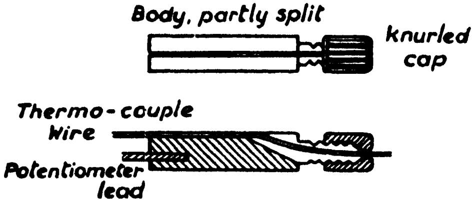

FIG. 52.—Joint for thermo-couples.

The above formulæ are based on the assumption that the cold junctions, that is, the points at which the wires of the couple make contact with the leads, are at 0°.

Although the cold junction may be maintained at any convenient temperature and an appropriate correction made, it is preferable to arrange that it shall always be at 0° by joining the couple wires to the leads by some such device as is shown in Fig. 52, which avoids bending the thermo-couple wires,[2] and enclosing each pair in a thin tube, immersed in a Dewar vacuum flask containing crushed ice.

The wires constituting the couple should be 0·6 mm. thick and 60-100 cm. long, in order that the cold junctions may be at a safe distance from the furnace. To insulate one wire from the other, it is enclosed in a capillary tube, which may be of silica or other

[1] L. Holborn and A. L. Day, *Amer. J. Sci.*, 1899, [iv], **8**, 165; J. A. Harker, *Phil. Trans.*, 1904, **203**, A, 343. For a detailed comparison of a large number of thermo-couples see H. Euler and K. Guthmann, *Arch. Eisenhüttenw.*, 1935, **9**, 73.

[2] R. J. M. Payne, *J. Sci. Instruments*, 1934, **11**, 231.

refractory material according to the temperature and the nature of the substances in contact with it, whilst the whole is enclosed in an outer protecting tube, as described above. Outside the furnace, the wires are separated by being threaded through doubly bored fireclay rods or beads of insulating material. The leads are of insulated copper wire.

In the simplest method of measuring the thermo-electromotive force developed by the couple, the leads are connected directly with a galvanometer, such as a millivoltmeter, on the scale of which 1° C. = 0·0001 volt, at 1000°, a platinum platinum-rhodium couple being used. Such instruments are often provided with a scale graduated directly in temperatures, but the readings should be carefully calibrated from time to time by determining the freezing-points of pure metals. The following freezing-points are in common use for calibration :—

Tin	231·9°
Lead	327·3°
Zinc	419·5°
Aluminium-copper eutectic	546·4°
Aluminium-iron eutectic	653·2°
Silver-copper eutectic	779·4°
Sodium chloride	801°
Silver	960·5°
Gold	1063°

together with the boiling-points of water (100°) and sulphur (444·7°). The freezing-points of silver and copper are much lower in presence of air.

The accuracy of the millivoltmeter type of instrument is not very high. It is suitable for measuring annealing temperatures or for determining freezing-points when very high accuracy is not required, but it is not satisfactory as a means of investigating a series of alloys. The accuracy may be largely increased by the use of a suspended coil instrument with mirror, the readings of the spot of light reflected on a scale being taken. It is not worth while, however, to increase the sensitiveness of the galvanometer very greatly, as the direct method of measurement is subject to certain errors, depending on the change of resistance of the couple itself with temperature, which limit its accuracy.

For greater accuracy the E.M.F. should not be read directly, but should be balanced against that of a standard cell, a potentiometer being used to effect the balance. A special construction of the potentiometer is required, the E.M.F. to be measured being very small, whilst it is essential that readings should be taken in rapid succession. A null method does not provide the required rapidity of manipulation, and the device, due to Stansfield,[1] of compensating the greater part of the E.M.F., leaving a small outstanding part to

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[1] A. Stansfield, *Phil. Mag.*, 1898, [v], 46, 59.

be read on a scale in the usual manner, is generally adopted. A large standard cell or a small secondary battery is used to produce the balancing E.M.F. and a sensitive galvanometer is used for reading. The sensitiveness may be so chosen that the whole range of the scale, some 60 cm. long, represents only 10° or 15°. When the spot of light has reached the end of the scale, the resistance of the potentiometer is altered, so reducing the balance E.M.F. and bringing the spot back to the beginning of the scale. This plan is only suitable for slow cooling, as otherwise the time required for the oscillations of the galvanometer to die down may cause the loss of a reading. It is modified when the "inverse-rate" method (p. 93) is used.

In the various difference methods[1] the difference of temperature between the specimen under examination and the furnace is measured at frequent intervals or continuously. Since the temperature of the furnace is not so readily or so accurately determined as that of a body enclosed in it, Roberts-Austen proposed the device of placing a neutral body, such as a mass of platinum, near to the body under examination and under the same conditions of temperature as it.[2] The neutral body is one which gives a perfectly regular cooling curve; it must not, therefore, present any discontinuity of thermal properties within the range to be observed. Platinum is obviously the most suitable substance for the purpose, although nickel may be used successfully for ranges of temperature which do not include its transformation point. The neutral body should be as nearly as possible of the same shape and size as the body investigated, in order that they may cool with equal rapidity. The difference in specific heat of the two metals causes a departure from uniformity in cooling; but this error may be to some extent eliminated in plotting the curves, as described below.

In Roberts-Austen's method of working, the two thermo-couples, placed in holes drilled in the specimen and the neutral body respectively, are connected so that the E.M.F.'s produced tend to neutralize each other, that is, the platinum wires of the two couples are connected together, the other wires being connected with the galvanometer. So long as the bodies are cooling at the same rate, the galvanometer does not indicate the passage of any current; but any development of heat, caused by a polymorphic change in the specimen, gives rise to a difference of temperature $(\theta - \theta_1)$ between the two bodies, so that the galvanometer coil is deflected. The temperature θ of the specimen is observed at the same time, either by a separate thermo-couple, or by the shunting of one couple through a second galvanometer. The former arrangement is more suitable for accurate work, and is illustrated diagrammatically in Fig. 53.[3]

The specimen S and the neutral body N are contained in the

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[1] This term is more accurate than *differential.*

[2] *Fifth Report, Alloys Research Committee*, 1899.

[3] H. C. H. Carpenter and B. F. E. Keeling, *J. Iron Steel Inst.*, 1904, i, 224.

cylindrical electric resistance furnace A. The thermo-couple B is connected directly with the potentiometer, whilst the two couples C and D are so connected that their platinum-rhodium wires are joined, and their platinum wires lead to the galvanometer, G_1, the deflections of which measure $\theta - \theta_1$. K_1, K_2 and K_3 are cold junctions, maintained at 0°. The balancing E.M.F. is furnished by the accumulator P, and is checked from time to time by means of the standard cells Q, of 1·019 volts each. R_1 and R_2 are resistance boxes, of which R_1 can be used for balancing Q against P until the deflection of the galvanometer G_3 becomes zero, R_2 having the resistance 1019 ohms. The potentiometer consists of four sets of nine coils each, arranged in two rows, and connection may be made between them at any two points by the plugs E and F. The coils in the left-hand are of 2 ohms each, and those in the right-hand half of the potentiometer 0·2 ohm each. Each 0·2 ohm between E and F then corresponds with about 400 microvolts. The thermo-couple being connected by the key, balance is found to the nearest 400 microvolts, and the outstanding E.M.F. is read off by means of the galvanometer G_2, which is a sensitive suspended coil instrument, with mirror, giving a deflection on the scale of 8 mm. for 1°, so that very small changes in $\theta - \theta_1$ may be read off.[1]

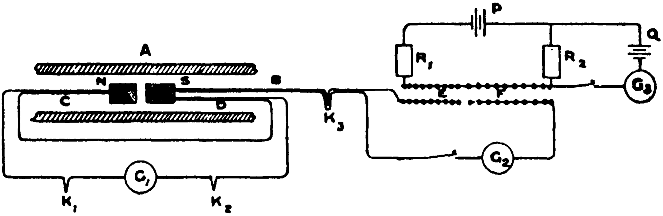

FIG. 53.—Potentiometer and difference method.

In the electrical resistance pyrometer, advantage is taken of the change of resistance of a platinum wire with temperature.[2] This method of pyrometry is admirably adapted to work of great precision, since very minute differences of temperature may be determined by its means. It is, however, less suited to the work of thermal analysis than the thermo-couple, on account of the greater difficulty of reading, and also of the comparatively large mass of the thermometer portion of the instrument, which renders it difficult to follow rapid fluctuations of temperature. The method is interesting as having been employed by Heycock and Neville in their investigations of the freezing-points

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[1] A mechanically driven potentiometer, for use with the plotting chronograph, has been constructed, and saves much labour (R. J. M. Payne, *J. Sci. Instr.*, 1935, **12**, 348). By the use of a photo-electric cell it has been made completely automatic (*ibid.*, 1936, **13**, 158).

[2] H. L. Callendar, *Phil. Trans.*, 1887, **178**, A, 161 ; H. L. Callendar and E. H. Griffiths, *ibid.*, 1891, **182**, A, 119.

of metals and alloys.[1] The end portions of the freezing-point curves, which are of great importance as giving information as to the molecular condition of alloyed metals, were, in particular, determined by these investigators with great precision.

In the original form of instrument the platinum wire is wound on a mica frame enclosed in a porcelain tube. In a later form the wire is wound on a quartz rod, which is then slipped into a thin quartz tube, the latter being finally fused on to the rod, so embedding the wire in quartz. This gives a very narrow bulb, occupying little more space than a thermocouple.[2] The resistance is measured by a Wheatstone bridge arrangement, which may be made self-registering. In industrial practice the resistance pyrometer is used for the determination of the transformation temperatures of steel, when a large mass, of several kilogrammes, may be employed, the instrument being connected with a Callendar recorder.

The optical pyrometer depends on the comparison of the radiation emitted by the specimen with that from a standard source, only rays of a particular wave-length being selected for comparison. In the disappearing filament instrument [3] an electric glow-lamp is used as the standard source, the current passing through it being adjusted until the image of the filament just disappears on the field illuminated by the radiating body, a red glass being interposed to select a certain group of radiations. With the cuprous oxide glass used by Holborn, the radiations transmitted have their centre at $\lambda = 0{\cdot}643\ \mu$. The relation between the current passing through the filament and the temperature, assuming the emitting object to have the properties of a black body, is given by a parabolic formula. The intensity I of the monochromatic radiation varies with the temperature, according to Wien's law:

$$I = C\lambda^{-5}e^{-\frac{c}{\lambda T}},$$

where T is the absolute temperature, and C and c are constants. Very high temperatures may be measured by using a tungsten filament as the standard source. The instrument is readily calibrated by observing a series of melting-points of pure metals.

Optical pyrometers only give the correct temperature if the emissive power of the object is that of a black body. This is not often the case, but "effectively black" radiations are emitted by surfaces in the interior of a uniformly heated space, so that the inner wall of a muffle, etc., may be considered as having the emissive power of a black body. This condition may be reproduced by inserting a refractory tube, closed at one end, into the furnace or crucible, the opening facing towards the pyrometer, which is arranged to form an image of the closed end of the tube. This gives the true temperature very closely.

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[1] C. T. Heycock and F. H. Neville, *Trans. Chem. Soc.*, 1895, **67**, 160.

[2] For details of construction, see J. A. Hall, *J. Sci. Instr.*, 1933, **10**, 4.

[3] L. Holborn and F. Kurlbaum, *Ann. Physik.*, 1903, [iv], **10**, 225; L. Holborn and S. Valentiner, *ibid.*, 1907, [iv], **22**, 1.

The optical pyrometer is useless for measuring temperatures if flames or heated vapours having a high absorptive power intervene between it and the object. An advantage in dealing with very high temperatures is that the radiation increases very rapidly with the temperature, namely, in proportion to its fourth power, and very small differences of temperature are therefore measurable. Further, the radiation equations used in their calibration are in close agreement with the gas scale throughout the whole observed range, and extrapolation may therefore be resorted to with confidence.

Although the optical pyrometer is of great value for the measurement of temperatures in annealing and similar processes, it is not often convenient for the determination of thermal curves, but is sometimes essential in determining melting-points in a range in which thermo-couples are not satisfactory. The disappearing filament pyrometer is sighted on the metal in the form of a wire or cone, enclosed in a furnace which has been arranged, by the use of diaphragms, to give black-body conditions in the part under observation, the moment at which the wire or cone melts being observed by the eye.[1] A modification of the method, which allows of the taking of a thermal curve over a range of temperature, consists in immersing a refractory tube, having a spherical end, in a crucible filled with the molten metal. The interior of the bulb thus becomes a black body. This gave good results for gold. It was used, with a different form of crucible (Fig. 45), in the determination of the melting-point of iron.[2] By making the black-body chamber open downwards, and by passing a stream of hydrogen during the operation, the effects of metallic vapours are eliminated. A prism at the base of the apparatus reflects the light into the pyrometer.

THE COOLING CURVE.

The simplest form of cooling curve is that illustrated in Chapter II., in which the temperature of the mass is directly plotted against the time.[3] In its construction the readings of the galvanometer are taken at equal intervals of time and utilized directly for the construction of the curve.

The taking of direct cooling curves has been replaced, in most research laboratories, by that of inverse rate curves, but the theoretical simplicity of the direct curve is a great advantage, especially for the purposes of students, and it is worth while to consider means of rendering it more accurate. Using a mirror galvanometer, either alone or with a potentiometer, the spot of light may be made to fall on a recording surface which is moved at a constant rate, and the

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[1] F. H. Schofield, *Proc. Roy. Soc.*, 1929, **125**, A, 517 ; in an earlier form the method was used by G. K. Burgess, *Bull. U.S. Bur. Stand.*, 1907, **3**, 345.

[2] C. H. M. Jenkins and M. L. V. Gayler, *Proc. Roy. Soc.*, 1930, **129**, A, 91.

[3] Frankenheim, *Ann. Physik.*, 1836, [ii], **39**, 376 ; F. S. Schaffgotsch, *ibid.*, 1857, **102**, 293.

curve traced by hand. In the simple form of apparatus used by Heycock, and used regularly in the Cambridge Laboratory, a sheet of paper is attached to a wooden panel, the weight of which is balanced, while it is moved vertically by a cord passing over a pulley and attached to a float in a cylinder from which water is allowed to escape through a tap. A cross bar serves as a rest for the hand while tracing the curve as the spot of light from the galvanometer moves horizontally across the paper. Simple as is this device, it has proved satisfactory in research work on metals of comparatively low melting-point.[1]

In an investigation of the ternary alloys of lead, tin and antimony, a vernier potentiometer was used, together with a drum covered with paper and rotated by clockwork. A needle point carried by a vernier scale was moved by hand along a graduated scale parallel with the axis of the drum. The needle was set at the reading corresponding with the setting of the potentiometer, and when the galvanometer reading reached zero, the needle was depressed so as to puncture the paper. The potentiometer and needle were then set to the next reading and the process repeated.[2] Such a method, which is suitable for slow rates of cooling, gives very satisfactory results.[3]

When a large range of temperature is involved, the direct curve has the disadvantage of occupying a large amount of space, which makes its plotting on such a scale as to show sufficient detail impracticable. This is one of the reasons for the general adoption of the inverse-rate method, but it must not be supposed that this modification adds to the accuracy of the experimental determinations, although it makes changes of direction more immediately obvious. It is equivalent to the plotting of a differential coefficient, representing the change of slope, and it therefore indicates sharply the beginning of a transformation, but is liable to give a false impression as to the progress of the change. It must therefore be interpreted with caution, and it is for this reason that the writer prefers, for teaching purposes, to lay stress on the direct curve, or on a curve obtained by a difference method.

The difficulty of giving a quantitative interpretation to the direct curve arises from the fact that the rate of cooling is not uniform, being different at the beginning and at the end of the change of state. Direct cooling curves may, however, be so modified as to yield quantitative information, by the employment of an electric furnace, the temperature of which is diminished at a uniform rate by the gradual increase of resistance in the external circuit, or by the passage of the specimen through a furnace in which a uniform temperature gradient exists. The means of effecting this have been described on page 69.

A perfectly inert body cooled in this way at a sufficiently slow

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[1] D. Stockdale, *J. Inst. Metals*, 1930, **43**, 193.

[2] F. D. Weaver, *J. Inst. Metals*, 1935, **56**, 209.

[3] The Brearley curve tracer is a device of this kind.

rate will at each moment be only slightly hotter than the furnace, and the readings of a thermo-couple in contact with it, plotted as a temperature-time diagram, will give a straight line. If a molten metal is cooling at a sufficiently slow rate, the difference in the specific heats of the liquid and solid will have little influence on the form of the cooling curve; the two branches would then be nearly in the same straight line. The area included between the observed curve and the base line is proportional to the heat liberated during freezing.[1] This area may be measured by means of the planimeter.

When the change under observation is not the freezing of a liquid, but the transformation of one solid phase into another, the liberation of heat is generally neither so great nor so instantaneous, and the indications on the time-temperature curve become uncertain and difficult to interpret. They are brought out more clearly by the device of plotting "inverse-rate" curves, in which the temperatures are taken as ordinates, and the inverse rates of cooling (times taken for the temperature to fall through a definite small amount) as abscissæ. Denoting temperature by θ and time by t, the "direct-rate" curves have as co-ordinates θ and t, whilst the "inverse-rate" curves have as co-ordinates θ and $dt/d\theta$.[2] A development of heat appears on such a curve as a "peak," the position of which can be located without difficulty, but on account of the uncertainty as to the points at which the curve leaves the neutral line and returns to it, a quantitative interpretation is not feasible. The "inverse-rate" method is of interest as having been employed by Osmond in his original work on the allotropy of iron and its alloys with carbon.[3] For accurate work a chronograph is required to mark seconds on a tape, a key being depressed each time that the E.M.F. decreases by a fixed amount. In this way the time taken by the specimen to cool through 1° or a smaller interval is recorded.[4]

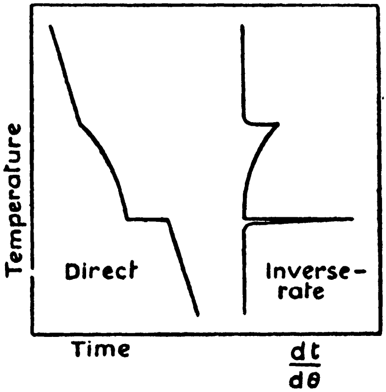

FIG. 54.—Cooling curves.

The taking of inverse-rate curves is greatly facilitated by the use of

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[1] W. Plato, *Z. physikal. Chem.*, 1906, **55**, 721; 1907, **58**, 350; 1908, **63**, 447.

[2] The different types of cooling curves are discussed and compared by G. K. Burgess, *Bull. U.S. Bureau Stand.*, 1908, **5**, 199; and W. Rosenhain, *Proc. Phys. Soc.*, 1908, **21**, 180.

[3] F. Osmond, *Mém. Artill. Marine*, 1887, **15**, 573; *J. Iron Steel Inst.*, 1890, i, 38; *Compt. rend.*, 1890, **110**, 242, 346.

[4] F. Wüst, *Metallurgie*, 1906, **3**, 1.

the plotting chronograph.[1] The paper on which the record is to be made is mounted on a horizontal drum, and the points are recorded by a stylus, which can be depressed, making a mark by pressure on a sheet of carbon paper placed between the paper and the drum, or by puncturing the paper. A light wooden rod, carrying the stylus, is moved parallel with the axis of the drum at a constant rate, being driven by a governed motor. The observer watching the galvanometer presses his key, and the action brings about the depression of the stylus by means of an electro-magnet. Immediately contact has been made, another electro-magnet lifts the rod off its contact with the friction drive and causes it to touch a wheel which is rotating rapidly in the opposite direction. This returns the rod to the zero position, where a small solenoid retains it without rebound. As soon as the second magnet is released, springs press it into contact with the motor-driven wheel, and it again starts on its outward journey. At the same time the drum is rotated by one step through the action of suitable gearing. This step represents the interval of temperature which has been selected for the construction of the curve, whilst the travel of the rod represents the time taken for that fall of temperature to occur. This apparatus is in general use at the National Physical Laboratory, and has given complete satisfaction. A typical curve is reproduced in Fig. 55.

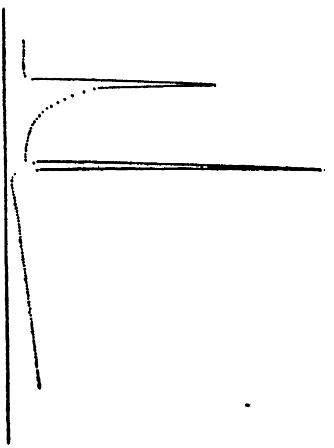

FIG. 55.—**Inverse-rate curve, taken with automatic potentiometer.**

A method of plotting, giving very well-marked arrests, suitable for the measurement of arrest times, has been employed in the study of the ternary alloys of mercury.[2] Pure mercury, which remains liquid within the range covered by the experiment, is cooled under the same conditions as the alloy under investigation. Readings are taken of the time at which the mercury and the alloy respectively reach certain temperatures, that is, time readings are taken every 5° or 2°. This necessitates a very slow rate of cooling, and the co-operation of two observers. The two sets of readings, plotted separately, give two curves, of which the mercury curve is smooth, whilst the alloy curve presents the aspect of an ordinary temperature-time curve with an arrest. The time readings of the mercury curve are now subtracted from those of the alloy curve at the same temperatures, and the differences are plotted against temperature. In this derived curve, the ordinates are θ, and the abscissæ $(t - t_0)/\Delta\theta$.

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[1] W. Rosenhain, *J. Inst. Metals*, 1915, **13**, 160; 1929, **42**, 31.
[2] E. Jänecke, *Z. physikal. Chem.*, 1906, **57**, 507; 1907, **60**, 399.

Examples of the ordinary curve, and of the derived curve corresponding with it, are shown in Fig. 56. The arrest-time is very easily measured on the latter. The dip in the curves at the beginning of freezing is due to undercooling, as will be explained in Chapter XII.

Marked arrests are only obtained on a heating or cooling curve when there is a phase change accompanied by the absorption or release of a certain quantity of latent heat. There are, however, important changes in solid alloys which are not phase changes and have no latent heat. They involve a change of specific heat, spread over an interval of temperature. On a cooling curve they are indicated only by a slight change of direction, which is easily overlooked. The usual physical methods of determining the specific heat are excluded, as they involve quenching, and it is also desirable to be able to make a series of determinations as the temperature is continuously varied. For this purpose a simple method has been devised.[1] The specimen is completely enclosed in a copper block which can be heated in a furnace at a uniform rate. The difference in temperature between the specimen and the block must be kept small, and a small heating coil is inserted in the specimen so that a known quantity of heat can be supplied to it at intervals, the power input being measured by a calibrated ammeter and voltmeter. The specimen (Fig. 57) is in the form of a hollow vessel with a cover making

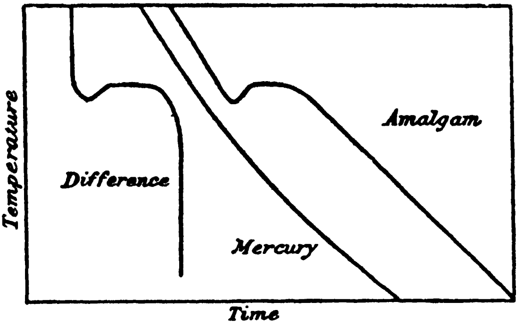

FIG. 56.—Jänecke's method of plotting cooling curves.

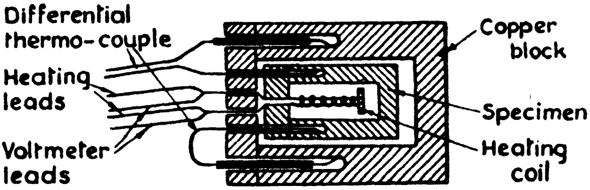

FIG. 57.—Apparatus for determining specific heats (Sykes).

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[1] C. Sykes, *Proc. Roy. Soc.*, 1935, 148, A, 422; C. Sykes and W. Jones, *J. Inst. Metals*, 1936, 59, 257.

good thermal contact. It is supported on three short silica rods. The temperature of the copper block, T_2, is measured by a thermocouple and potentiometer, and the difference of temperature between specimen and block, $T_1 - T_2$, by a thermo-couple and mirror galvanometer. After steady heating conditions have been reached, the power input to the coil is varied so that the rate of change of the difference of temperature, $\frac{d}{dt}(T_1 - T_2)$ is about 0·1° per minute. The values of $T_1 - T_2$ are observed over the range 0·5° to $-$0·5°, and $\frac{d}{dt}(T_1 - T_2)$ is obtained for $T_1 = T_2$. Readings of T_2 against time t are taken at intervals of five minutes. This curve gives the value of $\frac{dT_2}{dt}_{t=t_0}$ and the specific heat, s, is then found by the formula

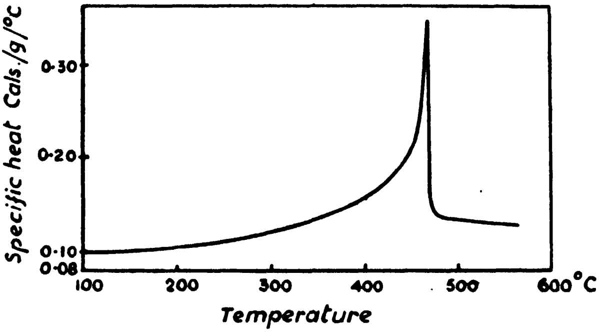

FIG. 58.—470° transformation in brass.

$$s = \frac{0{\cdot}24V \times A}{M\left(\frac{d}{dt}(T_1 - T_2) + \frac{dT_2}{dt}\right)_{t=t_0}},$$

where M is the mass of the specimen and the numerator represents the input of power. Measurements are made alternately when $\frac{d}{dt}(T_1 - T_2)$ is negative and positive. Errors due to heat transfer are then opposite in the two cases. A curve showing the change of specific heat at the 470° transformation in brass (p. 340), as obtained by Sykes by this method, is shown in Fig. 58. The ordinary inverse rate curve gives a single cusp, and does not indicate the true character of the change.

DILATOMETRY.

Most transformations in the solid state are accompanied by a change of volume, and this fact is used as a means of investigation of alloy systems. The dilatometric method has an advantage over the thermal method in being independent of time, so that the specimen may be held at a given temperature for any length of time in order to attain equilibrium, and the cooling or heating then resumed, whilst a transformation temperature may be passed through as slowly as may be desired. The measurements almost always take the form of determinations of changes of length, volume dilatometers having been little used except in the study of amalgams, although experience with a differential gas dilatometer [1] shows that the method might be adopted with advantage for constitutional studies. It is usually assumed, however, that the change of length is a measure of the change of volume, an error only being involved when the specimens are markedly anisotropic. When this is known to be so, as in the examination of single crystals of non-cubic metals, the X-ray method (p. 219) is to be preferred. Forged bars sometimes show distinct anisotropy when examined by means of the dilatometer.[2]

In the practical construction of instruments for such work, advantage is commonly taken of the negligible expansion with heat of vitreous silica, which can therefore be used as a neutral body. A simple form of instrument consists of a vertical silica tube, closed below, and containing a shorter tube of the same material, supporting the specimen, a cylindrical rod 2·5-3 cm. long. The rod is turned to a smaller diameter or made convex at both ends, so that it fits into the supporting tube and into another silica tube which prolongs its length upwards.[3] The movement of the specimen relatively to the containing tube is indicated by an Ames dial, which magnifies the displacement. A thermo-couple wedged into a saw-cut in the specimen passes out through a refractory tube, and provision is made for using either a vacuum or an atmosphere of inert gas, the dial and upper part of the apparatus being enclosed in a bell-jar. A heating furnace surrounds the part of the tube containing the metal specimen, or for a smaller range of temperature it may be immersed in a water or oil bath.

Another type of instrument uses two rods, one being of the material to be tested, and the other of an alloy with a known coefficient of expansion which varies uniformly over the range to be covered. The relative changes of length may then be magnified in one of several ways, and the apparatus may be made self-recording.

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[1] W. E. Goodrich, *Trans. Faraday Soc.*, 1929, **25**, 531. The dilatometer used was modified from an earlier form, C. J. Smith, *Proc. Roy. Soc.*, 1927, **115**, A, 554. See also E. Cohen and H. L. Bredée, *Z. physikal. Chem.*, 1929, **140**, 199.

[2] J. H. Andrew, J. E. Rippon, C. P. Miller, and A. Wragg, *J. Iron Steel Inst.*, 1920, i, 527.

[3] P. Hidnert and W. T. Sweeney, *U.S. Bur. Stand. J. Res.*, 1928, **1**, 771; modified by F. M. Walters and M. Gensamer, *Trans. Amer. Soc. Steel Treat.*, 1932, **19**, 608; and by R. C. Gale, *J. Sci. Instr.*, 1930, **17**, 131. Gale's dilatometer is made by Messrs. Griffin & Tatlock.

In its simplest form[1] two parallel rods were used, one end being pivoted by a knife-edge and groove, a small mirror being held between the free ends. Any difference in the expansion of the two metals was then indicated by a tilting of the mirror. This principle has been adopted in many later instruments. The two metallic rods, for example, are placed in horizontal silica tubes, and prolonged at each end by silica rods, fitted as above to make good contact. The two ends, extending beyond the heated zone, impinge against two of the corners of a right-angled triangular frame which carries a concave mirror, the other corner bearing on a fixed pivot. The arrangement is shown diagrammatically in Fig. 59, *a* and *b* are the ends of the two rods to be compared, and p_1 and p_2 the points by which they respectively bear on the light invar triangle which forms the optical lever. p_3 is the pivot on which the lever turns. Light from a source S falls on to the mirror M and is reflected to N, the axes of co-ordinates being OX and OY, parallel with the shorter edges of the triangle. If the two rods expanded equally, the point would follow a line parallel with OX. On the other hand, if the expansions of the two rods be unequal, the point will trace a line MN inclined to the axis. It is usually arranged that the standard material shall be an alloy with a lower coefficient than that of the specimen under examination. Should the specimen undergo a change on heating which involves a contraction, this change being reversed on cooling, but at a lower temperature, a condition which often obtains in practice, the resulting diagram takes the form shown in Fig. 60. The coefficient of expansion of the standard bar being known, the temperature scale is given by the co-ordinate OX_1.

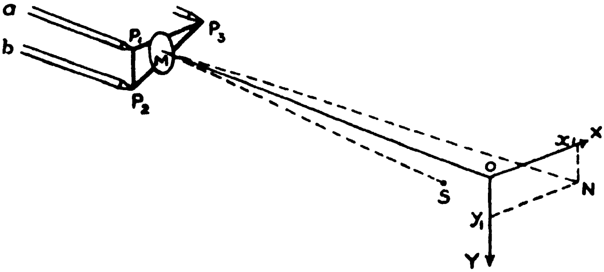

FIG. 59.—Diagram of Chevenard dilatometer.

It is possible to use only the one metallic rod, the other being replaced by a rod of silica. The temperature co-ordinate must then be obtained in another way. This is done by causing the beam of

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[1] P. Chevenard, " Analyse dilatométrique des matériaux," Paris, 1929. The instrument was first described in *Rev. Métall.*, 1917, 14, 610. In its modified form it is supplied by Aciéries d'Imphy. Other modifications have been made by H. Esser and P. Oberhoffer, *Stahl u. Eisen*, 1926, 46, 142; F. Bollenrath, *Z. Metallk.*, 1933, 25, 163; R. A. Ackley and F. M. Walters, *Metals and Alloys*, 1936, 314.

light to be reflected twice in the course of its path, the second reflection, in a plane perpendicular to the first, being from the mirror of a galvanometer which indicates the temperature of a thermocouple, as in the Saladin method[1] for taking thermal curves. The Leitz universal dilatometer[2] is so constructed that either of these methods may be used, and the experiments can be carried out in a vacuum or in an inert gas. The movements of the luminous point are recorded photographically in most modern dilatometers, the friction at pivots causing difficulty in the many lever instruments using tracing pens. The Leitz instrument is so arranged that thermoelectric and conductivity measurements may be made with the same apparatus.

An entirely different means of magnifying the changes of length of a metallic specimen, with the object of greater refinement in the detection of transformations in the solid state, depends on the change in capacity of an electrostatic condenser brought about by varying the distance apart of its plates. This is the principle of the Whiddington ultra-micrometer,[3] and has been applied in several different ways to the purposes of dilatometry.[4] In the form now used at the National Physical Laboratory,[5] which is intended for the determination of critical points, and not for absolute measurements, the movements of the specimen displace one plate of a small condenser, which forms part of the series grid capacity of a valve circuit. In this way small changes in the capacity cause large changes in the mean steady anode current of the valve. A continuous record of this anode current is made on a thread recorder, which at the same time records the temperature of the specimen. The arrangement of the plates at the top of the dilatometer is such that the expansion of the specimen diminishes the capacity of the condenser by separating them. The furnace tube is wound with platinum ribbon, and the apparatus may be evacuated or filled with an inert gas. The recorder draws two curves, one connecting expansion in length with time and the other temperature with time. These are combined graphically to give a length-temperature curve.[6]

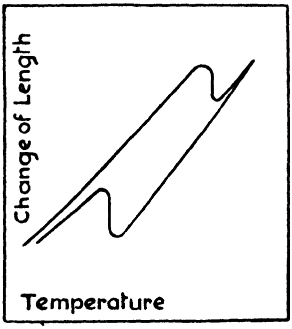

FIG. 60.—Heating and cooling curves by dilatometer.

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[1] Saladin, *Assoc. inter. Méth. Essais*, 1903, Feb.; H. Le Chatelier, *Rev. Métall.*, 1904, **1**, 134.

[2] H. Esser, *Mitt. Leitz-Werke*, 1933, No. 55.

[3] R. Whiddington, *Phil. Mag.*, 1920, [vi], **40**, 634.

[4] H. Lloyd, *J. Sci. Instruments*, 1929, **6**, 81; J. H. Handley, *ibid.*, 84.

[5] W. E. Prytherch, *J. Sci. Instr.*, 1932, **9**, 128; J. L. Haughton and F. Adcock, *ibid.*, 1933, **10**, 178.

[6] J. L. Haughton and W. T. Griffiths, *J. Sci. Instruments*, 1924, **1**, 225.

CHAPTER VI.

THE PREPARATION OF MICRO-SECTIONS.

THE preparation of thin, transparent sections, such as are employed in the study of rocks and minerals, is not possible for metals and alloys, which remain opaque in the thinnest slices. It is therefore necessary to examine prepared surfaces by means of reflected light. Whenever the metal is sufficiently soft to allow of it, the specimen is sawn to the required size with a hack-saw. With a little practice it is not difficult to cut sections of regular form, with parallel faces, from a piece of metal held in a vice, by means of a hand-saw, but a mechanically driven hack-saw has obvious advantages. Brasses, bronzes, etc., are more easily sawn than such tough metals as copper or aluminium, in cutting which some practice is required to overcome the drag on the teeth of the saw. Soap solution should be applied to lubricate the saw and to prevent heating, unless the alloy is of such a composition as to be affected chemically by water or alkali, in which case turpentine may be employed. Electrolytic calcium may be cut by moistening the saw with alcohol.

A convenient size for micro-sections is from 15 to 25 mm. square, and from 7 to 10 mm. in thickness. Circular specimens have the advantage of having no corners which might tear the polishing cloth. Larger specimens may, of course, be necessary when it is desired to include the whole of some structure or flaw. Specimens which are too thick are apt to rock slightly when held in the hand during grinding and polishing, so that the surfaces become rounded instead of flat. If too thin, the sections may "buckle," so that the centre becomes hollowed, and escapes polishing.

Care must be taken to ensure that the micro-section is representative of the metal under examination. When there is any doubt as to the specimen being homogeneous, sections should be cut from both the outer and inner portions. Much useful information is often obtained by cutting serial sections, representing the change of structure on proceeding from the surface to the centre of an ingot or of a forging. Ingots which have been cast in iron moulds have a chilled outer layer which may be quite different in structure and even in composition from the general mass. An outer layer should also be removed from small specimens which have been annealed or quenched in the laboratory, as surface changes are likely to occur during heating, even when care has been taken to avoid the access of air, copper-zinc alloys losing a portion of their zinc, steels becoming superficially decarburized, etc.

Many alloys are too hard to be cut with a saw, or so brittle as to crumble under the pressure. It is then necessary to break off a piece with a hammer, and to grind a flat surface. Hard alloys which are not brittle, such as certain steels, must be cut with a Carborundum disc. For very hard alloys, such as white cast-iron or ferro-alloys, an emery or Carborundum wheel must be used for grinding, care being taken that the supply of water is sufficient to prevent heating. For alloys which are friable without being so hard as white cast-iron, a more satisfactory plan is to prepare a flat surface by grinding by hand on a Carborundum block or with Carborundum on a lead lap moistened with water or turpentine. A torn or pitted surface is less likely to be produced in this way than when a mechanically driven wheel is used. The specimen should not in any case be allowed to become hot by friction. When a piece of metal is felt by the fingers to be distinctly hot, the surface which is being rubbed is at a considerably higher temperature, and in some specimens, as of steels hardened by quenching, important structural changes may be produced.

If the alloy is not too brittle, the sawn surface may now be made approximately flat by means of a file. For this purpose a flat file is held in the left hand, with the end resting on the bench, and the specimen, held by the thumb and finger of the right hand, is drawn lightly up and down its surface. The proper pressure to be applied varies with the nature of the metal or alloy, and can only be determined by experience. It is to be remembered that the teeth of the file strain the metal, especially if soft, to some depth below the surface, and the lines of strain may reappear after polishing. It is often better to avoid the use of a file, and to prepare the surface of the specimen by rubbing with a circular motion on a piece of coarse emery cloth laid on the bench. Sharp edges and corners should be removed with the file before proceeding further, in order to prevent tearing of the cloth or paper used in the later processes.

Steels and the harder alloys are conveniently prepared on a "linisher," or mechanically driven endless belt of fabric coated with abrasive. Rubbing on a No. 1 emery paper, either with a to-and-fro or with a circular motion, should leave the specimen ready for the next series of operations.

Thin sheets and wires cannot be held rigidly enough to be ground, and they must be mounted in some way. When the surface of a thin sheet is to be examined, the specimen should be cemented to a piece of thicker metal to serve as a support. Cross-sections may be embedded, as below, or they may be held, singly or in bundles, in a small clamp (Fig. 61). Wires may be fixed into a hole or slot in a small steel block, or embedded. When the specimen is of small size or of irregular shape, or when the edge has to be preserved, as in the examination of fractures, embedding is most convenient.

White fusible metal has been most commonly used for this purpose, as it is readily cast round the specimen, and can be ground and polished with it, but it has the disadvantage of forming an electrolytic couple with the metal under examination, and in etching the border is very liable to show anomalous effects. The writer prefers to avoid its use. Sealing wax is a convenient material, being cast round the specimen in a metal ring. Bakelite, or other synthetic resin, is, however, preferable. The powdered form, containing wood dust or other filling, is used, and is packed round the specimen in a brass ring, about 3 cm. diameter. A small press is necessary, which may be obtained commercially or made by adapting a disused hardness testing machine. The mould is heated electrically to 170°-180°, the bakelite packed round the specimen or specimens, and pressure applied by the ram and maintained for about three minutes. When cold, the whole mass is ground as if it were a solid piece of metal.[1]

When delicate detail at the edge of the specimen has to be preserved, it is better to protect it by depositing metal electrolytically until a thick mass has been built up, and to polish this as a whole. This plan was adopted by Rosenhain for the purpose of examining slip-bands, the height of which was only 1 μ, in cross-section.[2] Copper was deposited on the stepped surface, and the detail remained clear at a high magnification. When steel fractures are under examination, copper is better avoided on account of its electrolytic action, and iron is most conveniently deposited. A chloride solution, containing 288 g. of ferrous chloride and 57 g. of sodium chloride in a litre, is used with a current density of 5 milliamps./cm.^{2} at first, raised to double that value after a time. At 80° the iron is deposited at about 0·04 mm. thickness in an hour.

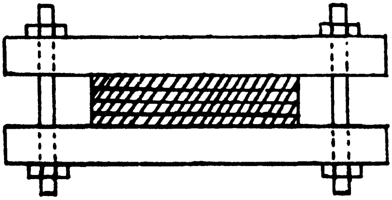

FIG. 61.—Clamp for holding sheet specimens.

PREPARATION OF A SMOOTH SURFACE.

The preparation of a surface suitable for polishing is most often obtained by rubbing on emery paper. Emery papers prepared for jewellers' use are generally employed, and can be obtained in four grades, 0, 00, 000, and 0000, the last being the finest.[3] The rubbing is preferably carried out by hand, although rotating discs are often used. In order to carry it out, the emery papers are placed on a

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[1] For the detailed technique, using various types of resin, see H. J. Taffs, *J. Roy. Microsc. Soc.*, 1936, **56**, 300.

[2] W. Rosenhain, *Proc. Roy. Soc.*, 1905, **74**, 557.

[3] F. F. Lucas, *Trans. Amer. Soc. Metals*, 1936, **24**, 1, uses Aloxite papers for this purpose, beginning with No. 240 and finishing on No. 400.

hard support, such as plate glass or cast iron. Before using a new paper, the surface should be well rubbed with a piece of steel (an old micro-section) to remove any coarse particles.

The specimen, held between the fingers, is now rubbed backwards and forwards on the paper 0 with a slight pressure, care being taken to avoid tilting on reversing the direction, which would cause rounding of the edges. The paper is held flat by the stretched fingers and thumb of the other hand. The rubbing is continued until, on examination with a hand lens, no scratches are seen except the parallel series due to the 0 paper. The process is now continued with the finer papers. On passing from one paper to another, the specimen is turned through a right angle, so that the new scratches cross the old at right angles. In this way it is easy to see when the coarser scratches have been effaced. On leaving the last emery paper, the surface should reflect the image of a lamp or window brilliantly, and should only show very fine parallel scratches under a lens.

The papers are mostly used dry, but it is necessary to add a liquid in some special cases. Thus fully quenched steels undergo slight tempering with even a small rise of temperature, and this may be avoided by covering the paper with a mixture of glycerol and water during the whole process of grinding. When soft alloys, such as those of aluminium, are being prepared, it is advisable to soak the paper in paraffin just before use.[1]

Many laboratories use an abrasive powder on rotating discs in place of hand rubbing on emery papers. A succession of wheels is used, on which fine washed emery or Carborundum is dispersed in water on fine canvas, followed by tripoli powder on broadcloth. This process is much more rapid than hand rubbing, but some metallographers prefer the slow process, which is more easily controlled.

A complete departure from ordinary practice has, however, been made with great success, in the examination of the softer metals, especially of aluminium. This consists in the preparation of the surface by planing instead of by grinding, a microtome being used.[2] The microtome must be of heavy construction, the Jung sledge instrument,[3] intended for the preparation of sections of timber, being used for the purpose. With a knife kept in good condition, sections only 2 μ thick can be cut, and if the instrument be set to cut with increments of 2 μ a surface is soon obtained which is so smooth as to show fine detail even under high magnification. With lead and its alloys, for which rather deep etching is necessary, the specimen can be etched directly without polishing, but for the light alloys of aluminium, for which cutting with the microtome has, in some laboratories, superseded grinding, a final polishing is given.

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[1] D. Hanson and S. L. Archbutt, *J. Inst. Metals*, 1919, **21**, 291.

[2] F. F. Lucas, *Trans. Amer. Inst. Min. Met. Eng.*, 1927, **75**, A, 481.

[3] R. Jung and Co., Heidelberg. Supplied by Messrs. Carl Zeiss.

POLISHING.

The process of rubbing on emery paper is really one of cutting. Microscopical examination shows that the particles of emery cut grooves in the metal, the section of each groove being approximately parabolic. A certain amount of plastic deformation also occurs in the neighbourhood of the groove, this being the greater the coarser the scratch. Hence the final scratches should be very fine in order to avoid the presence of a deep surface layer of strained metal. The effect of the emery on brittle metals, however, is to break out small conchoidal chips, as in grinding glass, the chips being smaller the finer the emery. It was long supposed that the effect of polishing with powders on cloth was merely to continue this process, the grooves or pits becoming so fine as not to be visible under the microscope. The researches of Lord Rayleigh,[1] Osmond and his collaborators,[2] and Beilby,[3] have shown, however, that the process of polishing is essentially different from that of grinding. The full bearing of these investigations will be discussed in Chapter XVI., but here it will be sufficient to say that the production of a polished surface consists in the formation of a thin layer of " flowed " metal on the surfaces, the irregularities of the scratched surface being partly rubbed away and partly filled up. This plastic behaviour of the surface layer is readily observable even in such a brittle metal as antimony.

The powders employed in polishing are the oxides of aluminium, iron, magnesium, and chromium. Rouge (ferric oxide) is widely used in commercial polishing processes, but causes heavy surface flow, and should be avoided in metallographic work. Chromium oxide is valuable for stainless steels and similar alloys, whilst alumina is the most generally useful of all oxides. It is mostly prepared by igniting ammonium alum at 1000°-1100°, but suitable powders are now obtainable commercially, and there is no advantage in preparing one's own polishing material. " Diamantine " was formerly used, but is expensive, and " Abradum " has proved very satisfactory.

For the final polishing of steels and of the harder alloys, magnesia gives the best results, being least liable to cause surface flow, and giving fine detail without removing non-metallic inclusions. It was first recommended by Rosenhain, and is preferably used after a good surface has been produced by polishing with alumina. The " heavy " variety is employed and must be stored out of contact with air. During its use on the wet pad it absorbs carbon dioxide, forming crystalline magnesium carbonate, which has a gritty texture. It should therefore never be allowed to dry during or after use, and the cloth should be washed, and even stored, in water containing a

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[1] *Proc. Roy. Inst.*, 1901, **16**, 563.

[2] F. Osmond and G. Cartaud, *Rev. gén. des Sciences*, 1905, **16**, 51. A summary of work on the subject.

[3] *Proc. Roy. Soc.*, 1903, **72**, 227 ; *Electrochem. and Metall.*, 1903, **3**, 806.

little hydrochloric acid. For the very finest work, Lucas (*loc. cit.*) recommends the use of an air elutriator in order to obtain a very fine powder (average diameter of particles 0·176 μ) free from grit.

Hard cutting alloys, consisting mainly of tungsten carbide, must be ground with boron carbide and paraffin on a copper disc, and polished with the finest diamond dust.[1]

A textile fabric must be used as a support for the polishing powder. A fine cloth is generally preferred, and must be of close and even texture, without any ribbed pattern. Fine broadcloth is suitable, as is the cloth used for some military uniforms. For most purposes the material known as "selvyt," a kind of velveteen sold as a polishing cloth, is very convenient, as although it wears out more quickly than a heavier cloth, its texture is suitable, and it is cheap and easily renewed.

For hand-polishing, the wet cloth is simply stretched by the fingers on a sheet of plate glass or slate. Mostly, however, the process is carried out mechanically, the cloth being stretched over a disc of wood or aluminium which is revolved at a speed of 400 to 600 r.p.m. The disc is conveniently mounted on the spindle of a variable speed motor, as shown in Fig. 62, this being better than the driving of a number of discs from a single motor by means of belts.

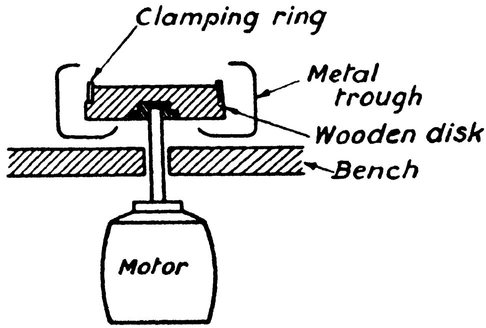

FIG. 62.—Polishing disc.

The wet cloth, having been thoroughly washed, is stretched over a disc by means of a brass ring. The polishing powder is added dry, and rubbed into the cloth by the finger. It being remembered that a single particle of grit may produce extensive scratching, care must be taken to remove any gritty particles, which are readily detected by the sensitive tip of the finger and removed by drawing to the edge. The disc being set in motion, the specimen is held between the finger and thumb, and is pressed on to the cloth with an even pressure, care being taken to avoid tilting. For most metals the pressure should be hardly more than is necessary to keep the specimen from flying off the disc. Skill can only be acquired by practice. The rotation of the disc being counter-clockwise, the specimen is slowly moved in circles clockwise, so that its relative direction is constantly changing. The cloth must be kept wet, and from time to time a little more powder should be added. This is

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[1] S. L. Hoyt, *Trans. Amer. Soc. Steel Treat.*, 1930, 17, 54.

best done by having the powder in water contained in a wide-mouthed bottle which is closed with a cork having a V-notch, from which the water, carrying polishing material in suspension, is shaken on to the cloth. Should the cloth be allowed to become dry, "seizing" is likely to occur, and particles of powder will be attached to the metal so closely as to be impossible to dislodge without tearing the surface. The specimen is examined from time to time with a hand lens to see whether the scratches are disappearing. During the last stages of the polishing of steels for examination under high powers, Lucas recommends the addition of a little soap solution, which makes it easier to wash away the powder from the surface. When polishing is seen to be complete, the specimen is well washed under running water, with liquid soap if necessary, then in distilled water, and lastly in alcohol, and dried quickly, an electric hair-drier being useful for the purpose. When finished the specimen should present a uniform mirror-like surface under the microscope, unless either of the following conditions is present:

1. The constituents differ markedly in colour. In copper-antimony alloys rich in antimony the structure is well seen on polishing without etching, as the compound Cu_2Sb, which is present as one of the constituents of the eutectic, is violet in colour, and outlines the antimony crystals with great distinctness. The same may be said of the alloys of aluminium and gold, the compound $AuAl_2$ (Roberts-Austen's purple alloy) being strongly coloured.

2. The constituents differ greatly in hardness. The hardest constituent may be found to present itself in relief, even when precautions have been taken to avoid wearing away the soft parts. Thus in polishing white bearing metals containing copper and antimony in a base of tin or of tin and lead, the hard needles of the copper-tin constituent will almost always be found to project above the soft matrix, and thus to be visible without etching. It is usually desirable to avoid polishing in relief, and to reveal the structure in other ways. Relief is most likely to be developed if the cloth used is thick and soft.

3. The alloy is porous. Dark irregular patches are seen. Cavities in the specimen cause serious difficulties in polishing, since they readily retain particles of dirt, emery, or polishing material which may become dislodged in the subsequent process of polishing, and give rise to deep scratches. A porous specimen should therefore be thoroughly washed in a stream of water after each stage. When the cavities are coarse, as when defective castings or cracked specimens are under examination, it is advisable to fill them with a plastic material, such as shellac, before rubbing on fine emery paper.

4. Non-metallic inclusions are present. Special care in polishing is necessary when it is wished to study the non-metallic inclusions present in a metal, as their size is usually small, and they may be covered up by the flow of metal during polishing. On the other hand, particles of abrasive may become embedded in the metal during

its preparation for the microscope, and are then readily mistaken for inclusions. In the earlier stages of polishing, when movement has been mainly in one direction, each inclusion will be seen under the microscope to have a "tail," indicating the direction of flow, and in the later stages care must be taken, by polishing lightly and continually changing the direction, to eliminate these markings. Some workers[1] prefer to avoid wet polishing when examining inclusions, and to use instead a disc covered with billiard cloth charged with a commercial polishing mass, composed of alumina or rouge mixed with stearin and cast into a cake. The author prefers careful polishing with magnesia.

ETCHING.

In general, further treatment is required to bring out the structure of an alloy. This usually consists in attacking the surface of the specimen by a chemical reagent which acts preferentially on one or more of the constituents, or which acts along certain directions in a homogeneous metal. The variety of etching reagents is great, and only the more generally useful can be described here.

Hydrochloric acid.—The concentrated acid is useful for many white metals, the basis of which is tin. The specimen is immersed in the acid for a few seconds, the process being watched with a hand lens. When sufficiently etched, it is removed, rinsed in water, lightly dried with a cloth, and examined.

Dilute hydrochloric acid is a convenient reagent for metals containing large amounts of tin. An alcoholic solution, prepared by diluting 5 c.c. of concentrated acid to 100 c.c. with alcohol, is the most regular in its action. Alloys containing free zinc require a much more dilute acid.

Nitric acid.—The concentrated acid is used for metals which can only be attacked by its means. Alpha brasses have their crystalline structure revealed by dipping for a moment in the concentrated acid, and then rinsing rapidly in water. Nitric acid, D 1·2, is a more generally useful reagent. It etches phosphor-copper, copper-silver alloys, etc., very clearly, giving bold contrasts which are very suitable for photography. Much weaker solutions are used for the more reactive metals. For silicon steels a dilute solution should be used at first, the concentration being increased until the grain structure is seen clearly. A 2 to 4 per cent. solution in alcohol is the most useful reagent for steels, whether annealed or hardened. Should its action be too rapid, it is diluted, or amyl alcohol is substituted for ethyl alcohol, this being very suitable for pure iron.

Picric acid.—This reagent, introduced by Ischewsky,[2] is in general use for etching steel in the unhardened condition, in the form of a 5 per cent. solution in alcohol. It usually develops the structure of

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[1] C. R. Wohrman, *Trans. Amer. Soc. Steel Treat.*, 1928, 14, 81; S. F. Urban and R. Schneidewind, *Metal Progress*, August, 1932, 39.

[2] *Stahl u. Eisen*, 1903, 23, 120.

the steel without indicating the grain boundaries, but by adding a few drops of nitric acid these are brought out clearly. The coloration, which gives good photographic contrast, is due to the deposition of a film of carbonaceous matter, so that the specimen should be washed with alcohol and dried by air without wiping.

Sodium picrate.—This reagent is used in a strongly alkaline solution to stain iron carbide and a few other compounds. It is usual to add a cold saturated solution of picric acid to a 50 per cent. solution of sodium hydroxide, and to immerse the steel specimen in the boiling solution, five minutes or more being required to stain the carbide black. This method has its dangers, as the temperature is high enough to bring about changes in the constitution of a quenched steel, and erroneous conclusions have been drawn from such etching. When quenched steels are being examined for free carbide the temperature of the sodium picrate reagent should not be higher than 70°, the time of attack being correspondingly lengthened.[1] The reagent also darkens sulphides, nitrides and sometimes phosphides. The effect is caused by the attack of alkali hydroxide on the anodic parts of the surface, the picrate acting as a depolariser, so that a hydroxide of iron is deposited as a film on the cathodic constituents.[2] Other oxidizing agents have been used in place of picric acid, especially for the carbides of alloy steels. Among these are potassium ferricyanide,[3] and hydrogen peroxide.[4] A solution containing 10 g. of potassium ferricyanide and 10 g. of sodium hydroxide in 100 c.c. of water will darken the carbides of high-speed steel without heating.

Ammonia.—Ammonia solution, diluted 1 : 3, is useful for etching alloys of copper, especially the brasses and bronzes. Exposure to air is necessary, so that instead of immersing the specimen it is better to rub it lightly with a wad of cotton wool dipped in the reagent. Immersion in ammonia to which hydrogen peroxide or ammonium persulphate has been added is often effectual.

Sodium or potassium hydroxide.—These are used in 5 per cent. solutions for etching alloys containing high proportions of zinc or aluminium. The black deposit formed is removed by dipping in a solution of chromic acid.

Ferric chloride.—This reagent, employed with great success by Heycock and Neville in their study of the copper-tin alloys,[5] is generally useful for bronzes. It is prepared by adding a syrupy solution of ferric chloride to concentrated hydrochloric acid, and diluting with water, the correct dilution having to be found by trial. Like ammonia, it is apt to develop latent scratches, and a specimen which has appeared to be well polished may therefore appear badly scratched after etching. It is also useful for austenitic steels.

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[1] E. Maurer and G. Riedrich, *Arch. Eisenhüttenw.*, 1930, 4, 95.

[2] R. Mitsche, *ibid.*, 1935, 9, 311 ; see H. Hanemann and A. Schrader, *ibid.*, 1931, 4, 475.

[3] T. Murakami, *Sci. Rep. Tôhoku Univ.*, 1918, 7, 217.

[4] M. Yatsevitch, *Rev. Métall.*, 1918, 15, 65.

[5] *Phil. Trans.*, 1903, 202, A, 1.

Aqua regia is necessarily employed for many alloys of gold and of the platinum metals. It is generally necessary to raise it to a temperature just below its boiling-point, but a mixture of one part nitric acid, five parts hydrochloric acid, and six parts water, gives good results when cold, pure gold taking about an hour to etch.

Ammonium persulphate.—A 10 per cent. solution of this salt etches brass and other copper alloys very clearly, without staining. The surface must be quite free from grease, and should therefore be washed in dilute sodium hydroxide before immersion in the reagent. Prolonged etching develops geometrical etch-figures with a great variety of alloys.

Hydrofluoric acid.—This reagent is used in the form of a 10 per cent. solution for etching aluminium and light alloys, the crystalline structure of which it develops.

Copper ammonium chloride.—In neutral and acid solutions this is used for the deep etching of steels, as described below. In ammoniacal solution it etches copper and its alloys, and is convenient when fairly deep etching is required, as in determining the orientation of crystal grains.

Chromic acid, in the form of a nearly saturated solution, etches brasses very clearly. A mixture of 94 g. of concentrated nitric acid and 6 g. of chromic acid is the best reagent for etching zinc. A few drops of the solution are added to 50 c.c. of water.[1]

Mixtures of nitric and hydrochloric acids with glycerol, the proportions being varied according to the composition of the alloy, are useful for alloys containing chromium, including the stainless steels.[2] A mixture of concentrated nitric and glacial acetic acid, diluted if necessary with acetone, may be used for nickel and its alloys, which are otherwise difficult to etch, and the same acids, mixed with glycerol, give good results with alloys of lead.[3]

Electrolytic etching.—It is often convenient to assist the etching process by means of an electric current, the specimen being made the anode in a solution of an electrolyte. This may be ammonium nitrate or any other neutral salt. Le Chatelier[4] obtained the best results with copper-tin alloys by using sodium thiosulphate. The solution is placed in a beaker, and the specimen supported below the surface by a bridge of platinum wire or foil, the cathode being of platinum foil or gauze. An adjustable resistance is inserted in the circuit with an accumulator. A 10 per cent. solution of citric acid gives very clear etching with alloys of copper and nickel in all states, and this solution is also successful with silver, which is otherwise very difficult to etch.[5] Should the specimen appear patchy, a drop of nitric acid is added to the solution. An ammoniacal solution of

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[1] G. Timoféef, *Rev. Métall.*, 1914, **11**, 127.

[2] J. R. Vilella, *Iron Age*, 1926, **117**, 761.

[3] J. R. Vilella and D. Beregekoff, *Ind. Eng. Chem.*, 1927, **19**, 1049.

[4] *Bull. Soc. d'Encouragement*, 1896, [v], **1**, 559.

[5] F. Adcock, *J. Inst. Metals*, 1921, **26**, 362 ; 1922, **27**, 73.

ammonium molybdate gives good results with a remarkably wide range of alloys. A combination of methods is sometimes useful; thus Adcock found that the grain boundaries in cupro-nickel (80 per cent. copper, 20 per cent. nickel) could be revealed by electrolytic etching, leaving a tarnish which could be removed by dipping in chromic acid, after which the inner structure of the crystals could be seen on etching lightly in bromine water. Stains on the surface of copper alloys are conveniently removed by means of a solution of potassium cyanide. Etch-figures in brasses are beautifully developed by electrolytic etching in a 5 per cent. solution of sodium chloride.[1]

Etching with alkaline ferricyanide followed by electrolytic etching in sodium hydroxide solution develops the structure of the hard alloys, consisting of cemented tungsten carbide.[2] A mixture of nitric and hydrofluoric acids may also be used.

Heat-tinting.—When heated in air, many metals and alloys become coated with a film of oxide, which remains adherent and shows the colours of thin films. Since different constituents oxidize with unequal rapidity, Stead based on this fact a very delicate method of distinguishing between certain of the constituents of iron and steel. The specimen is best embedded in sand on a metal plate or in a porcelain capsule, and heated with a small flame until the colours appear. The oxidation can be stopped at any required point by plunging into mercury. To obtain successful results, the surface of the specimen must be thoroughly clean and dry, as the presence of moisture in cavities of the metal causes the formation of irregular coloured rings. It is advisable to heat the specimen, previously freed from grease, to 120°, and then to rub on clean, warm flannel, before heating to a higher temperature.

This method gives remarkably beautiful results with steel, cast-iron, and certain copper alloys, especially those containing antimony or silver. As an example of its use, the effect of heating steel or iron containing phosphorus[3] may be mentioned. At 280° the carbide of iron, cementite, becomes reddish-brown. The phosphide becomes pale yellow in 10 minutes, salmon in 15, and on further heating assumes a characteristic (heliotrope) shade of blue.

Polishing in relief.—This method is less used than in the early days of metallography, when the choice of etching reagents was more limited. Using a soft bed, such as chamois leather, the harder constituents of many alloys may be shown in relief, but there is some loss of sharpness. Eutectic structures in the light alloys of aluminium may often be developed successfully by polishing with one of the commercial polishing liquids on "selvyt," the specimen being then cleaned by rubbing on clean dry selvyt.

Polish-attack.—Following a technical practice of colouring steel by rubbing with an aqueous extract of liquorice root, Osmond[4] adopted

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[1] C. H. Desch and S. Whyte, *J. Inst. Metals*, 1913, **10**, 304.

[2] G. J. Comstock, *Trans. Amer. Soc. Steel Treat.*, 1930, **18**, 993.

[3] J. E. Stead, *J. Iron Steel Inst.*, 1900, ii, 137.

[4] "Étude des Alliages," 1901, 277.

the plan of rubbing steel specimens on parchment moistened with a 2 per cent. solution of ammonium nitrate, with rouge or calcium sulphate as a polishing powder. This method gave beautiful results, and rendered great service in the early studies of the structures of steels, but has now been superseded. Combined polishing and etching are, however, of great advantage in the examination of specimens which readily tarnish. Copper alloys may be rubbed on a polishing pad moistened with ammonia, and staining is prevented.[1]

Lead, which presents special difficulties in polishing on account of its softness, gives very clear structures when ground on emery paper covered with paraffin, and then etched by wetting with an acid solution of ammonium molybdate (as used for phosphorus analysis), rubbing on selvyt moistened with the same reagent, and washing.[2] For examination under high powers, the specimen is further etched with the nitric acid acetic acid-glycerol reagent.

	A[3].	B[4].	C[5].	D.	E.
Cupric chloride	1·0 g.	10 g.	10 g.	6 g.	5 g.
Hydrochloric acid	100 c.c.	20 c.c.	20 c.c.	10 c.c.	40 c.c.
Ferric chloride	30 g.	—	—	6 g.	—
Magnesium chloride	—	40 g.	40 g.	—	—
Stannous chloride	0·5 g.	—	—	—	—
Alcohol	—	to 1000 c.c.	—	100 c.c.	25 c.c.
Water	1000 c.c.	—	180 c.c.	—	30 c.c.
Methyl alcohol	—	—	100 c.c.	—	—

Special etching methods.—In determining the distribution of certain impurities in steel, mainly phosphorus and oxygen, advantage has been taken of the fact that a thin film of copper may be deposited on relatively pure iron by contact with certain solutions, but that the presence of impurities hinders the deposition, so that the less pure portions of the structure remain bright. Three varieties of the reagent, A, B and C, are shown in the table.

A reagent of this class has also been used to show strain lines in steel.[6] Some, but not all, mild steels, when suitably etched, develop lines which indicate clearly the regions of strain in the metal, and this fact finds applications, discussed in Chapter XVI. Solution D is used to show the lines on a large scale, whilst their fine detail is seen under higher magnification after etching in solution E.

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[1] O. F. Hudson, *J. Inst. Metals*, 1915, **13**, 193.

[2] B. Jones, *ibid.*, 1933, **52**, 73.

[3] W. Rosenhain and J. L. Haughton, *J. Iron Steel Inst.*, 1914, i, 615. This reagent, with half the water replaced by alcohol, was used by P. Oberhoffer, *Stahl u. Eisen*, 1916, **36**, 798.

[4] J. E. Stead, *J. Iron Steel Inst.*, 1915, i, 140.

[5] H. Le Chatelier, *ibid.*, 196.

[6] A. Fry, *Krupp. Monatsh.*, 1921, **2**, 117; *Stahl u. Eisen*, 1921, **41**, 1093; T. H. Turner and J. D. Jevons, *J. Iron Steel Inst.*, 1925, i, 169.

The light alloys of aluminium contain eutectics and small inclusions, often of several different kinds in a single alloy, and their identification is important in the study of age-hardening and other properties, as well as in the determination of their constitution. It is necessary to use several reagents in succession, and reference must be made to papers on the subject [1] for a statement as to the comparative effects of those reagents on the constituents. The identification depends on the observation of differences of etching which are sometimes minute.

The systematic use of several reagents in succession is also required for the identification of non-metallic inclusions in steel, and schemes have been devised for the purpose.[2] In this instance use is also made of polarized light, as described in Chapter VII.

The preservation of polished and etched specimens is a matter of some difficulty. The usual method of preserving microscopical preparations, by affixing a cover-glass with Canada balsam, is not available, as the presence of the cover-glass interferes with the subsequent examination under vertical illumination, causing scattering of light and "flare." The surface may be coated with a thin layer of a solution of nitro-cellulose in amyl acetate. The film thus obtained is very thin, and may be removed if necessary just before examination, by washing with the solvent. The most generally satisfactory plan is that of heating the specimen in an oven to near 100°, and packing in a labelled glass tube containing warm, dry cotton wool or in a desiccator. All specimens are most conveniently stored in an unmounted condition. Heat-tinted sections retain their appearance well.

MACRO-ETCHING.

When it is desired to study the arrangement of the crystals in an ingot or a forging it is necessary to examine a sufficiently large field. For this purpose deep etching with a reagent which has a selective action is used, and the etched surface is then examined at a low magnification or without any magnification. This process is known as macro-etching, and while of great technical importance is also of value in the scientific study of metals. Its chief application has been in the study of segregation in steel ingots [3] and in the control of forging operations in steel, the directions of flow of the metal being brought out clearly. Nitric acid is most commonly used for steels. It is not necessary to polish the surface, but only fine grinding marks should be visible. The surface is washed with 2 per cent. nitric acid, using pads of cotton wool, and the strength of the acid is gradually

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[1] D. Hanson and S. L. Archbutt, *J. Inst. Metals*, 1919, **21**, 291 ; E. H. Dix and W. D. Keith, *Proc. Amer. Soc. Test. Mat.*, 1926, **26**, ii, 317.

[2] See, for a very complete survey, C. Benedicks and H. Löfquist, "Non-Metallic Inclusions in Iron and Steel" (London, 1930) ; also C. R. Wohrman, *Trans. Amer. Soc. Steel Treat.*, 1928, **14**, 81, 255, 385, 539 ; A. Portevin and R. Castro, *J. Iron Steel Inst.*, 1935, ii, 237, and subsequent papers.

[3] An example is shown in Plate IXA.

increased, up to 10 per cent. This removes scratches and gives a clear picture of the structure. For photography the object is best laid on the floor in a room with a good diffused light, and the camera is attached to an overhead framework, so as to point downwards.

Cupric ammonium chloride is much used for macro-etching. An 8 per cent. solution was first used,[1] but many modifications have been introduced. The surface should be as free from scratches as possible, and if necessary a preliminary etching with nitric acid is given.[2] The solution deposits copper, and unless precautions are taken this may become so firmly attached as to leave an irregularly stained surface. It is advisable to begin by flooding the surface repeatedly with a neutral solution containing 120 g. of cupric ammonium chloride to the litre, and then to replace this by a solution of the same strength but with 50 c.c. of hydrochloric acid added.[3] With a little experience, the solution can be so handled as to give a deposit of copper which can be washed off, leaving a matt surface which may be brightened by rubbing lightly with fine emery paper. Should deeper etching be needed to bring out the structure, the proportion of acid is still further increased. Humfrey used this method of etching to produce permanent records without photography, applying printers' ink to the surface by a rubber roller, and pressing paper into contact with the inked surface as in an ordinary printing operation. This method had been used much earlier by Sorby [4] to produce the structure of deeply etched steels, and was called by him " Nature printing."

In the industrial examination of steels for heterogeneity, use is often made of a boiling acid solution, etching very deeply, but the results call for cautious interpretation, since they exaggerate defects in an irregular way.[5]

Copper alloys, such as bronzes, may be macro-etched by using an ammoniacal solution of cupric ammonium chloride. An unusual means of revealing the macro-structure of tin bronze consists in machining the surface with a fine tool in a shaping machine,[6] the difference in hardness between the eutectoid and the mass of the crystals producing a slight jump of the tool which shows the structure in relief.

Macro-etching of the light alloys of aluminium is carried out with a 20 per cent. solution of hydrofluoric acid, or by immersing several times in a 15 per cent. solution of cupric chloride, wiping off the loose deposit of copper, and finally cleaning by dipping in nitric or chromic acid.[7]

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[1] E. Heyn, *Mitt. k. Mat. prüf. Amt.*, 1898, **16**, 310.

[2] See the Reports of the Heterogeneity Committee of the Iron and Steel Institute, 1926-37, for details.

[3] J. C. W. Humfrey, *J. Iron Steel Inst.*, 1919, i, 273.

[4] H. C. Sorby, *ibid.*, 1886, i, 140.

[5] See J. P. Gill and H. G. Johnstin, *Trans. Amer. Soc. Steel Treat.*, 1933, **21**, 354.

[6] See Plate VI in (Sir) J. Dewrance, *J. Inst. Metals*, 1927, **37**, 21.

[7] W. Hume-Rothery, *J. Inst. Metals*, 1931, **46**, 239.

SULPHUR PRINTING.

The distribution of particles of sulphides in steel is related to the process of crystallization, and a method devised for the detection of sulphides is used as an alternative to macro-etching. This consists in pressing on to the surface of the steel (polished for a small specimen or smoothly ground for a large mass) a sheet of photographic printing paper, moistened with 5 per cent. sulphuric acid. Each particle of sulphide generates hydrogen sulphide, which produces a dark stain of silver sulphide on the paper, which is then washed and fixed in the ordinary way.[1] The reaction is not independent of other impurities, such as phosphorus and arsenic, and modifications have been proposed[2] with the object of making it unambiguous. Plate IXB is a sulphur print of a steel ingot having a highly segregated interior.

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[1] R. Baumann, *Metallurgie*, 1906, 3, 416.

[2] H. J. van Royen and E. Ammermann, *Stahl u. Eisen*, 1927, 47, 631.

CHAPTER VII.

THE MICROSCOPICAL EXAMINATION OF PREPARED SECTIONS.

ALTHOUGH several special types of microscope, each possessing some advantages, have been designed for the purpose of examining the structure of alloys, it is quite possible to obtain satisfactory results with any microscope of good mechanical construction. Since metals and alloys, being opaque, are necessarily examined by reflected light, the substage, condensers, and other appliances which add greatly to the cost of a good microscope, may be dispensed with, whilst certain special illuminating devices are required in their stead. It is nevertheless true that a microscope, designed with a view to metallographic work, offers far greater convenience, especially when many different sections have to be examined in rapid succession. The beginner, however, who possesses a fairly good ordinary microscope stand, need not be deterred by his lack of the elaborate appliances described in the makers' catalogues, and in the following account of the microscopical equipment employed in metallography his requirements will be kept in view.

The principal modification found in metallographic microscope stands is the provision of means of raising and lowering the stage. The reason for this arrangement is that when the object is illuminated by means of a device inserted in the tube of the microscope, as described below, it is convenient to fix the position of this illuminator once for all, so that it always occupies the same position relatively to the source of light. When, owing to the use of an objective of different working distance, or to the introduction of metal sections of different thickness, it is required to vary the distance between the stage and the front lens of the objective, it is convenient to effect this by racking the stage up or down, leaving the body-tube in which the illuminator is placed untouched. But even this modification, although undoubtedly effecting a great saving of time and trouble, is not indispensable for accurate work.

Since the principal source of difference between metallographic and ordinary microscopical manipulation lies in the illumination of the specimen by reflected, instead of by transmitted, light, it will be convenient to begin the description of the appliances used with the illuminator.

In the simplest method a beam of light is allowed to impinge obliquely on the surface of the section, as in Fig. 63. With a truly plane surface the whole of the beam is reflected as by a mirror, and passes entirely out of the field of the objective. To an eye placed at the end of the microscope tube, therefore, the surface of the metal appears perfectly black, none of the reflected rays being received by the eye. Should the specimen be etched, however, the surface will not be plane, but will present a number of elevations or depressions, composed of intersecting crystal faces. Suppose that some of these faces, as at *a*, *a*, have such an inclination to the surface as a whole that the rays which they reflect have a vertical direction. These rays will enter the microscope, and the areas *a*, *a* will consequently appear bright. In an etched portion of the specimen there will usually be numerous small facets having the required inclination, and the etched area will therefore appear to be irregularly illuminated, and to have a granular appearance, owing to its roughness. On the other hand, those areas which have not been attacked by the etching reagent retain their original smoothness, and since they reflect the incident beam outside of the field of the objective, they present the appearance of dark areas on a light background. Much use was formerly made of parabolic mirrors for concentrating the oblique rays, and a refinement of this method is described later.

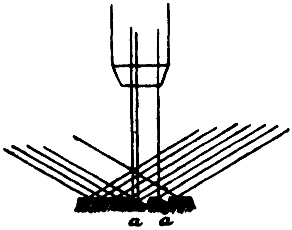

FIG. 63.—Oblique illumination.

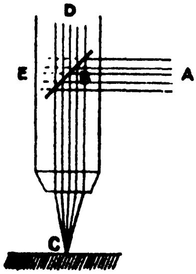

FIG. 64.—Vertical illumination with plate.

Most metallographic sections are best examined under vertical, or nearly vertical, illumination. A beam of light is introduced into the tube of the microscope above the objective, this beam being then deflected so as to pass through the objective, and after reflection from the surface of the metal to retrace its path, passing up the body-tube of the microscope to the eyepiece end. Two different types of illuminating device have been employed for this purpose. In the first, known as the Beck vertical illuminator, a thin plate of glass, with parallel surfaces, is placed at an angle of 45° to the optical axis, as shown in Fig. 64.[1] The rays from the source of light, entering the tube in the direction AB, are in part reflected from the surface of the glass plate, and pass downwards in the direction BC. The

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[1] This device was first used by V. von Lang, *Anz. kais. Akad. Wiss. Wien*, 1872, 9, 175. Lucas (see refs. later) uses a plate at an angle of 67½°, which gives the maximum reflection. This involves an additional prism outside the illuminator to correct the deflection of the beam.

rays reflected from the object travel back in the direction CBD, passing through the glass plate on the way. A considerable loss of light is unavoidable on this system. Only a part of the beam AB is reflected downwards, the remainder passing on in the direction BE and being lost, and, in a similar manner, only a part of the returning beam passes through the plate without change of direction, the remainder being reflected from the face, and passing uselessly out of the tube towards the source of light. In spite of these disadvantages, the Beck illuminator is to be preferred, as being less liable to produce false or distorted images than any instrument in which, as described below, only a part of the objective is illuminated. For most metallographic work it is not essential that the small plane reflector should be optically worked so that its two faces are truly parallel. An ordinary thin microscopic cover-glass, tested for flatness, gives satisfactory results. If too thick, defects due to astigmatism are produced.

The Beck illuminator is often constructed with such a small disc that the whole aperture of the objective is not utilized, as the turning of the plate into a plane inclined to the axis at 45° causes its projection to become an ellipse. The reflector should be so large that when inclined the whole of the back lens of the objective is covered by it. Sliding and pivoting adjustments, which are provided with some microscopes, are undesirable. There is only one correct position for the plate illuminator.

For use with very low powers, where the working distance between lens and object is great, a large square cover-glass, mounted on a hinge, may be placed *below* the objective, as suggested by Stead.[1]

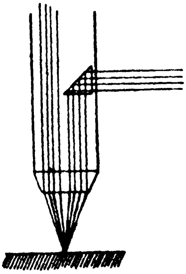

FIG. 65.—Vertical illumination with prism.

In the second form of vertical illuminator, the thin glass plate is replaced by a small right-angled prism, giving total reflection. Since the prism necessarily blocks out a portion of the beam, it is necessary to arrange it so that only one half of the area of the tube is thus occupied. The reflected ray, after passing twice through the objective, returns through the other half of the tube, passing at the back of the prism, as shown in Fig. 65. The prism is capable of a certain amount of rotation, by which the inclination of the incident light may be changed within certain limits.

Silvered half-discs and other forms of reflector have been designed, and are supplied with some microscopes, but in the author's experience they have no advantages and they involve a real sacrifice of definition. The two forms described above answer all requirements. By stopping portions of the aperture, so that the illumination becomes slightly oblique, structures in relief may be made more obvious by the casting of shadows,[2] but although the revelation of slightly more

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[1] *J. Iron Steel Inst.*, 1897, i, 42.

[2] H. S. George, *Trans. Amer. Soc. Steel Treat.*, 1923, **4**, 140; C. Benedicks and E. Walldow, *Zeitsch. wiss. Mikroskopie*, 1920, **36**, 193.

detail is claimed, the effect is not pleasant, and it is greatly preferable to polish the specimen in such a way as to avoid relief, and to make the fullest use of high resolution.

Whatever be the construction of the vertical illuminator, the prism or disc is enclosed in a short tube which screws into the lower end of the microscope body-tube, the objective, again, screwing into it. In order to avoid internal reflections, which give rise to loss of light and to "flare," the distance between the reflector and the back lens of the objective should be as short as possible. Nose-pieces and sliding objective changers increase this distance slightly, and are preferably used with objectives in short mounts.

The introduction of the vertical illuminator increases the distance between the lower end of the body-tube and the stage and it may be found, when working with low-power objectives, that the tube has been racked up to its furthest limit before focus is obtained. With a microscope specially constructed for metallography this is remedied by racking the stage down. With an ordinary small microscope the difficulty may sometimes be overcome by placing the specimen to be examined *below* the stage, attaching the glass slide by means of rubber bands, and viewing the surface through the central opening of the stage, thus securing an increased working distance. If the microscope has a racking sub-stage, this may very conveniently be employed as a stage with simple attachments which will readily suggest themselves. By such devices as these, satisfactory results may be obtained with an instrument such as is to be found in any laboratory.

The next fitting to be considered is the stage. Since metallographic specimens are only ground flat on a single surface, they are often otherwise irregular in shape. In order to examine them, it is necessary to set the flat polished surface accurately perpendicularly to the optical axis. Most metallurgical microscopes were formerly fitted with tilting or levelling stages for this purpose, but this is a useless encumbrance and hinders accurate work. It is rendered entirely unnecessary by the adoption of a simple device due to Stead. This consists in mounting the specimen in such a way that the surface to be examined is accurately parallel with that of the glass slip. On placing the slip on the stage this parallelism is retained, and no further adjustment is needed. For this method of mounting, the only apparatus required consists of a number of rings, cut from a piece of brass tube about 3 cm. diameter, of heights varying from 4 mm. to 16 mm., the edges being accurately parallel. Such rings are readily cut on a lathe. The micro-specimen is laid, with the smooth surface downwards, on a sheet of glass, and a ring of suitable height placed over it. A small quantity of plasticine is placed on the specimen, and an ordinary glass micro-slip is pressed down until it is in perfect contact with the brass ring (Fig. 66). The slip, with the specimen now adhering to it, is lifted, turned over, and placed on the microscope stage, and requires no further levelling.

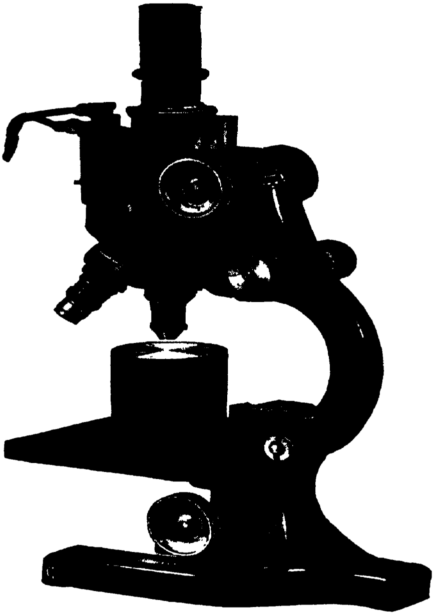

Fig. 68. Cooke table microscope

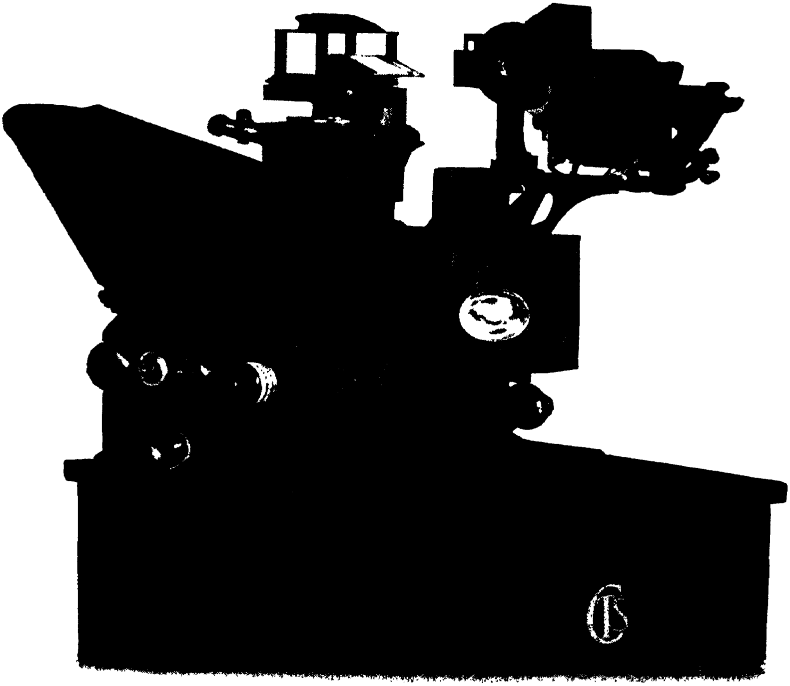

Fig. 72. Vickers microscope

Unless great care be taken to avoid rubbing of the specimen against the glass, delicate structures may be injured, and where many specimens have to be examined it is convenient to use a mounting device, due to Rosenhain,[1] which avoids any contact. This depends on the principle of auto-collimation. The stand (Fig. 67) carries a small telescope, with eyepiece E and object glass O. H is a small diaphragm, and the distance HR is made equal to RF, where F is the principal focus of O. P is a parallel polished plate of glass, silvered on the under side and mounted on a spherical seating. When a bright lamp is placed in front of H, an image of H is formed at F, and is seen on cross wires. The specimen to be examined is mounted on a slip with plasticine and the slip is then laid on the plate P. The specimen is then tilted by the fingers until the image of H again falls on the cross wires. The accuracy of setting is high, and the process only occupies a few seconds.

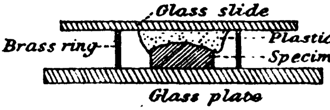

FIG. 66.—Mounting device.

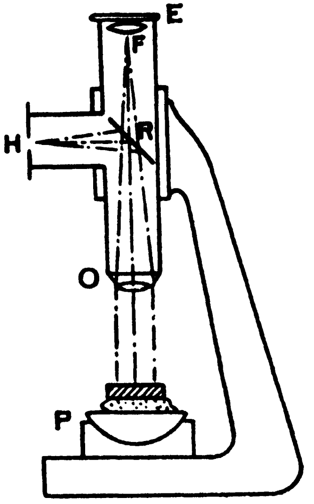

FIG. 67.—Rosenhain levelling instrument.

The provision of mechanical movements to the stage, and of means of rotating it, greatly adds to the convenience of the worker, and the former is in fact indispensable when working with any but low powers. Rotation is necessary when observing structures under oblique illumination. The mechanism does not differ from that employed in microscopes intended for observations by transmitted light. Detachable mechanical stages are supplied by several makers, and these give smooth movements, whilst they can be removed to set the flat stage free for large specimens. A large, roomy stage, free from projections, is convenient when a variety of specimens has to be dealt with. Typical bench microscopes for use in a vertical or inclined position are shown in Figs. 68 (on plate) and 69.

In laboratories in which many specimens have to be examined, especially if photo-micrographs are to be taken, it is of advantage to use a stand which is designed with a view to metallographic work. For photographic purposes, the horizontal position is to be preferred to the vertical, on account of the greater rigidity and freedom from vibration, as well as for the increased convenience and comfort of the observer. The first instrument of this kind was that devised by Martens for use in the

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[1] W. Rosenhain, *J. Inst. Metals*, 1915, **13**, 160.

Charlottenburg laboratory.[1] This form is the parent of several later instruments.

The Martens type of microscope has the advantage that no additional reflecting surfaces are introduced into the system, and it has been used, with certain improvements, by Lucas in all his work on the photo-micrography of metals at very high magnifications.[2] The instrument is made by Messrs. Carl Zeiss. The focussing, as in all these special forms of microscope, is effected by racking the stage and not the body-tube. The fine adjustment, however, is in most forms attached to the body-tube in the ordinary way. An entirely different construction was adopted by Le Chatelier,[3] in whose instrument the specimen under examination is placed face downwards on the stage, the illuminating beam entering through a horizontal collimating tube, and being reflected upwards by a totally reflecting prism into the objective, a second prism directing the reflected beam into the tube containing the eyepiece. The principle has now been adopted by most of the makers of instruments for photo-micrographic work with metals. The convenience of such microscopes is very great, and few metallographic laboratories are without one or more of them, but they have certain disadvantages, and there are indications, one of which is mentioned below, that new departures in design may revert to a plan which avoids inverting the specimen. With the inverted microscope, it is impossible to see the face of the specimen, as is desirable when searching for particular fields, whilst the fact that the prepared face of the metal is in contact with the stage makes it liable to be scratched if moved about. Further, the additional reflections involved in changing the direction of the beam of light introduce the possibility of optical errors. From the mechanical point of view the advantage

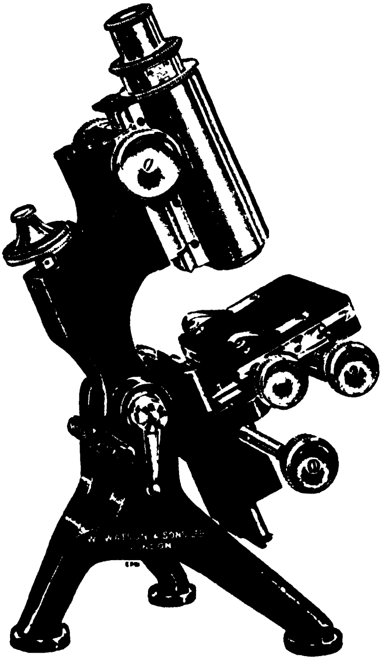

FIG. 69.—Watson microscope.

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[1] A. Martens and E. Heyn, *Mitt. k. techn. Versuchs-Anst.*, 1899, **17**, 73.

[2] F. F. Lucas, *Trans. Amer. Soc. Steel Treat.*, 1933, **21**, 1112; and for the development of this method and its results, by the same author, *J. Franklin Inst.*, 1926, **201**, 177; *Congr. Intern. Essai Mat.*, Amsterdam, 1927, 123.

[3] H. Le Chatelier, " Étude des Alliages," 1901, 421.

is usually on the side of the inverted instruments, some of which are marvels of ingenuity in their facilities for changing from one mode of illumination to another and for preserving fixed directions for the illuminating beams. The modern forms have a massively supported stage, with a locking lever to the coarse focussing adjustment, so that heavy specimens may be placed on the stage without injury.

The Zeiss " Neophot " (Fig. 70) is typical of this form of construction. The lamp, body carrying the stage and illuminating devices, and camera, are all mounted on an optical bench. The figure shows only the microscope proper. The rotating stage is placed above the objective, and the box below contains both a plane glass and a prism illuminator, the change from one to another being made by pushing a pin. In this instrument a dark-ground illuminator and polarizing prisms are also attached, and can be introduced into the system by small movements. The coarse and fine adjustments are made by the milled heads seen below on the right, the fine adjustment having two speeds.

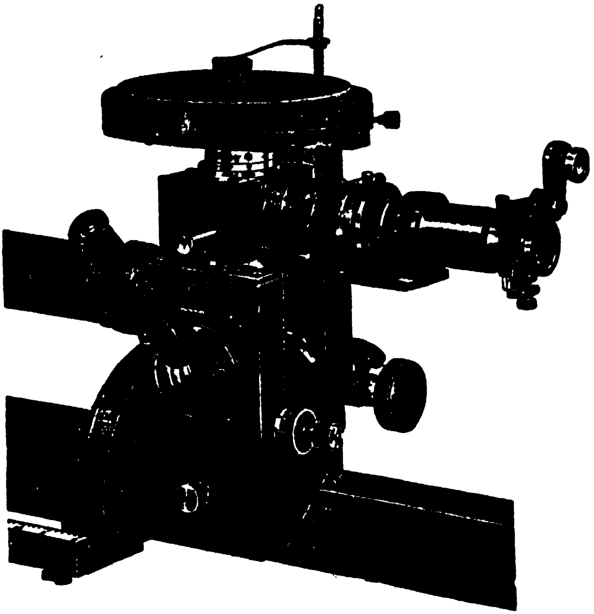

FIG. 70.—Zeiss " Neophot " microscope.

For low magnifications, from 4 to 25 diameters, the objective is replaced by a combined lens and illuminator which is placed beneath the stage.

Inverted microscopes on a horizontal optical bench are also made by Messrs. Leitz, Reichert, Beck, and Bausch and Lomb. These differ in detail, but the general plan is similar. When selecting an instrument, special attention should be paid to rigidity. A stage supported on slender pillars is too flimsy to remain steady during focussing and moving the mechanical stage, and in the best inverted microscopes a very solid construction is adopted. For macrophotography, a second optical bench, hinged to the first and swinging out to a position at right angles, is sometimes provided, carrying a lamp and the necessary lenses for directing either an oblique or a vertical beam on to the surface, the low-power lens being then attached to the camera, as in ordinary photography.

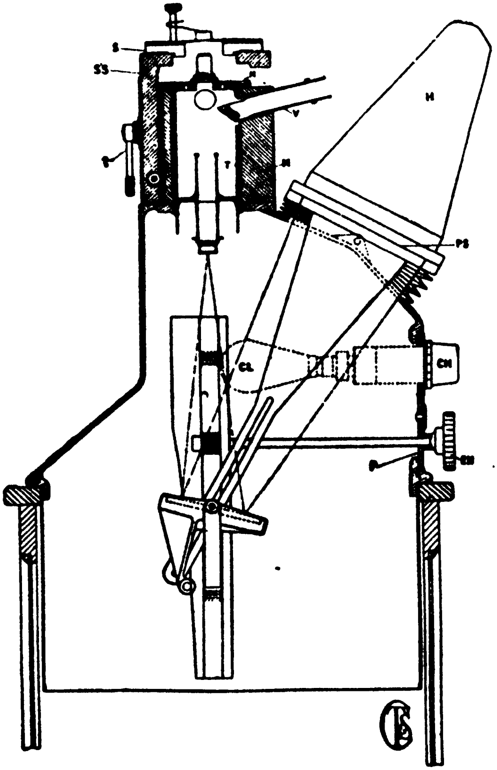

FIG. 71.—Section of Vickers' microscope.

The optical bench arrangement is very apt to be affected by vibration. Some makers suspend the whole instrument from four springs, but the swinging is unpleasant, and it is better merely to support the ends of the bench on several thicknesses of sponge rubber, this simple plan having been found quite effective, even in a room subject to disturbance by neighbouring traffic. The load is distributed over the rubber by cast-iron plates, or the cushions may be enclosed in iron shock-absorbers.

The Vickers microscope,[1] although of the inverted type, departs widely from the conventional plan. Designed in the first instance to give freedom from vibration, the parts are of massive construction, the usual tube carrying the objective, for instance, being replaced by a heavy casting. The eyepiece is placed vertically below the objective, thus avoiding a prism for turning the beam at right angles, and the bellows camera is dispensed with, the image being reflected by

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[1] R. L. Smith, *J. Roy. Microsc. Soc.*, 1930, **50**, 378. The instrument is made by Messrs. Cooke, Troughton & Simms. A smaller and very compact microscope on the same principle is made by Messrs. Reichert

a mirror of polished metal which can be raised or lowered to alter the camera length. The ground glass screen is arranged in a sloping desk, which tilts with the displacement of the mirror, so that it is always perpendicular to the optical axis (Fig. 71). A side tube for visual observation is drawn out of the path of the rays when the camera is being used. The general appearance is seen in Fig. 72 (on plate). The stage and coarse adjustment are massive, and very heavy specimens may be examined with safety. The fine adjustment is unusual. The objective carrier forms part of a large nut, having a fine internal thread, the upper part of the microscope tube being threaded externally, so that fine focussing is done by turning a pinion which engages with teeth on the nut. This gives an exceptionally slow motion to the fine adjustment, a point in which some metallographic microscopes of the inverted type are defective. The lamps are carried on an arm, which can be raised when required for transmitted light or for macro-photography. The camera incorporates a holder for illuminating a glass positive for the comparison of the grain size or other characteristic of a specimen with a standard.

The Leitz "Panphot" is a vertical instrument with a horizontal stage, the parts being arranged on the principle of an optical bench, the body consisting of a massive casting which also carries a camera of the reflex type. The eyepiece being inclined forwards by inserting a reflecting prism, the observer has the support of the body away from him instead of as in the usual vertical microscope. The illuminating beam, whether for reflected or transmitted light, passes through openings in the casting. This instrument is adaptable to a great variety of purposes.

The objectives to be used in metallographic investigations require careful selection. Since metallic specimens are examined without a cover-glass, which would cause excessive surface reflection and consequent loss of clearness, all objectives must be corrected for uncovered objects. Further, in order to avoid internal reflections, the back lens of the objective should be as close to the vertical illuminator as possible, and it is therefore advisable to have special short mounts, which have the additional advantage of reducing the height to which the body-tube has to be racked up.

Although apochromatic objectives are most usually recommended for all work of a high class, it is important to note that the conditions in metallography differ from those in biological work with the microscope. Differences of colour are eliminated by using a colour filter with a narrow band of transmission when photographing fine structures. Achromatic objectives have the advantage of giving a flatter field than apochromats, and as the back lens of the combination is more strongly curved, the risk of "flare" is lessened. Objectives by different makers differ to some extent in this matter of curvature of the back lens, and the point should be noted in making a choice. Achromats being cheaper than apochromats, and flatness of field being important when structures are to be photographed, the choice will most often fall on them, in which case care should be taken to use the colour filter which is found to give the best results with each.

The most convenient focal lengths are 25, 8, 6, 4 and 2 or 3 mm. with 50 mm. if low magnifications be required. The 2 and 3 mm. objectives are usually designed for oil immersion, and have a high numerical aperture, 1·40. Cedar-wood oil is commonly used, and must be carefully removed from the face of the lens after use, by means of lens paper moistened with xylene. A suitable bottle, with oil in the inner vessel and benzene in the outer, thus keeping the rod with which the oil is applied clean, is shown in Fig. 73.

An objective with N.A. 1·60 was designed by Abbe and used as early as 1885, but found little application until recently, when it has proved of great value in metallographic work. The immersion liquid was monobromonaphthalene, but as this deteriorates with time, Lucas, who has made much use of the objective, has preferred monochloronaphthalene.[1] It is corrected for yellowish-green light.

More recently, an objective of 1·60 N.A., working with monobromonaphthalene, has been constructed by Messrs. Beck.[2] This is a monochromat, being corrected for use with light of a single wave-length, that of the blue line in the mercury arc, with $\lambda = 4359$ Å. In practice, this light is too feeble,[3] and a Pointolite has been used with a Wratten 50L filter, which transmits light very near to this wave-length. The objective gives very high resolution, and represents the best solution of the problem of combining high resolving power with a flat field and absence of flare. Monobromonaphthalene is easily removed from the lens and the specimen by means of a few drops of acetone.

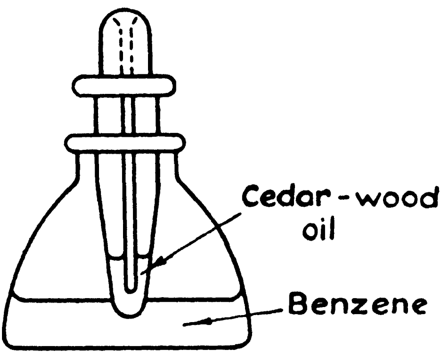

FIG. 73.—Bottle for immersion oil.

The formula for the resolving power, $\delta = 0{\cdot}5\lambda/\text{N.A.}$ (p. 130) shows that increased resolution is obtainable by using light of shorter wave-length. Blue light is therefore advantageous in work with high powers, but it is well to note that the visual and the photographic focus may not then coincide exactly, and this must be determined by trial. A logical extension of the plan of shortening the wave-length is to use ultra-violet light, and this has been attempted on many

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[1] F. F. Lucas, *J. Franklin Inst.*, 1934, **217**, 661.

[2] H. Wrighton, *J. Roy. Microsc. Soc.*, 1933, **53**, 328. The computation is due to R. J. Bracey, of the Sci. Instr. Res. Assocn.

[3] Mercury lamps giving very intense illumination are now available.

occasions. The reflecting power of most metals in the ultra-violet region is low, and this is disadvantageous. It has been necessary to use a spark as a source of light, and focussing is then exceedingly troublesome. Special quartz objectives and eyepieces are necessary, and as the numerical aperture is low, the advantage of the short wavelength is largely counterbalanced. It is unlikely that the principle will find wide application in metallography, although in special instances remarkable results have been obtained. Particulars are given by Lucas and by Wrighton. On account of the number of reflections in quartz objectives, there is considerable flare. This has been greatly lessened by the ingenious design of a lens-mirror objective.[1]

Ordinary Huyghenian eyepieces are used with achromatic objectives; but the specially designed compensating eyepieces should always be used with apochromats to utilize their advantages fully. The eyepieces should be of low or medium power (× 4 and × 8 being the most useful) as the loss of light in metallographic examinations is so great that a high-power eyepiece gives a very dimly illuminated field. A number 2 eyepiece will also be found convenient for ordinary routine work. When the apparatus is arranged for photography, a projection eyepiece is often preferred. This is an eyepiece of low power (the × 2 is the most generally useful) in which the lower lens produces an image in the plane of the diaphragm, which is then magnified by the upper combination. In order to focus this image the tube holding the upper combination may be moved in and out, revolving in a helically cut slot. The position is indicated on the cap by a pointer travelling round a dial (Fig. 74). When projecting on to a screen, this part of the eyepiece is moved until the image of the diaphragm appears perfectly sharp on the screen. The position of the lenses in the eyepiece depends on their distance from the screen.

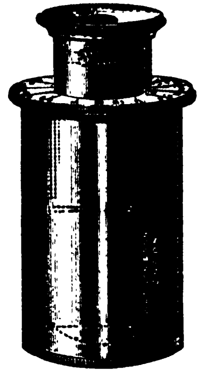

FIG. 74.—Projection eyepiece.

ILLUMINATION.

For visual observation, electric filament lamps are almost invariably used. Opal glass bulbs give a soft and uniform light, but become hot in use, so that if enclosed in a case good ventilation must be provided. A useful lamp for general purposes, giving enough light to be used for dark-ground illumination as well as with the ordinary illuminators, is one with a filament carrying a relatively heavy current at a low voltage. Such lamps, working at 6 volts, will carry as much as 5 amperes, and can be further overloaded for a short

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[1] B. K. Johnson, *J. Sci. Instruments*, 1934, **11**, 384.

time. They are best run on alternating current with a transformer and also an adjustable resistance. The lamp should be enclosed in a metal housing, provided with a holder for a ground glass screen and for light filters, and well ventilated. Such lamps are now supplied by several makers. For table microscopes an adjustable stand is desirable, allowing both alteration of height and tilting.

There are advantages in making the source of illumination an integral part of the microscope, so that all adjustment of the height of the lamp to the position of the vertical illuminator is avoided. In the earlier forms of this device, a small filament bulb was placed in a tube at right angles to the tube of the microscope, with a lens and an iris diaphragm interposed. This made a heavy attachment, projecting awkwardly and imposing a strain on the microscope tube. These disadvantages are overcome in the design due to Beck and Wrighton (Fig. 75) in which the side tube is bent at right angles, so as to be parallel with the tube of the microscope, and to impose no appreciable strain. The lamp is of the kind used in pocket torches, taking current at 4 volts from an accumulator or a transformer, and a ground glass and iris diaphragm are fitted in the attachment. This illuminator may be used even with microscopes which are not provided with means of raising and lowering the stage.

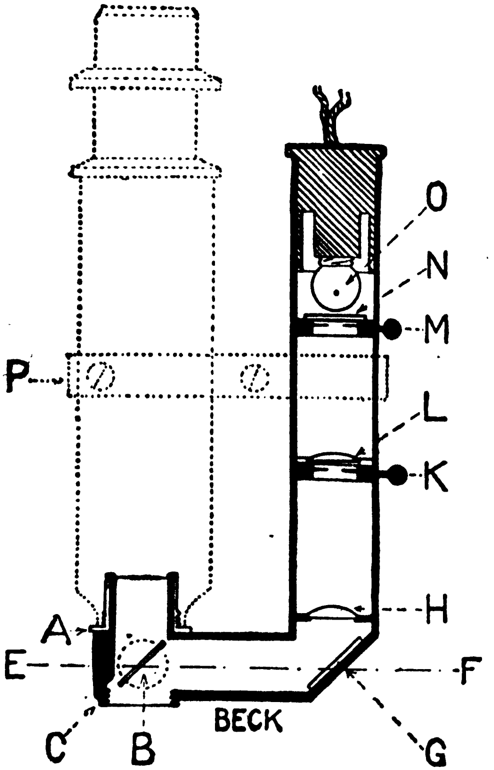

FIG. 75.—Beck-Wrighton illuminator.

Most instruments for photo-micrography are arranged for use with a small arc lamp. The carbons are from 5 to 7 mm. diameter, and either a hand or clockwork feed is provided. Clockwork is convenient, if the adjustment be correct, but excellent results may be obtained from a hand-feed lamp, only an occasional touch to the feeding head being necessary. Such lamps take 5 or 6 amperes, and only require a resistance for connection to the lighting circuit. Larger lamps of the same kind are made to take as much as 14 amperes, but are only required for such purposes as dark-ground photography with short exposures. The small lamp is all that is needed for most metallographic work.

The carbon arc gives an intense illumination, and with the present quality of carbons the light is very steady. With a properly constructed lamp the source of light remains central between the movements of the carbons. However, the rods burn away quickly, and it is inconvenient to have to interrupt a series of examinations in order to change them. For this reason enclosed tungsten arcs of the " Pointolite " type have been much used, these requiring no adjustment. They are somewhat more elaborate, having to have a separate starting switch. The disc of the 100 candle-power lamp is of very uniform intensity, so that it lends itself well to critical illumination, in which an image of the source is focussed on to the objective. It is not intense enough for photographic work with microscopes involving many reflections, but some workers prefer it, even for work with high powers, using instruments in which the path of the rays is as direct as possible. The 500 c.p. lamp has a much larger luminous disc,

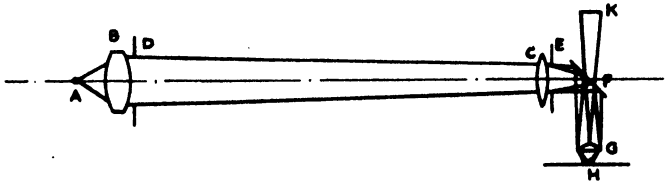

FIG. 76.—**Beck system of illumination.**

but the position of the arc does not remain constant enough for really critical work. It is probable that enclosed arcs will in time be replaced by filament lamps of high intensity.

The relative positions of the lamp, condensing lenses, and any diaphragms that may be interposed is important for the good performance of the microscope.

For a table microscope, but provided with a self-contained illuminator, the simplest arrangement is that of a filament lamp, enclosed in a dark housing with an aperture closed by a fine ground glass. This is brought up to the level of the aperture of the vertical illuminator, and no lens is used. A stop can be inserted in the path of the light to cut out stray rays which cause flare. To obtain good resolution and to avoid false structures, " critical " illumination is necessary, that is, the aperture of the objective must be fully utilised. In order that the field may be cut down as required without restricting the cone of light which fills the objective, the diaphragm must be at the same distance from the back lens of the objective as is the focal plane of the eyepiece, that is, it must be equal to the " tube length " of the microscope. For photographic work the arrangement shown in Fig. 76 is to be recommended.[1] A is the source of light, B is an aplanatic

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[1] H. Wrighton, *J. Roy. Microsc. Soc.*, 1927, **47**, 107 ; C. Beck, *ibid.*, 116.

condenser, C a small lens of about 13 cm. focus, D and E iris diaphragms, F the plane glass reflector, G the objective, H the object, and K the eyepiece. The lens B forms an image of the source of light on the lens C, being so placed that the image fills the aperture of the lens. This image is then focussed on to the back lens of the objective, being reflected at right angles on the way. The distance of the diaphragm E from the reflector being the same as that from the reflector to the eyepiece image, the diaphragm D may be used to control the beam of light so that it just fills the back lens of the objective, whilst E is used to cut down the field without altering the image. This cutting down is often necessary to exclude stray light, the improvement in definition being due to the removal of glare.

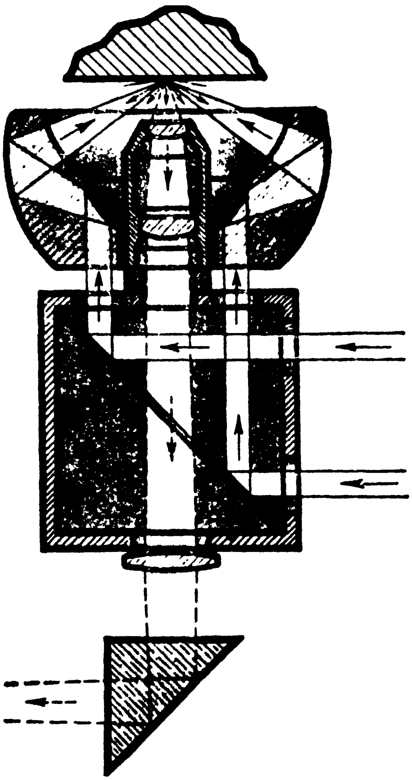
FIG. 77.—Leitz dark-ground illuminator.

Oblique illumination, mentioned above, is only practicable with low powers, as the beam of light has to pass between the objective and the specimen at a suitable angle. Since the beam falls only from one side, the effect is usually unsatisfactory. "Dark-ground" illumination, in which a hollow cone of rays is used, has long been employed in microscopical work with transmitted light, but its introduction into metallography is recent. The arrangement of Messrs. Leitz, in their large metallographic microscope, is shown in Fig. 77. Light is reflected from a plane-parallel glass, in this case upwards, and brought by internal reflections inside the glass system of lenses into the form of a hollow cone, surrounding the objective. The same makers have embodied this system in a series of "Ultropak" objectives for use on ordinary microscopes. These are fitted with a self-contained illuminating system at right angles to the tube of the microscope. Immersion as well as dry lenses are made on this plan.

In ordinary vertical illumination, the objective acts as a condenser towards the rays, which pass through it twice: before and after reflection by the object. With dark-ground illumination, the rays only traverse the objective once, so that the scattering of light by the various surfaces within the combination is reduced to one-half.

The appearance of an object under dark-ground illumination stands to that under vertical illumination in the relation of a negative to a positive. A perfect mirror surface appears perfectly black, whilst lamellar and similar structures appear bright, usually with strong contrast, which can be varied by altering the angle of the cone by means of a screw adjustment. The device is particularly useful in the examination of deeply etched or pitted specimens, as when studying surface corrosion. Pits which appear under vertical illumination merely as black spots may be examined in detail, the colour or form of the corrosion product contained in them being clearly seen. The system also lends itself well to isolated crystals, which appear flat and dead under the ordinary objectives.

For very low magnifications, microplanars and similar lenses, such as the Zeiss Tessars, are used. For magnifications of 15 to 25 diameters, the use of the anastigmats supplied with hand kinematographic cameras is recommended [1] as giving a large and flat field with good definition. The lens is reversed from its ordinary position, the front surface being made to face into the camera.

When the microscope is arranged for photographic work, with an intense source of light, it is necessary to cut down the intensity if the image is to be examined directly before projection on to the ground-glass. Dark glasses, which can be obtained in several different depths, are interposed between the source and the illuminator, a slip being provided for holding them. For photographic exposures the dark glass is replaced by a colour filter. These filters are usually of gelatin, dyed with a suitable dye, and preserved between glass plates, which need not be optically worked if they are placed in the outer part of the system. Wratten filters may be obtained with any required absorption. A light greenish-yellow filter is useful for general purposes, but with high-power lenses a bluish-green filter is desirable, whilst for monochromats a filter must of course be used which transmits only a narrow band including the wave-length for which they are corrected.[2] Liquid filters, containing solutions of copper sulphate and other salts, were formerly recommended, but the range of gelatin filters now available makes them unnecessary.

When an arc lamp taking a heavy current is used, it is essential to interpose a water trough with parallel sides near to the source, to absorb a large part of the heat rays, otherwise damage may be done to the cementing material of the objectives as well as to gelatin filters, but when the illuminating arrangements are such as to allow of the use of less powerful lamps this may be dispensed with.

Most often, a horizontal camera is used, mounted either on the

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[1] R. H. Greaves and H. Wrighton, "Practical Microscopical Metallography," London, 1933.

[2] The Eastman Kodak Co. supplies a list giving the ranges of absorption of all Wratten filters.

same optical bench as the microscope or, as in the large Zeiss instrument used by Lucas, on a separate table at right angles to it. It is usual to make the camera bellows in two parts, so that either moderate or great extensions may be used. Some workers still prefer to use a vertical camera with a microscope of the normal (not inverted) type, the only inconvenience being the height of the focussing screen above the table. A long camera is very rarely necessary, it being better to obtain magnification in other ways, or to enlarge negatives after they have been made.

Much has been written on the advantages of using very high magnifications in metallographic work, and it is important to determine how far magnification may be carried with any real gain in the revelation of detail. By using a higher eyepiece, or by increasing the camera length, any desired increase in magnification is obtained without difficulty, but such a device does not increase the resolving power of the objective, and when carried beyond a certain limit gives only the same result as would an enlargement of a negative taken with the same objective but a lower total magnification. Most of the photographs of the structure of steels at a magnification of 2000 diams. or more are of this character, the supposed advantages being quite illusory. On the other hand, such a photograph as that of chromium carbide particles at 4000 diameters by Lucas[1] undoubtedly shows particles with great clearness which have only just come into view, and are not seen at a lower magnification. The ordinary computation of resolving power, however, indicates a lower value for the greatest useful magnification, and the reason for the paradox has to be sought.

The resolving power of an objective is usually defined as the minimum distance between two lines which can be separated optically by the lens, as given by the formula

$$\delta = 0{\cdot}5\ \lambda/\text{N.A.},$$

where δ is the smallest distance between two lines which can be resolved; λ is the wave-length of the light used for illumination, and N.A. is the numerical aperture. Assuming that an angle of at least 2′ must be subtended for the image to be perceived by the eye, and taking λ as $0{\cdot}55\ \mu$ for daylight, the greatest possible resolution for an objective of N.A. 1·40, is given by $\delta = 0{\cdot}19\ \mu$, and the highest useful magnification is 741 diam.[2] If an angle of 2′ be considered too small for comfort, and the value of 4′ be taken, the magnification becomes 1481 diam. For an objective of N.A. 1·60, the highest which is practicable, the magnifications become 847 and 1693 respectively. It is certain that in all but a few exceptional conditions nothing is gained by magnifying further. However, the Abbe theory of resolution is based on the separation of the lines of a grating by transmitted light, and does not necessarily fix the limit of size

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[1] F. F. Lucas, *J. Franklin Inst.*, 1934, **217**, 661. (Fig. 32 of paper.)
[2] E. Abbe, *J. Roy. Microsc. Soc.*, 1882, [ii], **2**, 460.

of, for instance, a single lamella or particle which can be rendered visible. Lord Rayleigh[1] has pointed out that visibility is not the same thing as resolution, and an elementary experiment of his is instructive. When a piece of very fine wire gauze is viewed through a minute pin-hole, it is impossible to see the structure of the gauze at a distance of a few inches, whilst a single wire of the same thickness can still be seen when several feet beyond the pin-hole. The resolution of fine grating-like structures, whilst of importance to the observer of diatoms by transmitted light, is a problem which rarely presents itself to the metallographer, working with reflected light, and examining structures which consist mainly of discrete particles Hence the existing theory does not indicate the limit to which magnification may be carried with useful effect in the metallographic microscope. At the same time, a warning should be given against the use of excessively high magnification. It is not only that the structures which call imperatively for such high powers do not often present themselves, but to obtain any advantage from the increased resolution the preparation of the specimens for examination must be unusually perfect. The success of Lucas in resolving the fine structure of hardened steels is probably due as much to the precautions taken in polishing the specimens as to the increased optical quality of the microscope. For most purposes, including even the examination of carbide particles in alloy steels, a magnification of 1500 diam. is as great as is required.

When, however, micrographs have to be reproduced by a half-tone process, higher magnifications may be used in order that the images of particles may be at least 0·5 mm. across, as otherwise they may be lost or rendered indistinct in reproduction. Such a fine photograph as that showing lamellæ of cementite only 0·16 μ apart clearly resolved at a magnification of 2500, using an objective with an aperture of 1·60 and blue light,[2] would not show the structure if reproduced by a half-tone process. The published plate is an actual photograph on a glossy paper.

To obtain the maximum resolution it is essential that the aperture of the objective be utilized to the full. "Stopping-down" by means of a diaphragm may be necessary to avoid flare or to obtain some depth, but only at the cost of reducing the power of seeing fine detail. The blocking of a portion of the aperture by crescent-shaped diaphragms, or by the use of a prism illuminator instead of a plane plate, sacrifices definition.

Two glass screens are required for focussing purposes. One of these should be of very fine-grained ground glass, the other of clear glass. In focussing an object the ground glass screen is first inserted, the iris diaphragm being opened far enough for the field to be illuminated brightly. The specimen is then moved about on the stage until a suitable field is selected. It is advantageous to have the size

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[1] Lord Rayleigh, *Phil. Mag.*, 1896, [v], **42**, 167.
[2] H. Wrighton, *J. Roy. Microsc. Soc.*, 1933, **53**, 328.

of the plate to be used ruled in pencil on the ground glass, so that it may be seen at once what portion of the field falls within the limits of the plate. The iris diaphragm is then closed until the detail appears clearly up to the edges of the marked area. When the focus appears sharp, the ground glass screen is replaced by the clear glass, and the final focussing performed with the aid of a focussing glass applied to the screen. If a colour filter is to be used, this should be inserted before the final focussing. The screen is now withdrawn and replaced by the dark slide, and the exposure made in the usual way. It is advisable to reinsert the focussing screen after exposure, in order to see whether the necessary movements have caused any displacement.

Care must be taken to exclude all extraneous light. The connection between the eyepiece of the microscope and the camera should not be made rigidly, but by means of a velvet sleeve with elastic collars or of an adaptor of blackened brass, shown in section in Fig. 78.

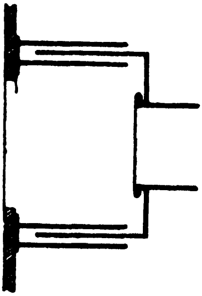

FIG. 78.—Light-tight connection.

Although as a rule the photographic method is at once the most convenient and the most trustworthy means of recording structure, it may sometimes happen that there is an advantage in making a drawing of some particular specimen. This may be called for by the appearance of some structure in a deeply etched alloy, the features of which cannot be simultaneously brought into focus, or by the colorations produced by heat-tinting, which are lost unless some process of colour-photography is employed. For students beginning the subject, the practice of drawing structures is strongly to be recommended as the best means of impressing the details on the memory. Examples of artistic drawings, sometimes in colour, are the illustrations to papers by J. O. Arnold, executed by F. Ibbotson and J. H. Wreaks.[1] The task is facilitated by the use of a device, such as the camera lucida or the Abbe reflector, for projecting the microscopic image on to the drawing paper. The drawing of the outline is then reduced to mere tracing. Even without such devices it is not difficult with a little practice to apply the left eye to the microscope, and to watch the pencil and paper with the right, the process then becoming one of drawing from a copy. As in all microscopical work, it is important that the worker should accustom himself to using both eyes in turn for observations, the eye not applied to the microscope being kept open. Neglect of this precaution leads to fatigue and strain.

THE USE OF POLARIZED LIGHT.

Polarized light, which is invaluable in the examination of transparent sections of rocks and minerals, also finds application in

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[1] *J. Iron Steel Inst.*, 1905, ii, 27; 1914, i, 306, etc.

metallography. The microscope should have a rotating stage and means of centring the object. In the simplest method of use, a polarizing Nicol prism is inserted in the beam of light before entering the vertical illuminator, and a second Nicol prism, used as an analyser, is placed in the tube of the microscope. A sensitive quartz plate is placed below the analyser. The rotation of the plane of polarization of the light reflected from a surface which is not isotropic is detected by a change of colour when the specimen is rotated.[1] The method is only qualitative, but it serves to distinguish anisotropic metals or phases unetched or only lightly etched from those which are isotropic. A more refined method, also due to Koenigsberger, makes use of interference fringes, but is less convenient for ordinary metallographic work. A hexagonal metal, such as zinc, appears isotropic if the basal plane happens to lie in the surface, but other sections appear anisotropic. The first method has been made more delicate by the use of other types of quartz plate.[2] It is possible in this way to determine, for instance, the orientations of the several constituents of a eutectic.

When a metal is etched deeply, polarization effects are seen on rotating the specimen, even when the metal is isotropic, owing to the scattering of light from the facets of the etch-figures.[3]

Polarized light proves particularly useful in the study of inclusions. Thus under ordinary vertical illumination, cuprous oxide and cuprous sulphide are very similar in appearance, whilst between crossed Nicols the oxide assumes its true ruby-red colour, whilst the sulphide remains greyish-blue.[4] The ternary character of some eutectics may be made distinct in the same way. That certain globular non-metallic inclusions in steels are transparent has been shown by the appearance of a dark optical cross when examined between crossed Nicols, and the changes produced in the inclusions by forging may be followed by the changes in the crystalline arrangement of the silicates within the inclusions.[5]

Several of the larger metallurgical microscopes are now provided with attachments by means of which the change from ordinary to polarized light may be made rapidly without moving the specimen.

MICROSCOPY AT HIGH TEMPERATURES.

Information as to the structure of metals and alloys at high temperatures has usually been obtained by quenching and subsequent etching. Etching the metal while hot has, however, been employed

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[1] J. Koenigsberger, *Metallurgie*, 1909, **6**, 605.

[2] K. Endell and H. Hanemann, *Z. anorg. Chem.*, 1913, **83**, 267; F. E. Wright, *Mining and Metallurgy*, 1920, No. 158.

[3] O. Jones, *Phil. Mag.*, 1924, [vi], **48**, 207. For the theory see M. Berek, *Z. Krist.*, 1934, **89**, 125.

[4] M. v. Schwartz, *Z. Metallk.*, 1933, **25**, 314.

[5] S. L. Hoyt and M. A. Scheil, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **116**, 405. A. M. Portevin and R. Castro, *J. Iron Steel Inst.*, 1935, ii, 237.

by several investigators. The structure of iron at a red heat was examined by etching with fused calcium chloride,[1] the grain boundaries thus developed being examined after cooling. Gaseous chlorine and hydrogen chloride have been used in the same way,[2] the structure of steel being very clearly developed. Even heating in a vacuum at a sufficiently high temperature will reveal the structure, owing to differential volatilization from different crystal faces, and this method has been used in the study of steel,[3] and has given striking pictures of crystal structure in the examination of silver.[4]

Furnaces in which the specimen can be kept under microscopical observation during heating have been constructed, the most convenient being one in which the furnace is closed below by a plate of transparent silica, the microscope being below the furnace. The cylindrical furnace has a tungsten winding and water-cooled ends.[5]

METALLOGRAPHY AT LOW TEMPERATURES.

Dental amalgams present special difficulties as the objects of metallographic examination, on account of the presence of liquid mercury, which makes them pasty at the temperature of the room. In the course of a study of their structure, it became necessary to carry out the whole of the operations of polishing, etching, and examining under the microscope, at a temperature below −40°. Mercury or liquid amalgams are filled into a small cylindrical mould of glass or ebonite closed at one end by a plane glass slip. After freezing by immersion in a paste of carbon dioxide snow and acetone and removing the end plate, the surface may be smooth enough for etching. Pasty amalgams are filled into a mould made up of two rings, one of which may be detached with the end plate, so that the frozen alloy projects beyond the mould, or when an ebonite mould is used it may be ground down together with the alloys. The combined mass is held in a wooden clamp, and ground down by hand on strips of emery paper in the ordinary way, each paper, however, being immersed in a paste of carbon dioxide snow and acetone. The final polishing may be on wash-leather, without any polishing powder, the pad being cooled

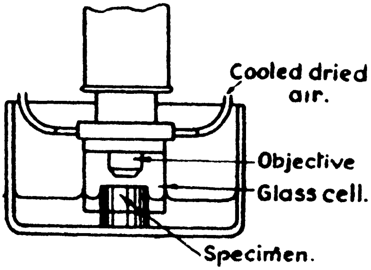

FIG. 79.—Low-temperature stage.

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[1] E. H. Saniter, *J. Iron Steel Inst.*, 1897, ii, 115; 1898, i, 206, 275.

[2] P. Oberhoffer, *Metallurgie*, 1909, **6**, 554; A. Baykoff, *Rev. Métall.*, 1909, **6**, 829.

[3] W. Rosenhain and J. C. W. Humfrey, *J. Iron Steel Inst.*, 1913, i, 221. The effect probably depends on the presence of traces of oxygen.

[4] W. Rosenhain and D. Ewen, *J. Inst. Metals*, 1912, **8**, 149; *Intern. Zeitsch. Metallogr.*, 1913, **3**, 276.

[5] H. Esser and H. Cornelius, *Stahl u. Eisen*, 1933, **53**, 532.

as before. The specimens are etched in 25 per cent. hydrochloric acid, cooled to $-60°$, and washed in cooled acetone without drying. A special attachment is used on the microscope stage, as illustrated in Fig. 79. A brass tube fits over the objective, and carries a glass tube which forms a chamber enclosing the specimen, cooled by passing a stream of dried air, saturated with cooled acetone.[1]

THE ELECTRON MICROSCOPE.

That there is an analogy between the refraction of a beam of light by a lens and the behaviour of a stream of electrons passing through electric or magnetic fields was first shown by Busch.[2] On account of the wave properties associated with the electron, a beam of electrons travelling at a high speed may be made to converge to a focus, so that an instrument having a close analogy with an optical microscope may be constructed, capable of giving a magnified image which may be made visible by a fluorescent screen or recorded on a photographic plate. This instrument has found application in metallography, and is likely to prove a valuable auxiliary to the ordinary microscope, owing to the higher resolving power which is possible, and to the fact that metals may be conveniently examined at high temperatures by its means.

The equivalent wave-length of the electrons composing a beam is given by the formula

$$\lambda = \sqrt{(150/P)} \times 10^{-8} \text{ cm.,}$$[3]

where P is the potential drop in volts corresponding with the energy of the electrons. With a numerical aperture of 0·1, applying the usual formula for resolving power, $0{\cdot}5\lambda/\text{N.A.}$, this gives, for electrons with an energy of 50,000 volts, a resolving power of $0{\cdot}27 \times 10^{-4}\ \mu$. It is, at present, quite impracticable to apply such a magnification as would allow of this resolution being utilized, but with a magnification of 8000 diam. a resolution of $0{\cdot}05\ \mu$ has been obtained, so that the limits of the optical microscope have already been somewhat exceeded.

It is possible, however, that another advantage of the electron microscope may prove equally useful to the metallographer. This is its applicability to the photography of metals at high temperatures. As the heated specimen is far from the photographic plate, and no glass lenses are interposed, very high temperatures can be applied without difficulty. Moreover, the action of the electrons on the photographic emulsion is so intense that very short exposures suffice, and in this way it has been possible to observe the $\alpha - \gamma$ transformation in iron, the grain boundaries being made apparent by activation

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[1] W. Rosenhain and A. J. Murphy, *Proc. Roy. Soc.*, 1927, **113**, A, 1.

[2] H. Busch, *Ann. Physik*, 1926, [iv], **81**, 974.

[3] G. P. Thomson, " Wave Mechanics of Free Electrons," New York, 1930, p. 47.

with barium,[1] and even to make a kinematographic record of the process.[2]

The construction of the instrument, which is shown diagrammatically in Fig. 80, is simple, but to determine the best dimensions of the several parts, and the strength of the magnetic fields required, involves preliminary experiments.[3] It is not possible to examine metals directly by these means at atmospheric temperatures. However, by etching the surface and taking a thin cast in some transparent material which reproduces all the detail, transmission photographs may be taken, and in this way remarkably beautiful photographs of pearlite in steel at magnifications as high as 40,000 have been obtained.[4] Vinyl resin or some similar synthetic plastic is used for the casts. The large instruments used for such work are made by the Radio Corporation of America.

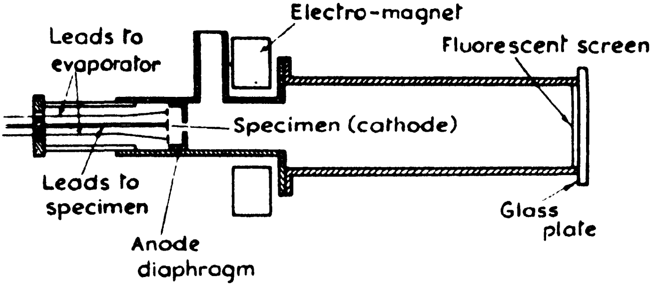

FIG. 80.—Electron microscope.

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[1] E. Brüche and W. Knecht, *Z. techn. Physik*, 1935, **16**, 95.

[2] W. G. Burgers and J. J. A. Ploos van Amstel, *Nature*, 1935, **136**, 721.

[3] For further particulars see M. Knoll and E. Ruska, *Z. Physik*, 1932, **78**, 318; E. Brüche, *ibid.*, 1935, **98**, 77; H. J. H. Starks, *Phys. Soc. Reps. on Progress in Physics*, 1936, **2**, 288 (with a survey of the literature).

[4] V. K. Zworikin and E. G. Ramberg, *J. Appl. Physics*, 1941, **12**, 692; V. J. Schaefer and D. Harker, *ibid.*, 1942, **13**, 427; V. K. Zworikin, *Metals Technol.*, 1943, *Tech. Publ.* 1594; C. S. Barrett, *ibid.*, *Tech. Publ.* 1637.

CHAPTER VIII.

THE CRYSTALLIZATION OF METALS AND ALLOYS.

WHILST the crystallization of solid components from molten alloys, and of salts from their solutions, are processes of essentially the same nature, there is one remarkable difference in the course of events in the two cases. Salts commonly separate from their solutions in the form of more or less perfect crystals, bounded by plane faces, and a small crystal continues to grow in all directions in which it is free, retaining the same or a closely similar general form, so that an octahedron remains an octahedron, the development of additional faces being only a subordinate feature. Metals and alloys, on the other hand, only exceptionally form crystals of this kind. As a rule, a small crystalline nucleus grows almost exclusively in the direction of certain axes, giving rise to elongated and much branched forms, the "dendrites," "crystallites"[1] or "crystal skeletons." None of the faces attain any great development, even under favourable conditions of cooling, and curved faces are frequent, the bounding surfaces being sometimes highly curved, to the complete exclusion of plane faces.

Exceptions to these rules occur on both sides. A few intermetallic compounds, as noticed below, crystallize from molten alloys in well-developed cubic, rhombic, or hexagonal forms, bounded by plane faces, whilst it is possible to cause many salts and organic compounds to assume the skeletal condition, especially by adding viscous or colloidal substances to the solution in which crystallization is taking place.[2] Viscosity, however, is not responsible for the peculiar behaviour of metals.

The mode of growth of such a skeleton has been studied microscopically in a number of substances by Lehmann. If we suppose crystallization to begin at a centre in the midst of the liquid, a minute crystal is first formed. Crystals can only grow in a super-saturated

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[1] The term "crystallite" was introduced by H. Vogelsang ("Die Krystalliten," Bonn, 1875) and has since been used continuously to denote a crystal skeleton. In recent years, however, physicists have used it to signify a minute fragment of a crystal, such as is produced in the breaking-up of a crystal by plastic deformation, and this use has become so general that the metallographer is reluctantly forced to abandon the word in its original sense, and to use alternative expressions. The term "dendrite" is appropriate to branched or tree-like forms.

[2] See O. Lehmann, "Molekularphysik," vol. i, Leipzig, 1888, where a vast amount of information respecting the growth of crystals is collected.

solution, and as soon as the layer of liquid adjoining the crystal ceases to be supersaturated, growth is interrupted, and can only recommence when the concentration of the layer has been increased by diffusion. As Lehmann has shown, the concentration gradient is steepest at the most sharply pointed angles of the crystal, and it is there that the most rapid growth occurs. Hence, if we suppose the minute nucleus to have the form of an octahedron, its growth takes place in six directions, which in this case coincide with the prolongations of the crystallographic axes. The skeletons thus formed are truly crystalline, and exhibit numerous octahedral faces. Growth soon sets in at some of the solid angles thus produced, with the result that a system of secondary axes, at right angles to the primary axes, is established, and this is succeeded by systems of the tertiary and higher orders, resulting in the filling up of the interstices of the skeleton. In a substance growing from the melt, the temperature gradient takes the place of the concentration gradient. A metallic crystal growing freely develops axially, the axes advancing more rapidly than the interaxial matter, tending to complete the crystal. Very fine examples of this mode of growth are sometimes seen in the crystals of iron projecting into the internal cavities, or "pipes," of slowly cooled steel ingots.[1] It is also common in native metals, the elongation in the direction of certain axes being very remarkable in the case of filiform gold, and of arborescent silver and copper, all of which are elongated in the direction of the octahedral axes.[2]

If the growth of the dendrite is confined in some directions, only a few of the possible skeletal axes are developed. The arrangement of axes is well seen when, as at the free surface of a cast mass, the dendrites are compelled to grow in a plane, the axes perpendicular to that plane being suppressed. The frost-figures produced by the freezing of deposited moisture on window frames are a familiar example of such branched or dendritic growths. Owing to the fact that most metals contract on freezing, the crystals which form on the surface of a metal or alloy are left in relief by the contraction of the mother-liquor, and this fact makes it possible to photograph them without developing the structure by etching.

Plate IA represents the surface of a mass of antimony cast in an open mould, and a similar appearance is characteristic of most readily fusible metals cast in the same way.[3]

The process of crystallization from any given centre must ultimately reach a limit owing to the interference of adjoining crystals. The growth of the axes is thus arrested, and the further solidification of metal takes place interaxially, axes of higher order being formed until the spaces are filled with solid matter. If we suppose the

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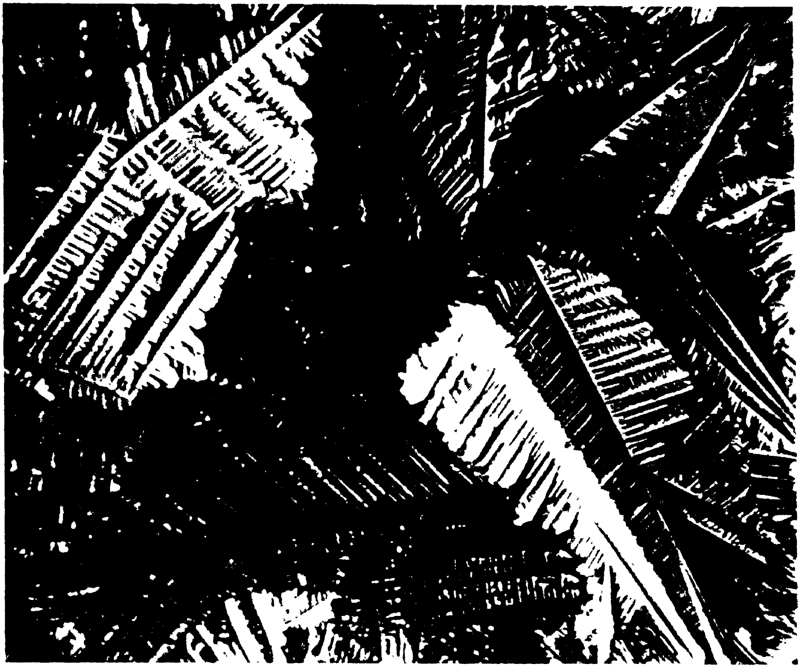
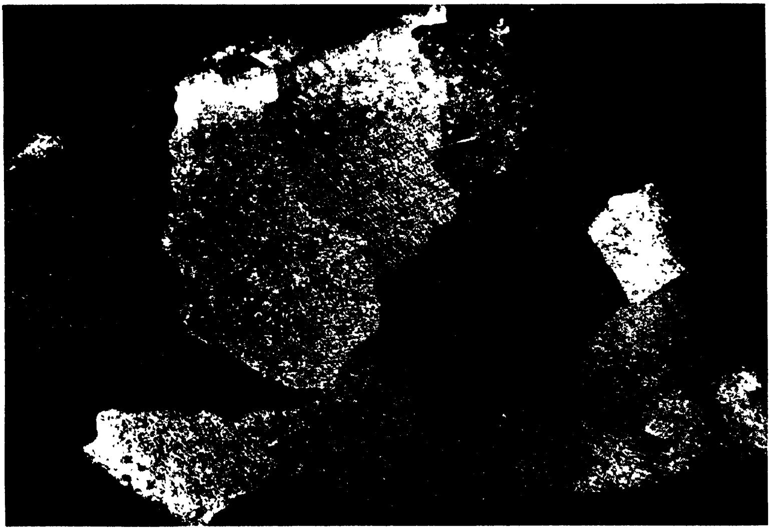
[1] D. Tschernoff, *Rev. Univ. Mines*, 1880, [ii], **7**, i, 129; E. F. Lange, *Mem. Manchester Phil. Soc.*, 1911, **55**, No. 24.

[2] The writer has reviewed the growth of metallic crystals in *J. Inst. Metals*, 1914, **11**, 57; and *Trans. Amer. Inst. Min. Met. Eng.*, 1927, **75**, A, 526.

[3] Another example is the surface of slowly cooled high-carbon steel, shown by N. Belaiew, "Crystallisation of Metals," London, 1922, Plate II.



A. Surface of cast antimony



B. Etched surface of cast lead. × 4

PLATE I

original distribution of the centres of crystallization to have been uniform, and growth to have taken place with equal velocity in the direction of each octahedral axis, the solidified mass will be divided up into exactly similar polyhedra. In any actual crystallization, the centres are not uniformly distributed, and the orientation of the axes of neighbouring crystals is not the same, so that the polyhedra vary in shape and size. They may retain a fairly regular polyhedral form, or may be quite irregular, as is seen in the section of cast lead, Plate Iʙ, or neighbouring crystals may grow to an unequal extent, giving rise to interlocked and complicated boundaries, often resembling the sutures of the cranial bones.

Surface tension undoubtedly plays a part in determining the forms of metallic crystals separating from the melt, as is shown by the rounding of the angles of such metals as have a relatively high surface tension. It was suggested by G. Quincke[1] that an actual separation into two liquid phases occurs just before solidification, so that the polyhedra have the form of foam-cells. Although the idea of a separation is certainly erroneous, the effect of surface tension is frequently to produce polyhedra which can be shown by statistical comparison to approximate closely to those which are found in a foam.[2]

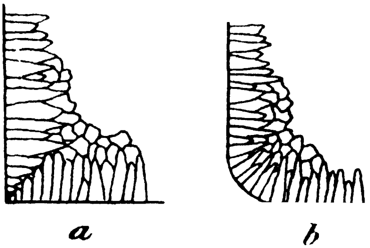


Fig. 81.—Crystal growth in ingots and castings.

The typical structure of a solidified metal is therefore that of approximately polygonal "grains," the boundaries of which are not crystal faces, but are due to interference during growth. Each grain is, to use the mineralogical term, an "allotriomorphic" crystal, the outline of which is determined by the presence of neighbouring grains. The form of the grains is somewhat different near to a cooling surface, as the dendrites which start from that surface have time to become long before their growth is interrupted by meeting with other skeletons, crystallization in the interior not setting in until later. The principal growth of the external skeletons is in a direction perpendicular, or nearly so, to the cooling surface, and elongated "columnar" crystals result. This fact is the cause of the weakness of castings having a rectangular outline. The two systems of crystals starting from two adjacent sides meet along a line bisecting the angle, as shown in Fig. 81. This line is a line of weakness, from the ease with which the crystals lying on opposite sides of it can be separated. The difficulty is avoided by rounding off the angle as at *b*.

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[1] See, for instance, *Ann. Physik*, 1902, [iv], **9**, 1; *Intern. Z. Metallogr.*, 1912, **3**, 23.

[2] C. H. Desch, *J. Inst. Metals*, 1919, **22**, 241; *Rec. trav. chim.*, 1923, **42**, 822; and, for further evidence of surface tension in solid metals, "The Chemistry of Solids," Ithaca, 1934, Chapter IV.

Metals deposited electrolytically also form skeletons perpendicular to the surface of the electrode, and lines of weakness are similarly produced at the junction of two systems of crystals starting from the surfaces of a V-shaped groove, making it possible to divide a sheet of electro-deposited metal along such a line with ease.[1]

The nature of the allotriomorphic crystals may be studied in a solid metal by polishing and etching.[2] In such an etched section as Plate Ib, the outlines of the grains are rendered visible by the unequal brightness caused by the varying orientation of the original dendrites. If we represent the crystals which first separate, and the grains formed by them, diagrammatically as in Fig. 82, and remark that etching with a chemical reagent develops the internal structure of a crystal grain by the production of minute facets, we see that these facets will vary in orientation from one grain to another. Light falling on an etched surface will only be reflected into the tube of the microscope by such facets as have the appropriate orientation, and facets having a different orientation will reflect the light outside the instrument, consequently some grains will appear light and others dark. Such an effect is easily distinguished from a true difference of chemical character between the grains by rotating the specimen on the stage of the microscope. If the difference is one of orientation only, those grains which appear dark in one position appear light under a different incidence of the illuminating beam, and conversely.

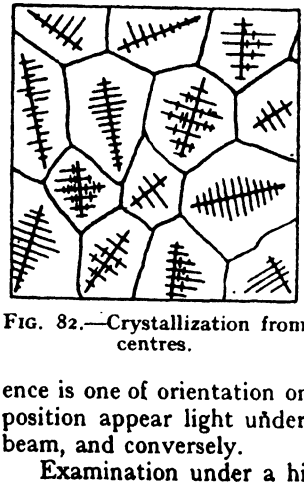

Fig. 82.—Crystallization from centres.

Examination under a higher power proves that the irregularities of surface are due to the exposure of crystalline facets. Crystals of a pure metal, suitably etched, show the formation of minute, regularly shaped "etch-figures," which usually take the form of negative crystals. The orientation and form of these may be employed to determine the crystalline system to which the substance etched belongs.[3] A few typical etch-figures are represented in Figs. 83 and 84, and in Plate Xb.

In pure metals or homogeneous solid solutions, the reflection of light from etched surfaces may be used to determine the orientation

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[1] W. De la Rue, *Mem. Chem. Soc.*, 1845, **2**, 300; A. K. Huntington, *Trans. Faraday Soc.*, 1905, **1**, 324.

[2] For a method of studying the arrangement of crystal skeletons in three dimensions, see C. H. Desch, *Proc. Roy. Phil. Soc. Glasgow*, 1912, 107; A. Portevin, *Intern. Z. Metallogr.*, 1914, **6**, 58.

[3] See especially, H. Baumhauer, "Resultate der Aetzmethode in der krystallographischen Forschung," Leipzig, 1894; A. P. Honess, "The Nature, Origin and Interpretation of the Etch-Figures on Crystals," New York, 1927. Etch-figures were first observed by F. J. Daniell, *Q.J. Sci.*, 1816, **1**, 24.

of a single crystal or of a grain exposed in the section. For instance, the cube face of copper usually gives pits of square outline, having their sides parallel with the edges of the cube. On illuminating obliquely and rotating the stage of the microscope, they will flash out four times in one rotation, at intervals of 90°. The octahedral faces give triangular pits, parallel with the edges of the octahedron, so that maximum brightness is obtained three times, at intervals of 120°. The dodecahedral faces, in copper as in most other metals, give furrows rather than pits, parallel with the shorter diagonal, so that only two maxima, 180° apart, are observed.[1]

This method is of value in determining the orientation of single crystals for use in experiments on mechanical deformation. By rotating an etched specimen and using a narrow beam of light, it is even possible to obtain patterns resembling those given by X-rays, and thus to fix the orientation of metallic crystals.[2]

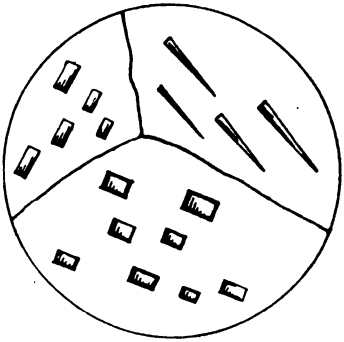

FIG. 83.—Etch-figures in iron.

Pure iron (ferrite) gives cubical etch-figures (Fig. 83) which may appear as triangular wedges when the section cuts the crystal grains at certain angles.[3] The pits obtained on a surface of pure lead [4] are negative cubo-octahedra, and their outlines are therefore either square or hexagonal, according to the orientation of the grain (Fig. 84). The microscopical appearance of such pits is deceptive; they often appear on examination to have the form of small crystals projecting *above* the general surface, and it is only by gradually altering the focus of the microscope that their true nature, as depressions *below* the surface, is recognized.

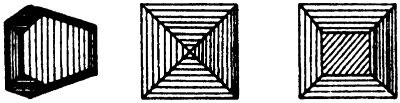

FIG. 84.—Etch-figures in lead.

Similar pits, very well defined in outline, are obtained by casting readily fusible metals, especially cadmium, in contact with glass or mica. The small air-bubbles enclosed between the metal and the smooth surface take the form of negative crystals, and are the true equivalent of etching-pits.[5] Such air-bubbles in cadmium are represented in outline in Fig. 85. Like the etching-pits, the orientation

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[1] G. Tammann and A. Müller, *Z. Metallk.*, 1926, **18**, 69; G. Tammann, *J. Inst. Metals*, 1930, **44**, 29.

[2] A. Schubnikow, *Z. Krist.*, 1931, **78**, 111.

[3] J. A. Ewing and W. Rosenhain, *Phil. Trans.*, 1900, **193**, A, 353; E. Heyn, *Z. Ver. deut. Ing.*, 1900, **44**, 433.

[4] J. C. W. Humfrey, *Phil. Trans.*, 1903, **200**, A, 225; H. A. Miers, *Min. Mag.*, 1898, **12**, 113.

[5] Ewing and Rosenhain, *loc. cit.*

of these negative crystals is constant within any one grain, but varies from grain to grain.

No essential difference in the mode of crystallization of a pure metal is made by the presence of a second metal in the liquid alloy, that is, a metal crystallizes from a solvent in the same way as from its own melt. Thus lead separates from a lead-silver alloy containing less than the eutectic proportion of silver in precisely the same way as from molten lead. The process is also the same when the crystals separating are those of a solid solution, except that there is then a possibility of a difference of composition between the skeleton first produced and the layers deposited subsequently. Under ideal conditions of cooling, these differences of composition are obviated by the continual readjustment of crystals and mother-liquor, as described on p. 27, and the solid product is then indistinguishable microscopically from a pure metal. Under ordinary conditions of cooling, however, diffusion is unable to keep pace with crystallization, and the crystals deposited consist of layers of progressively varying concentration. Etching with a reagent which attacks one of the component metals more than the other develops a structure in the crystal grains. For instance, an alloy of equal weights of nickel and copper, cooled in a small crucible and etched with hydrochloric acid and ferric chloride, presents the appearance shown in Plate IIA. The etching reagent acts on copper more readily than on nickel. The dendrites separating from the molten alloy are richer in nickel, the metal of higher melting-point, than the outer layers; they are therefore less attacked by the reagent, and appear as light "cores." The boundary between the light and dark areas is not sharp, the proportion of copper varying continuously from centre to periphery, but as etching is carried further the boundary moves inwards so that the size of the cores seems to diminish. Such a structure is characteristic of all rapidly cooled solid solutions. The development of cores by etching thus gives information as to the mode of growth of crystals, corroborating and supplementing that derived from the examination of cast surfaces.

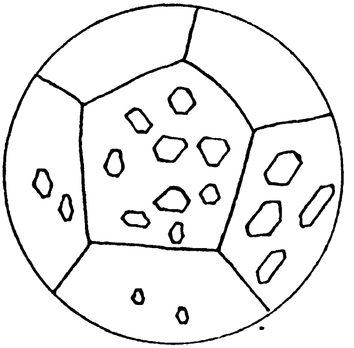

FIG. 85.—Casting-pits in cadmium.

Twinned crystals are sometimes observed in cooled metals which have not been subjected to strain, and are then known as "congenital twins"; but they are more often observed in metals and alloys which have been strained and subsequently annealed. Copper, and those alloys of copper which are isomorphous with copper, the so-called α solutions, show this strain-twinning very well. Plate IIB represents a specimen of "phosphor bronze," an α solid solution of

A. Copper 50, nickel 50 %. × 86

B. *a*- Tin-copper alloy, annealed. × 165

PLATE II

A. Copper crystallites in an alloy of silver and copper. × 200

B. Antimony 85, copper 15 %. × 86

PLATE III

tin and copper, after being strained and annealed. The arrangement of parallel laminæ, with alternating orientation, closely resembles that which characterizes the felspars in igneous rocks. The β solutions do not ordinarily undergo twinning when strained and annealed.

EUTECTIFEROUS MIXTURES.

In the process of crystallization of a constituent from a eutectiferous alloy, the separation at the cooling surfaces results in the concentration of the more fusible portions in the interior of the mass. It therefore happens in many instances that the whole or greater part of the constituent in excess forms long skeletons growing from the external surface inwards. Such highly-developed skeletons, often branched, are characteristic of many alloys, and are referred to as "arborescent," "dendritic," "pine-tree" or "fern" structures, from their general habit. Typical examples are seen in Plate III.

In the first of these, representing an alloy of silver and copper, the dendrites consist of copper, retaining a small quantity of silver in solution. They take the form of long primary axes, with well-developed secondary, but only a faint indication of tertiary, axes. The apparent breaking-up of the principal axes into isolated masses is due to the surface of the section cutting the dendrites obliquely, so that the principal axes lie partly above and partly below the plane of the section. The isolated masses are really sections through secondary axes nearly perpendicular to that plane. In Plate IIIB, which represents an alloy of antimony and copper, the dendrites are of pure antimony, and are composed of primary, secondary, and comparatively small tertiary axes.

A further example of a similar structure is illustrated in Plate IIA.

THE EUTECTIC.

A eutectic alloy consists, as has been shown, of an intimate mechanical mixture of two solid phases, produced by solidification at a constant temperature. The pattern produced by the intergrowth of the two phases takes a great variety of forms, and the beauty of many microscopic structures is owing to such patterns. The simple intermixture of small crystals of the two constituents, generally observed in mixtures of organic substances, and occasionally in igneous rocks, is rare amongst alloys. Metallic eutectics commonly show a definite orientation of one constituent, or else the two constituents are inter-laminated in curved forms, in which it is difficult to recognize crystalline structure.

A pure eutectic alloy, solidifying without undercooling, passes from the liquid to the solid state at constant temperature. The two constituents separate simultaneously, and the structure depends on the relative velocities of crystallization.[1]

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[1] R. Vogel, *Z. anorg. Chem.*, 1912, **76**, 425; F. E. E. Lamplough and J. T. Scott, *Proc. Roy. Soc.*, 1914, **90**, A, 600.

This process begins, like the crystallization of a pure metal, at a number of centres, and the interference of the systems leads to the formation of polyhedral masses or "colonies,"[1] resembling in general form the crystal grains of pure metals and solid solutions, but composed in this instance of an intergrowth of two phases. On etching, as the laminæ in neighbouring grains have generally a different orientation, the boundaries are developed, and under a low magnification the appearance is not unlike that of homogeneous crystal grains. Under oblique illumination, many eutectic alloys when etched present an iridescent lustre like that of mother-of-pearl, owing to the scattering of the incident light by the laminæ. This pearly appearance, first observed by Sorby in the eutectoid of iron and iron carbide, hence called by him "the pearly constituent," and by Howe "pearlite," is characteristic of such eutectic and eutectoid alloys as have a lamellar structure.

There have been many proposals for the classification of eutectics, as lamellar, globular, spherulitic, etc.,[2] but such distinctions are rather artificial, being based on superficial characters. Within a single colony the orientation of at least one of the constituents is uniform, as may be seen by examining the outlines of the particles, as in Plate VA, in which the small crystals of antimony are all parallel with one another and with the large crystal occupying the centre of the field. That the copper antimonide which forms the dark background is also parallel in orientation throughout the whole field is not so obvious, but may be shown by etch-figures, whilst in specimens of pegmatite, having a similar intergrowth of quartz and felspar, almost indistinguishable from the above, the parallelism may be proved by the simultaneous extinction between crossed Nicol prisms. A honeycomb structure is shown in the eutectic of white cast iron (Plate XVIIA). A coarsening of the structure towards the boundaries of the grains is very frequent, and is illustrated in Plate IVA. In many instances, the structure may be accounted for by growth radiating from a centre, giving a sheaf-like pattern (Plate IVA) resembling some of the spherulitic structures in rocks. Attention has been called to this similarity.[3] Slender rods, arranged in this sheaf-like form, appear as dots when the section cuts them transversely, and this accounts for the characteristic appearance of such eutectics as that of copper and cuprous oxide.[4]

That the outlines of the constituents of a eutectic are so frequently rounded, giving no indication of their crystalline form, is to be attributed to high surface tension. Although there are no satisfactory methods of determining the surface tension of a solid, it is a remarkable fact that when the metals are arranged in order

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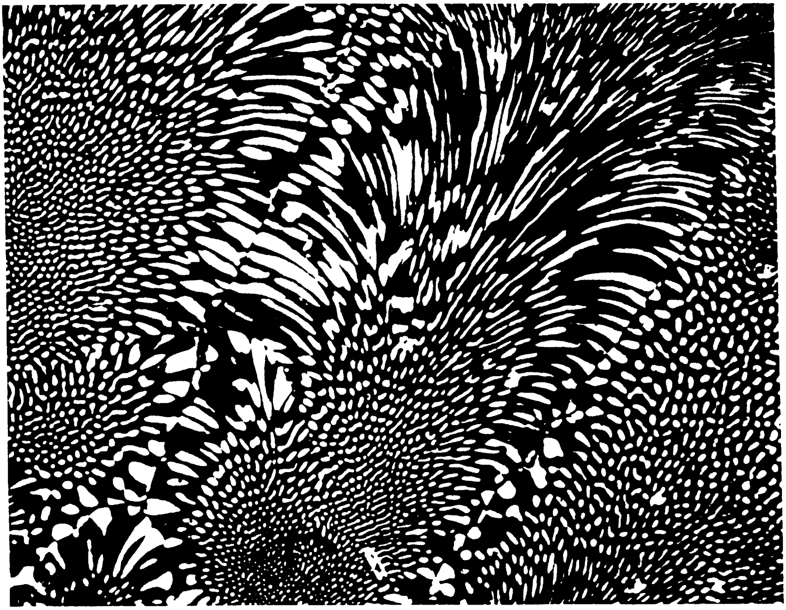
[1] C. Benedicks, *Intern. Z. Metallogr.*, 1911, **1**, 184.

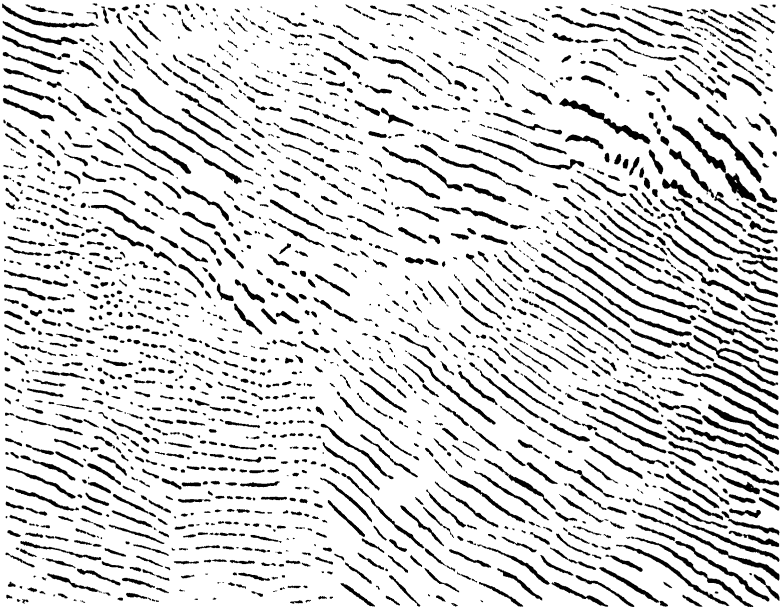
[2] J. E. Stead, *Proc. Cleveland Inst. Eng.*, 1900, February; *Metallographist*, 1902, **5**, 110; F. L. Brady, *J. Inst. Metals*, 1922, **28**, 369; A. M. Portevin, *ibid.*, 1923, **29**, 239.

[3] J. H. Teall, *Quart. J. Geol. Soc.*, 1907, **57**, lxii.

[4] L. W. Eastwood, *Trans. Amer. Inst. Min. Met. Eng.*, 1934, **111**, 181.

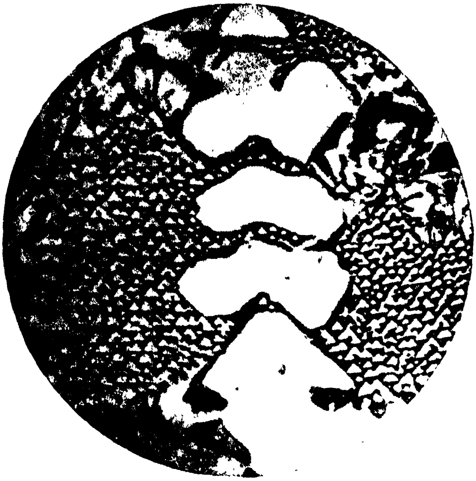


A. Eutectic of copper and copper phosphide. × 450



B. Eutectic of zinc and cadmium. × 600

PLATE IV



A. Alloy of antimony and Cu_2Sb. × 200

B. Antimony 75, copper 25 %. × 86

PLATE V

of their surface tensions in the liquid state[1] those metals which appear at the head of the list, such as copper and gold, usually form rounded dendrites and rounded particles in eutectic alloys, whilst those having low surface tensions, such as antimony, form dendrites and particles with sharp angles. Also, a metal has a greater tendency to form rounded dendrites, the higher the temperature at which it separates from an alloy, as may be seen by comparing alloys of copper and bismuth of different concentrations.[2]

It seems likely that the particles of one of the constituents of a eutectic have a common orientation within any one grain, as mentioned above. Whether there is a definite relation between the orientations of the two constituents will depend on the correspondence of the two crystal lattices. When these are closely related, or have some dimensions in common, something of the nature of parallel growth may be expected, corresponding with the orientation of potassium nitrate crystals on a crystal of calcite, and similar examples.[3]

When a eutectic alloy has a very fine grain, it is often difficult to reveal its structure by etching. The eutectic of silver and copper is an example. In some portions of the field even prolonged etching leaves the surface smooth, and it has been stated [4] that rapidly cooled eutectic alloys are not etched by reagents of the usual strength, several examples being given. The effect is, however, merely due to flow of the surface during polishing, the fine detail being smeared over. When such care is taken in polishing as will avoid flow there is no difference in etching properties between the fine and coarse areas.

As the composition of the alloy departs in the one direction or the other from the eutectic proportion, the structure naturally changes. A small deviation may fail to bring about the appearance of the constituent in excess in the form of distinct crystals or crystal skeletons. If the departure from the eutectic composition be greater, crystals of the constituent in excess make their appearance, at first as small isolated masses, becoming united to form skeletons or larger crystals with further change in the composition. A comparison of Plates III and V will illustrate the variations of structure as the eutectic point is passed. In Plate IIIB the antimony is in excess, and its long crystal skeletons are separated by the eutectic of antimony and copper antimonide. Plate VA shows the eutectic structure, whilst in Plate VB the long dark crystals are those of the compound Cu_2Sb, now the constituent in excess. Other typical eutectic structures are shown in Plate IV.

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[1] The surface tension of liquid metals has been determined by a number of different methods. The best results are those of L. L. Bircumshaw, *Phil. Mag.*, 1926, **1**, 341 ; 1927, **3**, 1286 ; 1928, **6**, 510 ; 1931, **12**, 596 ; 1934, **17**, 181 ; T. R. Hogness, *J. Amer. Chem. Soc.*, 1921, **43**, 1621 ; G. Drath and F. Sauerwald, *Z. anorg. Chem.*, 1927, **162**, 301 ; W. Krause and F. Sauerwald, *ibid.*, 1929, **181**, 353.

[2] G. Tammann and K. L. Dreyer, *ibid.*, 1932, **205**, 77.

[3] T. V. Barker, *Trans. Chem. Soc.*, 1906, **89**, 1120.

[4] N. S. Kurnakow and A. N. Achnasarow, *Z. anorg. Chem.*, 1922, **125**, 185.

INGOT STRUCTURE.

The freezing of liquid metal in an ingot mould presents certain peculiarities, and as the structure of the solid ingot has an important influence on the properties of the metal after forging or other mechanical treatment, the process has been the object of much study. Steel ingots, being made up to very large sizes (200 tons or more) and representing by far the largest metallurgical production, have received most attention.[1] An ingot cast under normal conditions consists of crystals arranged in three ways ; a thin outer layer of " chill crystals," small in size and only forming a small fraction of the mass ; " columnar crystals," perpendicular, or nearly so, to the walls of the mould ; and " equiaxed crystals," with random orientation, in the interior. Owing to the shrinkage of the metal during cooling, a cavity or " pipe " is usually found in the upper part of the ingot. The general arrangement is seen in Plate IXA, which represents an ingot of silicon-iron. The chemical composition in this instance is almost completely homogeneous, but in the casting of ordinary steel some separation of the constituents takes place. In general, there is an increase in the soluble impurities : carbon, phosphorus, and sulphur, on proceeding from the outside to the centre, and from the lower part of the ingot to the upper, but this general statement is subject to qualifications, and local concentrations of impurities occur, which are not accounted for by any simple theory. This " segregation " of impurities is brought about by the operation of the general principles of the freezing of alloys, according to which the first crystals to separate are relatively pure, and those elements which lower the freezing-point accumulate in the last portions to freeze. These are found near to the pipe, the head containing which is cut off in the later processes. By regulating the cooling, the impure and piped zone is confined to the shortest possible portion in the upper part of the ingot.

A class of steel known as " rimming steel " is also manufactured, in which the liberation of gas during freezing has had the effect of leaving cavities or " blowholes " in the metal, so that the shrinkage is compensated for and there is little or no pipe. When the process is properly controlled, the blowholes are situated at a definite and uniform depth below the surface, as shown in Plate IXB. In such ingots, which are only made from steel of low carbon content, the purity of the outer zone of crystals is remarkable. The main segregation of impurities is immediately within the zone of blowholes.

In addition to this " major segregation," there is a segregation of impurities on a small scale, the less pure liquid together with sulphide inclusions being trapped between the growing branches of the dendritic crystals. This effect is recognized when the steel is etched.

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[1] The successive reports of the Heterogeneity Committee of the Iron and Steel Institute, from 1926 onwards, contain the most extensive series of observations on this subject, and also provide a full bibliography, to which reference should be made.

The outer zone of a rimming ingot is almost free from such "minor segregation."

The elements found in steel vary widely in their liability to segregation. In the examples studied by the Ingots Committee, the range of variation increased on the whole with increasing size of the ingot, and whilst manganese and silicon showed only small variations, the range of carbon content $\left(\frac{\text{max.-min.}}{\text{mean}}\right)$ reached 100 per cent., and that of sulphur and phosphorus over 200 per cent. The distance between the solidus and liquidus curves in the systems iron-manganese and iron-silicon is small, and this condition is usually associated with a low degree of segregation.

The segregation found in carbon steel ingots, in which the more fusible constituents are concentrated towards the centre and the upper portions, is termed "normal" segregation, but it actually proves to be exceptional, the more frequent effect, known as "inverse" segregation, being the enrichment of the outer zones of the ingots in those constituents which cause a lowering of the freezing-point of the solvent metal. This is common in non-ferrous alloys, and in steels which do not undergo transformation, such as the high manganese steels. In its most extreme form, it is indicated by the appearance on the outer surface of excrescences, composed of a fusible eutectic, as in bronzes showing the so-called "tin sweat."[1] Such exudations are particularly common in bronzes containing lead, and indicate a forcible expulsion of the most fusible part of the alloy through fissures in the solid wall of the ingot. Where such a gross effect is not visible, analysis will show a concentration in the same direction, as in the alloys of silver and copper, in ingots of which a lack of uniformity of composition had been found even in the eighteenth century.[2] Many explanations have been offered. One of these may be disposed of at once. The Ludwig-Soret effect[3] has often been invoked as the cause of segregation, whether normal or inverse. This consists in a migration from the hotter to the cooler portions of a liquid, the condition of equilibrium being that the product of the osmotic pressure and the absolute temperature shall be a constant. Such an effect undoubtedly exists, and has been demonstrated for alloys,[4] but it is far too small, and the time required to reach equilibrium too great, to produce appreciable effects in ingots and castings, besides which, the convection currents in an ordinary mould are enough to mask any small changes of concentration caused by diffusion.

Inverse segregation has been attributed to the pressure exerted by dissolved gases,[5] which escape on solidification, and this factor

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[1] R. Genders, *J. Inst. Metals*, 1927, **37**, 241.

[2] W. Roberts-Austen, *Proc. Roy. Soc.*, 1875, **162**, 481. This paper contains a survey of the early observations, with new experiments.

[3] C. Ludwig, *Ber. Wien. Akad. Wiss.*, 1856, **20**, 539; C. Soret, *Arch. Sci. phys. nat.*, 1879, [iii], **2**, 48; *Ann. Chim. Phys.*, 1881, [v], **22**, 293.

[4] M. Ballay, *Rev. Métall.*, 1928, **25**, 427.

[5] Genders, *loc. cit.*; G. Masing and O. Dahl, *Z. anorg. Chem.*, 1926, **154**, 189.

is probably sometimes of importance, but the effect has been found in the thin outer shell of an ingot which had been emptied before there had been time for any such pressure to be exerted.[1] It seems rather that in the process of freezing from the wall of the mould inwards, the dendritic crystals grow more rapidly in length than in breadth, so that gaps are formed between them into which the liquid is sucked.[2] A possible mechanism for the production of such gaps is known, namely the " crystal thrust " which is often exerted during the growth of dendrites,[3] resulting in the outer shell of a cast bar, for instance, occupying a greater volume than would be expected from the normal density of the alloy. It was from this cause that certain brasses and bronzes were thought to expand during freezing,[4] whilst actually the resulting bars were porous, with gaps between the dendrites. In the freezing of an ingot, the residual liquid, containing more of the dissolved elements than the shell, may thus be drawn into the outer zone in order to fill the gaps left by the thrusting apart of the neighbouring dendrites. The effect is greater, the greater the solidification interval of the alloy, that is, the difference of temperature between the liquidus and the solidus. The amount of inverse segregation bears a rough proportionality to that interval. At the same time, other factors may sometimes contribute to the segregation, and it may be varied, and its direction sometimes even reversed, by varying the rate of solidification.

A third form of segregation is of a more obvious kind. When the primary crystals differ greatly in density from the liquid, they will tend to float up or to sink, according as they are lighter or heavier, and the ingot then varies in composition vertically. The more rapid the solidification, and the more active the stirring, the less the segregation, but it is often a faotor of importance in the examination of alloys.

CRYSTALLIZATION OF INTERMEDIATE PHASES.

An alloy composed of a single intermediate phase, such as an intermetallic compound or a solid solution, crystallizes in the same way as a pure metal or a terminal solid solution. The typical structure of such an alloy is consequently that of a uniform substance, divided into polyhedra presenting themselves as fine polygonal boundaries in an etched section. When, however, the compound is accompanied by a eutectic, its development often differs in a marked degree from that of a single metal. The tendency to form crystals with plane

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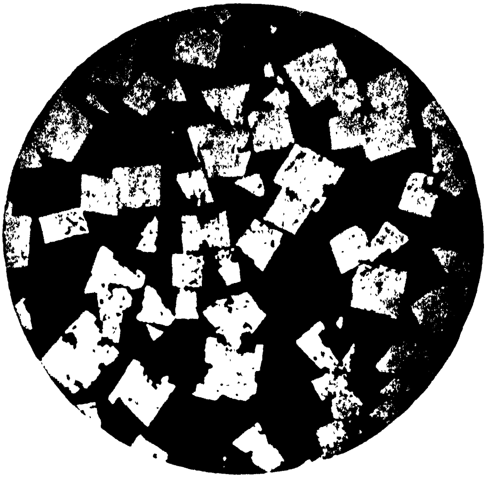
[1] W. Rosenhain and S. L. Archbutt, *J. Inst. Metals*, 1927, **37**, 275 ; W. Fraenkel and W. Goedecke, *Z. Metallk.*, 1929, **21**, 322.

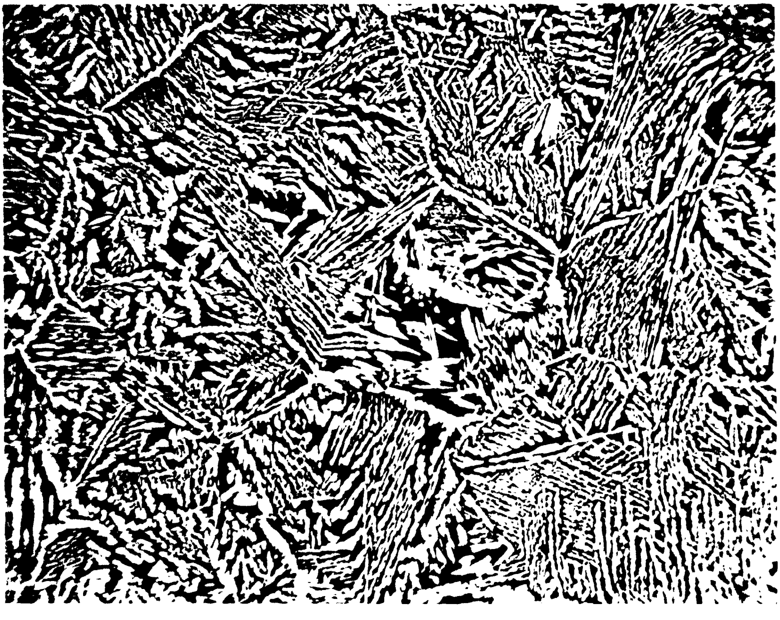
[2] O. Bauer and H. Arndt, *Z. Metallk.*, 1921, **13**, 497. For other surveys see S. W. Smith, *Bull. Inst. Min. Met.*, 1926, No. 257; G. Masing and E. Scheuer, *Z. Metallk.*, 1933, **25**, 173 ; J. H. Watson, *J. Inst. Metals*, 1932, **49**, 347.

[3] G. H. O. Volger, *Pogg. Ann.*, 1854, [ii], **93**, 66 ; C. H. Desch, *J. Inst. Metals*, 1914, **11**, 57.

[4] T. Turner and M. T. Murray, *J. Inst. Metals*, 1909, **2**, 98 ; and succeeding papers.



A. Alloy of tin and antimony. × 20



B. α-β Brass. × 120

PLATE VI

A. Copper 55, aluminium 45 %. × 86

B. α-β Aluminium-copper alloy. × 200

PLATE VII

faces, like the crystals of salts deposited by an aqueous solution, instead of skeletons, is much more pronounced among inter-metallic compounds than among the metals. A rhombic habit predominates. Cubic forms are rare, and such apparent cubes as are observed are probably less simple crystals, having a pseudo-cubic habit. An instance of this is seen in Plate VIA, the cubic or pseudo-cubic crystals of which consist of a solid solution approximating to the composition SnSb, and in Plate VIIA, in which the primary crystals are those of $CuAl_2$. Small crystals may unite to form skeletons. For instance, $FeSb_2$, which crystallizes in simple rhombs if present in small excess over the eutectic proportion, forms characteristic skeletons if in larger excess, and similar variations of habit are common.

The separation of crystals of a new phase from a homogeneous solid solution gives rise to characteristic structures, which are discussed in Chapter XX.

NON-METALLIC ELEMENTS IN ALLOYS.

The relations of the non-metals to each other and to the metals fall for the most part outside the scope of this work, but a few non-metals are capable of entering into associations which may be classed as true alloys. For example, steel and cast-iron are to be considered as alloys, although carbon is a non-metal. Its solutions in iron have an entirely metallic character, as has the carbide, Fe_3C, which crystallizes in hard, glistening plates. Manganese, chromium, and tungsten carbides are also metallic, but the easily decomposable carbides of aluminium, calcium, etc., have no metallic properties, and do not form alloys. Silicon is another alloy-forming element, and in fact may be considered for metallographic purposes as a metal, from the general resemblance of its behaviour in association with metals to that of a highly infusible metal. Even phosphorus unites with iron, copper, and tin, to form metallic phosphides. The structure represented in Plate IVA is characteristic of metals, and the compound Cu_3P, which is one of the constituents of the alloy, has all the properties of a hard, brittle inter-metallic compound.

Mixtures of this class do not retain the metallic character throughout the whole range of composition. When the proportion of the non-metallic component exceeds a certain limit, the mixtures have no longer the properties of alloys. It is often impossible to prepare the complete series, owing to the insolubility of the non-metal when a certain limit is exceeded (thus carbon cannot be dissolved in iron at any accessible temperature to a higher concentration than 7 per cent.) or to the high dissociation pressure of the combinations formed, causing the escape of the volatile component when the mixture is heated under atmospheric pressure. Thus the systems formed by iron, nickel, manganese, and copper with phosphorus have only been examined over a range of composition in which the phosphorus is less than about 15 per cent., this being the maximum quantity retained at the melting-point under atmospheric pressure.

Oxygen less often needs consideration as an alloy-forming element. Most oxides are virtually insoluble in molten metals, but copper eagerly absorbs oxygen when fused, the cuprous oxide produced dissolving in the metal to form a homogeneous solution. The freezing-point diagram is reproduced later (Fig. 105). Nickel behaves in a similar manner.[1] Cuprous oxide also dissolves readily in molten silver, forming a eutectic.[2] Other oxidizable metals absorb oxygen, but the oxide produced merely forms a dross on the surface. The behaviour of silver is unusual. Molten silver dissolves considerable quantities of oxygen, but rejects it at the moment of freezing, the escape of the dissolved gas giving rise to the well-known phenomenon of " spitting " observed when silver ingots are cooled.

Under higher pressure, however, oxygen lowers the freezing-point of silver, and a eutectic is formed, the reaction

$$4Ag + O_2 \rightleftharpoons 2Ag_2O$$

proceeding towards the right under increased pressure.[3] Conversely, under reduced pressure cuprous oxide dissolved in copper will dissociate, so that copper may actually be deoxidized by melting in a vacuum.[4] Other gases dissolve without evident formation of compounds. Very interesting results have been obtained by Sieverts,[5] who finds that the solubility of gases in metals generally increases with the temperature, with a sudden increase on passing from the solid to the liquid state. The solubility is proportional to the square root of the pressure. Hydrogen is dissolved in this way by copper, nickel, and iron, but is insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver, and gold. Its solubility in copper is unchanged by alloying with silver, increased by alloying with nickel or platinum, and diminished by alloying with gold, aluminium or tin, the effect being proportional to the quantity of the added metal as long as no change in constitution takes place. The solubility of hydrogen in molten aluminium has been determined on account of its technical importance. It also increases with the temperature.[6] Sulphur dioxide is insoluble in solid, but very soluble in molten copper. On freezing, a large part of the dissolved gas is retained mechanically.

MECHANICAL INCLUSIONS.

The microscopical examination of alloys frequently reveals inclusions of substances which have been mechanically entangled by

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[1] R. Ruer and K. Kaneko, *Metallurgie*, 1912, **9**, 419.

[2] C. H. Mathewson and C. H. Stokesbury, *Intern. Z. Metallogr.*, 1914, **5**, 193.

[3] N. P. Allen, *J. Inst. Metals*, 1932, **49**, 317.

[4] O. W. Ellis, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **106**, 487.

[5] A. Sieverts and W. Krumbhaar, *Ber.*, 1910, **43**, 893 ; *Z. physikal. Chem.*, 1910, **74**, 277 ; A. Sieverts, *ibid.*, 1911, **77**, 591.

[6] P. Röntgen and H. Braun, *Metallwirtsch.*, 1932, **11**, 459, 471 ; L. L. Bircumshaw, *Trans. Faraday Soc.*, 1935, **31**, 1439.

the fused alloy, and have not formed a part of the homogeneous system. Some practice is required to distinguish these accidental constituents from phases sharing in the equilibrium. Chief among them are the masses of slag enclosed in cast ingots. Steel commonly contains minute masses of silicates, in which a crystalline structure may be developed, and of manganese and iron sulphides, the latter forming globules of a characteristic "dove-grey" colour. The form of the globules is dependent on the treatment to which the metal has been subjected, rolled masses exhibiting an elongation of all enclosures in the direction of rolling. The examination of micro-sections for slag masses is of considerable importance in technical practice, on account of their influence on mechanical properties. Ferrous sulphide, for example, forms films separating the crystal grains, and is consequently a source of weakness when the steel is worked. The addition of manganese converts the sulphur into manganese sulphide, which collects in round or oval globules, which, as they do not interrupt the continuity of the metallic crystals, have less influence on the strength.[1]

The slag in wrought iron occurs in narrow, thread-like masses lying in the direction of rolling or working, so that in a longitudinal section they appear as narrow lines, or in a transverse section as round dots.

Crystalline enclosures are of less frequent occurrence. Well-defined crystals of stannic oxide are met with in bronzes which have absorbed oxygen during melting, as they do not separate readily from the molten metal. Minute crystals of corundum may also be observed in metals and alloys prepared by the aluminothermic method. Crystal skeletons of manganese sulphide have been observed in large steel ingots, and have the appearance of having solidified before the mass of the metal.[2]

ELECTROLYTIC DEPOSITS.

Although metals and alloys for metallographic examination have most often been made by fusion in the first instance, whatever mechanical treatment they may have had later, other methods of production are technically important. Electrolytic deposits are used as methods of protection and of ornament, and may be built up to considerable thickness in the repair of worn parts. Microscopically, their chief interest lies in the structure of transverse sections, but the appearance of the surface is often characteristic. A lustrous surface suggests a very fine grain, a matt surface one of somewhat larger crystals, and a markedly crystalline surface a coarse texture. Occasionally

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[1] See C. Benedicks and H. Löfquist, *Non-Metallic Inclusions in Iron and Steel*, London, 1930. Methods of identification are given by A. Portevin and R. Castro, *J. Iron Steel Inst.*, 1935, ii, 237; 1936, ii, 213; 1937, i, 223.

[2] A. A. Baykoff, *Ann. Inst. Polyt. St. Petersburg*, 1907, 8, 289. See S. Wologdine, *Rev. Métall.*, 1908, 5, 177.

the relation is less simple. A peculiar frosting of certain very fine-grained chromium deposits is due[1] to the formation of rounded aggregates.

An important conclusion from recent work on electrolytic deposits is that the size of the crystal grains is largely determined by the presence of non-metallic matter deposited together with the metal. When the acidity of the solution is low, the deposit contains fine admixed hydroxide, an effect which has been studied mainly in deposits of nickel.[2] Such deposits are relatively hard, but become softer on annealing, when the nickel oxide formed on heating, which is present at first as finely dispersed intercrystalline material, collects together in larger masses.[3] Complex anions may also enter into the deposit, as when copper, deposited from a complex iodide solution, carries sufficient iodine into the deposit on the cathode to make it sensitive to light.[4] Colloidal substances such as gelatin and dextrin are added in practical electrodeposition as a means of controlling the grain size of the deposits, and their action is largely mechanical, by presenting obstacles to growth.

The structure of an electrolytic deposit which has a perceptible grain size is usually columnar, the length of the crystals being parallel with the flow of the current, and therefore mainly perpendicular to the surface. Provided that the surface of the basis metal is clean and crystalline, the crystals of the deposit are frequently continuous with those of the basis metal,[5] a condition being that the crystal structures of the two metals must not be too widely different.

Alloys consisting of a single phase may be deposited in the same way as pure metals, and present similar appearances.

On account of differences in hardness and in electrolytic character between electrolytic deposits and the basis metal, a dark line of separation between the two will often be seen under the microscope. This may be a shadow caused by a difference of level, or a groove produced by local electrolytic action. Its true nature is determined by careful focussing and by varying the illumination.[6]

SINTERED MASSES.

Although alloys are mostly prepared by fusion, the cast material being subsequently shaped if necessary by mechanical means, a class of metallic bodies has come into existence, in making which powders

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[1] A. Portevin and M. Cymbeliste, *Rev. Métall.*, 1933, **30**, 323.

[2] D. J. Macnaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, 1931, **27**, 633; D. J. Macnaughtan, G. E. Gardam and R. A. F. Hammond, *ibid.*, 1933, **29**, 729.

[3] G. E. Gardam and D. J. Macnaughtan, *Trans. Faraday Soc.*, 1933, **29**, 755.

[4] M. Schlötter, J. Korpiun and W. Burmeister, *Z. Metallk.*, 1933, **25**, 107.

[5] A. K. Huntington, *Trans. Faraday Soc.*, 1905, **1**, 324; W. Blum and H. S. Rawdon, *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 305; A. W. Hothersall, *Trans. Faraday Soc.*, 1935, **31**, 1242.

[6] For a general survey of electrolytic deposits, see the Symposium in *Trans. Faraday Soc.*, 1935, **31**, 1043.

are united by pressure and heat, the result often being a uniform mass with cohesion equal to that of a fused product. The method was first applied to pure metals of such high melting-point that fusion in crucibles is impracticable. Tungsten, as used in the electrical industry, is the typical example. The metal, reduced by hydrogen from the purified oxide, is obtained in the form of a powder, which is pressed into bars and heated at about 1000° in hydrogen. This gives the mass sufficient strength to allow it to be handled, although it is still highly porous. It is then heated, again in hydrogen, by passing a heavy current through it in a vertical position, the upper contact being fixed and the lower dipping into mercury. A temperature of 3000° is reached, and the bar acquires such strength that it can be swaged to a round rod in hydrogen at 1300°. As the section is reduced the metal becomes more ductile, until at last it can be drawn into fine wire, even at the ordinary temperature.[1] The same process may be applied to other refractory metals, such as molybdenum and tantalum. Finely powdered iron is also pressed in this way for the production of magnetic cores. Even bearing metals have been made by mixing several constituents and compressing them at about 500°, according to the patent literature.

Iron in a state of high purity is obtained by the decomposition of iron carbonyl, $Fe(CO)_5$, in the form of vapour. The fine dusty particles thus produced fall to the bottom of the reaction vessel, and are then sintered without exposure to air, becoming so compact that the mass can be rolled into plates.[2]

This " powder metallurgy " has become an important part of industry. Among other developments, the production of porous masses, having good mechanical strength but being able to absorb and retain oil, so providing self-lubricating bearings, may be mentioned. Such objects as gears may be made to exact shape by moulding, thus avoiding the labour of machining from a solid block.[3]

A very important class of materials prepared by this method is that of the " hard alloys," consisting of metallic carbides bound into a compact mass by metallic particles, and used as cutting tools. These are usually known by trade names, such as Widia and Carboloy. Tungsten carbide, WC, in the form of powder, is mixed with a few per cent. of cobalt, prepared by reduction of the powdered oxide in hydrogen, and after pressing is sintered at about 1400°, preferably in a high-frequency vacuum furnace.[4] The product is so hard as to be used as turning tools, even for glass and porcelain, or as dies for the drawing of wire. Tantalum carbide is used in the same way.

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[1] W. D. Coolidge, *Trans. Amer. Inst. Elect. Eng.*, 1910, **29**, 961. Details are given by C. J. Smithells in " Tungsten," London, 1936; F. Skaupy, " Metallkeramik," Berlin, 1930.

[2] Details of the structure and properties of carbonyl iron are given by L. Schlecht, W. Schubard, and F. Duftschmid, *Z. Elecktrochem.*, 1931, **37**, 485.

[3] W. D. Jones, " Powder Metallurgy " (London, 1937), gives a survey of the subject. A very comprehensive symposium is " Powder Metallurgy," ed. by J. Wulff (Amer. Soc. Metals, 1942).

CHAPTER IX.

X-RAYS. PART I. THEORETICAL.

(By G. D. Preston.)

1. The application of the method of crystal analysis by means of X-rays has led to great advances in our knowledge of the structure of matter in the solid state. In this section a very brief description of the method will be given. The treatment of the subject has been carried out with the object of giving the metallurgist some account of the method, so that he may understand the kind of problem to which it can be applied, and be able to comprehend the different forms which X-ray photographs take. To this end the section is divided into two chapters, in the first of which a short and therefore incomplete account of some of the physical principles involved in the diffraction of radiation by a three-dimensional grating is given. Chapter X describes the experimental arrangements employed to obtain the data necessary for the analysis of a crystal, and indicates the different types of X-ray photograph that will be obtained in various circumstances.

Reference has been made in other parts of this book to crystals and the external regularity of form which first attracted attention to their properties. Before the introduction of X-rays it was by measurement of the angles between different faces that crystals were classified. In order to carry out this work a method of naming or numbering the facets of a crystal was necessary, and that most generally employed was due to Miller, and is now extensively used in X-ray crystallography. For this reason we will start our enquiry by a definition of the Miller indices of a crystallographic plane, which form a link between the older methods of crystal analysis, based on the study of the external form of crystals, with the newer X-ray methods, which give an insight into the structural factors which determine the external form assumed by a crystal.

2. *Law of rational intercepts.*

For axes of reference take any three lines OX, OY, OZ, parallel to three (not coplanar) edges, formed by the intersection of three faces of a crystal, Fig. 86. A plane parallel to a fourth face of the crystal intersects these axes in A, B, and C respectively. ABC is the parametral plane and the lengths OA, OB, OC are the parameters of the crystal. Any other face of the crystal, which cuts the axes in PQ, and R so that $OP = OA/h$, $OQ = OB/k$ and $OR = OC/l$, may be referred to these axes and parameters by the ratio of the intercepts

$$\frac{OA}{h} : \frac{OB}{k} : \frac{OC}{l}.$$

The numbers h, k, l are the Millerian indices of the plane. The fundamental experimental fact is that h, k, and l for the faces of crystals can always be expressed as small whole numbers, rarely exceeding 6 and usually 0, 1, 2, or 3. This is the law of rational intercepts. ABC, the parametral plane, is (111). A negative value of h would indicate that the plane intersected OX produced on the side remote from A; it is written $\bar{h}$, and so for k and l.

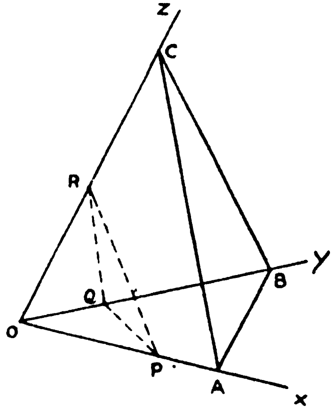


FIG. 86.—ABC is the parametral plane (111).

$OP = \frac{2}{3}OA$, $OQ = \frac{1}{3}OB$, $OR = \frac{1}{2}OC$. PQR is the plane $(\frac{3}{2}, 3, 2) = (364)$.

It will be observed that OA, OB, OC are not completely defined by the construction of the figure; any plane parallel to ABC would have led to the same result. Only the ratios of their lengths are fixed. For this reason crystallographers usually regard (111) and (222) as the same plane, the latter according to the definition being a plane parallel to ABC but bisecting OA, OB, and OC. We shall see later that for the purposes of X-ray analysis a more precise definition which involves a difference between the symbols (111) and (222) is convenient.

Metal crystals do not as a rule exhibit naturally developed crystal faces. The grain boundaries in a metal specimen are determined by the circumstances in which solidification took place and, with the exception of twin boundaries, are not generally crystallographic planes of the type defined above. To investigate the nature of a crystal the development of natural faces is essential if the external form only can be studied. X-ray methods are independent of the external form of a crystalline sample and indices can be assigned to planes of atoms although these planes have no observable external existence.

3. *Space lattices.*

The logical consequences of the law of rational intercepts or indices are developed in the science of mathematical crystallography. It is found that seven different crystal systems can exist and these are subdivided into 32 crystal classes. These classes are again divided into 230 space groups. For our present purpose the most important result of the mathematical treatment is that all these

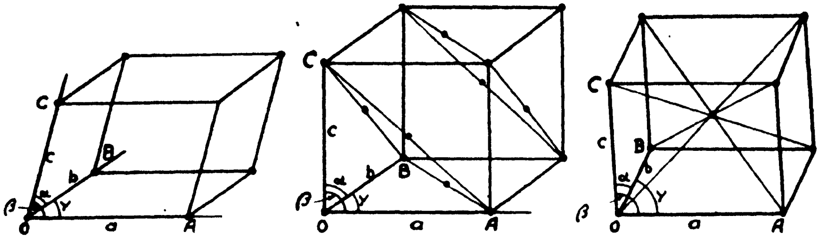


FIG. 87.—(*a*) Simple unit.

Γ_{tr}	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq \pi/2$
Γ_{m}	$a \neq b \neq c$	$\alpha = \beta = \pi/2,\ \gamma \neq \pi/2$
Γ_{o}	$a \neq b \neq c$	$\alpha = \beta = \gamma = \pi/2$
Γ_{t}	$a = b \neq c$	$\alpha = \beta = \gamma = \pi/2$
Γ_{r}	$a = b = c$	$\alpha = \beta = \gamma = \pi/2$
Γ_{rh}	$a = b = c$	$\alpha = \beta = \gamma \neq \pi/2$
Γ_{o}'	$a = b \neq c$	$\alpha = \beta = \pi/2,\ \gamma \neq \pi/2$
Γ_{h}	$a = b \neq c$	$\alpha = \beta = \pi/2,\ \gamma = \pi/3$ or $2\pi/3$

(*b*) Face centred unit.

Γ_{m}'	$a \neq b \neq c$	$\alpha = \beta = \pi/2,\ \gamma \neq \pi/2$
Γ_{o}''	$a \neq b \neq c$	$\alpha = \beta = \gamma = \pi/2$
Γ_{t}'	$a = b \neq c$	$\alpha = \beta = \gamma = \pi/2$
Γ_{r}'	$a = b = c$	$\alpha = \beta = \gamma = \pi/2$

(*c*) Body centred unit.

Γ_{m}'	$a \neq b \neq c$	$\alpha = \beta = \pi/2,\ \gamma \neq \pi/2$
Γ_{o}'''	$a \neq b \neq c$	$\alpha = \beta = \gamma = \pi/2$
Γ_{t}'	$a = b \neq c$	$\alpha = \beta = \gamma = \pi/2$
Γ_{r}''	$a = b = c$	$\alpha = \beta = \gamma = \pi/2$

230 space groups are built up on 14 different space lattices (Fig. 87), which are distributed among the seven crystal systems as follows :

System.	*Number of lattices.*	*Symbols.*
Triclinic . .	1	Γ_{tr}
Monoclinic . .	2	Γ_{m}, Γ_{m}'
Orthorhombic .	4	$\Gamma_{o}, \Gamma_{o}', \Gamma_{o}'', \Gamma_{o}'''$
Tetragonal . .	2	Γ_{t}, Γ_{t}'
Cubic . . .	3	$\Gamma_{r}, \Gamma_{r}', \Gamma_{r}''$
Rhombohedral .	1	Γ_{rh}
Hexagonal . .	1	Γ_{h}.

The most general lattice, the triclinic, is defined by six parameters, the lengths *a*, *b*, *c* of the edges OA, OB, OC of the unit parallelopiped and the three interaxial angles BOC, COA, AOB. The other lattices can be derived from Γ_{tr} by assigning special values to these parameters to give the resulting lattice a higher symmetry. For instance, by making the interaxial angles all equal to 90° the lattice becomes simple orthorhombic. If all the three edges are made equal and the three angles equal the lattice becomes cubic (if the angles are 90°) or rhombohedral (if they are not 90°).

It will be convenient to describe the lattice in terms of three unit vectors, α, β, γ parallel to OA, OB, and OC respectively. If a, b, c are the lengths of OA, OB, and OC then A, B, C are the extremities of the vectors $a\alpha$, $b\beta$, and $c\gamma$. Any other point of the lattice may be represented by a vector δ defined by

$$\delta = xa\alpha + yb\beta + zc\gamma \quad . \quad . \quad . \quad (1)$$

where x, y, and z are integers.

4. *Notation.*

The ideas to be described in the next section are very easily expressed in terms of vectors. A vector is a magnitude which can be represented by a straight line, having length and direction. The sum of two vectors OA and OB is defined to be the diagonal OC of the parallelogram of which the vectors OA and OB are adjacent sides (Fig. 88). It follows that the operation of addition is associative and commutative, i.e.

$$\alpha + \beta = \beta + \alpha$$
$$(\alpha + \beta) + \gamma = \alpha + (\beta + \gamma) = \alpha + \beta + \gamma.$$

The vector $-\alpha$ is equal in length to α but oppositely directed so that $\alpha + (-\alpha) = 0$.

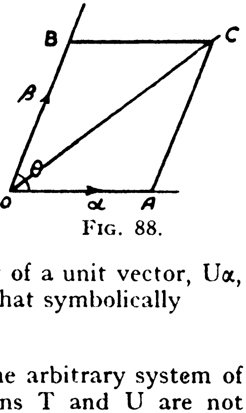


FIG. 88.

Any vector can be considered to be the product of a unit vector, $U\alpha$, "versor alpha," and a positive number $T\alpha$ so that symbolically

$$\alpha = T\alpha \,.\, U\alpha,$$

where $T\alpha$ "tensor alpha," is the length, in some arbitrary system of measurement, of the vector α. The operations T and U are not distributive for $T(\alpha + \beta)$ is not equal to $T\alpha + T\beta$ unless α and β are parallel vectors, i.e. unless $U\alpha = U\beta$.

The scalar product of two vectors α, β is written $S\alpha\beta$, "scalar alpha beta," and is defined to be numerically equal to minus the product of the lengths of α and β and the cosine of the angle, θ (less than π), between them, Fig. 88. In symbols where a and b are the lengths of α and β

$$S\alpha\beta = -T\alpha \,.\, T\beta \,.\, \cos\theta = -ab\cos\theta.$$

The operation S is evidently distributive and commutative, for by the definition

$$S\alpha\beta = S\beta\alpha$$

and $$S\alpha(\beta + \gamma) = S\alpha\beta + S\alpha\gamma$$

because the sum of the projections of any number of vectors on any line is the projection of their sum. If $S\alpha\beta = 0$ then α and β are perpendicular to one another.

The vector product of α and β, written $V\alpha\beta$, " vector alpha beta," is defined to be a vector perpendicular to α and to β of magnitude equal to the product of the lengths of α and β and the sine of the angle, θ, between them. Thus $T(V\alpha\beta) = T\alpha \,.\, T\beta \,.\, \sin\theta = ab \sin\theta$. We shall adopt the convention that if α and β are as shown in Fig. 88, then $V\alpha\beta$ is perpendicular to and drawn upwards from the plane of the paper. With this convention $V\beta\alpha$ is in the opposite direction, and therefore

$$V\alpha\beta = -V\beta\alpha.$$

The operation V is not commutative but it is distributive,

$$V\alpha(\beta + \gamma) = V\alpha\beta + V\alpha\gamma = -V\beta\alpha - V\gamma\alpha = -V(\beta + \gamma)\alpha.$$

If $V\alpha\beta = 0$ then α and β are parallel.

The product of two vectors α and β is defined to be the sum of their scalar and vector products :

$$\alpha\beta = S\alpha\beta + V\alpha\beta,$$

and therefore $$\beta\alpha = S\alpha\beta - V\alpha\beta,$$

so that $$S\alpha\beta = \tfrac{1}{2}(\alpha\beta + \beta\alpha),$$

and $$V\alpha\beta = \tfrac{1}{2}(\alpha\beta - \beta\alpha).$$

It follows that $$\alpha^2 = S\alpha^2 = -(T\alpha)^2,$$

and therefore $$\alpha = \alpha^{-1}S\alpha^2,$$

i.e. $$\alpha^{-1} = \frac{-\alpha}{(T\alpha)^2} = \frac{-U\alpha}{T\alpha}, \qquad (2)$$

that is the reciprocal vector α^{-1} is oppositely directed to α and its length is the reciprocal of the length of α, or, $U(\alpha^{-1}) = -U(\alpha)$ and $T(\alpha^{-1}) = (T\alpha)^{-1}$.

Any vector ρ can be resolved into the sum of vectors parallel to three (not coplanar) vectors α, β, γ in one way only. In fact

$$\rho S\alpha\beta\gamma = \alpha S\beta\gamma\rho + \beta S\gamma\alpha\rho + \gamma S\alpha\beta\rho. \qquad (3)$$

If we wish to resolve along $V\beta\gamma$, $V\gamma\alpha$, and $V\alpha\beta$

then $$\rho S\alpha\beta\gamma = V\beta\gamma S\alpha\rho + V\gamma\alpha S\beta\rho + V\alpha\beta S\gamma\rho. \qquad (4)$$

These formulæ are easily verified. If we multiply both sides of (3) by $\alpha\beta$, $\beta\gamma$, or $\gamma\alpha$ and take the scalar part of the product the equation is seen to be identically true. (4) can be verified in a similar manner by operating on both sides with $S\alpha$ (i.e. multiplying by α and taking the scalar part of the product), $S\beta$, and $S\gamma$. The scalar quantity $S\alpha\beta\gamma$ appearing on the left-hand side of the equations (3) and (4) is equal to the volume of the parallelopiped of which α, β, and γ are three adjacent edges.

5. *The Reciprocal Lattice.*

Returning now to the law of rational intercepts, we define the plane (*hkl*) to be that plane whose intercepts on the axes of the lattice are $\frac{a}{h}$, $\frac{b}{k}$, and $\frac{c}{l}$ respectively. In Fig. 86 OA, OB, OC are now the edges of the unit cell of the lattice, the vectors $a\alpha$, $b\beta$, and $c\gamma$ of equation (1), and if the plane (*hkl*) meets the axes in P, Q, R, then $OP = \frac{a\alpha}{h}$, $OQ = \frac{b\beta}{k}$ and $OR = \frac{c\gamma}{l}$. If σ is a vector from the origin, perpendicular to the plane (*hkl*) whose extremity lies in the plane, and if ρ is any other vector whose extremity lies in the plane, then the vectors σ and $\sigma - \rho$ are perpendicular to one another. Considering ρ as a variable the equation of the plane is

$$S\sigma(\sigma - \rho) = 0$$

or

$$S\sigma\rho = S\sigma^2.$$

Since the plane meets the axes in the extremities of the vectors $\frac{a\alpha}{h}$, $\frac{b\beta}{k}$, and $\frac{c\gamma}{l}$, these are values of ρ which satisfy the equation, i.e.

$$S\sigma\alpha = \frac{h}{a}S\sigma^2,$$

$$S\sigma\beta = \frac{k}{b}S\sigma^2,$$

$$S\sigma\gamma = \frac{l}{c}S\sigma^2.$$

If we write $V\beta\gamma = \alpha'$, $V\gamma\alpha = \beta'$, and $V\alpha\beta = \gamma'$ then multiplying these equations by α', β', and γ' respectively, and adding

$$\alpha' S\alpha\sigma + \beta' S\beta\sigma + \gamma' S\gamma\sigma = \left(\frac{h}{a}\alpha' + \frac{k}{b}\beta' + \frac{l}{c}\gamma'\right)S\sigma^2.$$

The left-hand side is identically equal to $\sigma S\alpha\beta\gamma$ by (4), so that dividing each side by $S\sigma^2$ and using the relation (2) we have

$$\sigma^{-1}S\alpha\beta\gamma = \frac{h\alpha'}{a} + \frac{k\beta'}{b} + \frac{l\gamma'}{c}. \qquad (5)$$

The vectors σ^{-1} therefore lie at the points of a lattice defined by the vectors $\frac{\alpha'}{aS\alpha\beta\gamma}$, $\frac{\beta'}{bS\alpha\beta\gamma}$, and $\frac{\gamma'}{cS\alpha\beta\gamma}$. This lattice is called the reciprocal lattice, and is very useful in considering the diffraction of X-rays by a crystal. Corresponding to every plane (*hkl*) as defined above there is a point in the reciprocal lattice at the extremity of the vector σ^{-1}; the distance from the origin to the extremity of σ^{-1} is the reciprocal of the spacing "*d*" of the plane (*hkl*). Provided *h*, *k*, *l* are prime to one another, successive planes of atoms in the lattice parallel to (*hkl*) are separated by a distance d equal to $T\sigma$. This can be seen in the following way:

The vector σ is perpendicular to the plane (*hkl*) and terminates on it. Let δ be the vector to any point in the lattice, then there will be a plane through the extremity of δ perpendicular to σ. The vector from the origin perpendicular to this plane will be $M\sigma$ where M is a number which we will now show to be an integer. The equation to the plane perpendicular to $M\sigma$ and passing through its extremity is

$$S\sigma\rho = MS\sigma^2.$$

If this passes through the extremity of δ then

$$S\sigma\delta = MS\sigma^2,$$

but

$$S\sigma\delta = axS\alpha\sigma + byS\beta\sigma + czS\gamma\sigma \qquad \text{by (1)}$$

$$= (hx + ky + lz)S\sigma^2$$

so that

$$M = (hx + ky + lz),$$

and is an integer because h, k, l, and x, y, z are integers. For the plane through the origin $M = 0$. The nearest plane to this is given by $M = \pm 1$ and its distance from the origin is $\pm \sigma$, the *M*th plane being at distance $M\sigma$ from the origin. All the planes parallel to (*hkl*) passing through points of the lattice are separated by vectors σ whose length is d (in the usual notation) the spacing of the planes (*hkl*).

If (*hkl*) are not prime to one another let them have a common factor N, so that they can be written Nh', Nk', Nl', where $h'k'l'$ are prime to one another. For the plane through the extremity of σ we would then find as above, putting $M = 1$,

$$N(h'x + k'y + l'z) = 1.$$

Since $h'x + k'y + l'z$ cannot equal the fraction $1/N$ (unless $N = 1$), it follows that there are no points of the lattice on the plane (Nh', Nk', Nl'). Corresponding to the indices (Nh, Nk, Nl) there is a vector σ_N^{-1}, which by (5) is equal to $N\sigma^{-1}$, in the reciprocal lattice. As will be shown later this vector is associated with the Nth order diffraction spectrum of the plane (*hkl*) in the same way that σ^{-1} is associated with the first order.

The value of d, for purposes of computation, has to be expressed in terms of the parameters a, b, c, and the interaxial angles A, B, C, of the lattice. A is the angle between the unit vectors β and γ so that $S\beta\gamma = -\cos A$ and $TV\beta\gamma = \sin A$. Squaring the expression for σ^{-1} we have

$$S\sigma^{-2}(S\alpha\beta\gamma)^2 = \frac{h^2}{a^2}S(\alpha'^2) + \frac{k^2}{b^2}S(\beta')^2 + \frac{2}{c}S(\gamma'^2) + \frac{2hk}{ab}S\alpha'\beta' +$$

$$2\frac{kl}{bc}S\beta'\gamma' + \frac{2hl}{ac}S\alpha'\gamma'.$$

In this expression $S(\sigma^{-2}) = -\frac{1}{d^2}$,

$$S(\alpha')^2 = -T(\alpha'^2) = -(TV\beta\gamma)^2 = -\sin^2 A,$$
$$S\alpha'\beta' = -S\alpha\beta - S\beta\gamma\, S\alpha\gamma = \cos C - \cos A \cos B,$$
$$(S\alpha\beta\gamma)^2 = 1 - \cos^2 A - \cos^2 B - \cos^2 C + 2 \cos A \cos B \cos C.$$

These substitutions give the value of d for different planes (hkl) in the triclinic lattice. The somewhat formidable formula is greatly simplified for lattices of higher symmetry.

For the monoclinic system $A = B = 90°$ and we find

$$\frac{1 - \cos^2 C}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2 \sin^2 C}{c^2} - \frac{2hk}{ab} \cos C.$$

For the orthorhombic $A = B = C = 90°$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}.$$

For the tetragonal $A = B = C = 90°$ and $b = a$

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}.$$

For the cubic $A = B = C = 90°$ and $c = b = a$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}.$$

For the rhombohedral $C = B = A$ and $c = b = a$

$$\frac{1-3\cos^2 A+2\cos^3 A}{d^2} = \frac{1}{a^2}(h^2+k^2+l^2)\sin^2 A - 2(hk+kl+lh)(\cos A-\cos^2 A).$$

In the hexagonal $A = B = 90°$, $C = 120°$, $b = a$,

$$\frac{3}{4d^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{3l^2}{4c^2} + \frac{hk}{a^2}.$$

6. *The diffraction of waves by a crystal.*

The points of a space lattice are supposed to be associated with material particles (atoms or ions) all similar and similarly orientated with respect to the lattice. Under the influence of a beam of radiation the particles become sources of energy, emitting waves. The phases of the radiation scattered by neighbouring particles are in a definite relationship, and reinforcement of the scattered wavelets will occur when the phase difference is an integral multiple of the wave-length L of the scattered and incident radiation. Let A, A_1, A_2 (Fig. 89) be a row of atoms (or ions) in the crystal, situated at equal intervals "*a*." A plane wave is incident on the row in the direction OA such that the angle $OAA_1 = \theta$ say. The scattered wavelets from A and A_1 reinforce in a direction AR if the path difference $PA + AQ$ is an integral multiple of L. If the angle QAA_1 is ϕ the condition for reinforcement is

$$mL = a \cos \theta + a \cos \phi.$$

AR is not necessarily coplanar with AA_1 and OA so that the directions in which the intensity maxima are found lie on the surfaces of cones of which AA_1 is the axis and the semi-vertical angle ϕ is determined by the above relation. This relation can be easily expressed in the vector notation. Let λ be a unit vector drawn from A towards the source of radiation, μ a unit vector drawn from A in the direction of the scattered radiation and α a unit vector parallel to the row of atoms AA_1 . . . . Then $S\alpha\lambda = -\cos\theta$ and $S\alpha\mu = -\cos\phi$ so the condition becomes simply

$$aS(\lambda + \mu)\alpha = -mL.$$

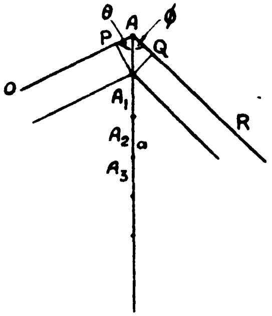


FIG. 89.—Diffraction by a row of equidistant points.

For a single row of particles there are always a number of directions corresponding to different integers m in which the intensity of the scattered radiation will be a maximum, provided the ratio L/a is not too great.

We now attempt to orientate a crystal so that the scattered wavelets from three (not coplanar) rows of atoms α, β, and γ will reinforce each other. In order that this may occur we must have simultaneously

$$\begin{aligned} aS(\lambda + \mu)\alpha &= -mL, \\ bS(\lambda + \mu)\beta &= -nL, \qquad (6) \\ cS(\lambda + \mu)\gamma &= -pL, \end{aligned}$$

b and c being the distances between successive atoms in the rows β and γ, and nL and pL being the path difference of the scattered wavelets from successive atoms in these two rows.

If these three conditions can be simultaneously satisfied, then the scattered wavelets from every atom in the crystal will be in phase and will reinforce one another. Because if $\delta = xa\alpha + yb\beta + zc\gamma$ is any atom, x, y, and z are integers, then using (6)

$$\begin{aligned} S(\lambda + \mu)\delta &= -(xm + yn + zp)L \\ &= -NL \end{aligned}$$

where N is an integer. But this is just the condition that the wavelets from the atom at the origin and from the atom at the extremity of δ shall differ in phase by N wave-lengths, and therefore if (6) are simultaneously satisfied the contributions from every atom in the crystal to the scattered beam are exactly in phase.

7. *Bragg's law.*

The conditions (6) imply a relation between the vectors involved. Taking *a*, *b*, and *c* over to the right-hand side, multiplying the equations by the vectors α', β', and γ' defined in § 5 respectively and adding, we find

$$\alpha'\mathrm{S}(\lambda+\mu)\alpha+\beta'\mathrm{S}(\lambda+\mu)\beta+\gamma'\mathrm{S}(\lambda+\mu)\gamma=\left(-\frac{m}{a}\alpha'-\frac{n}{b}\beta'-\frac{n}{c}\gamma'\right)\mathrm{L}.$$

The left-hand side is identically equal to $(\lambda+\mu)\mathrm{S}\alpha\beta\gamma$ (by (4)) so that

$$\lambda+\mu=-\mathrm{L}\left(\frac{m\alpha'}{a\mathrm{S}\alpha\beta\gamma}+\frac{n\beta'}{b\mathrm{S}\alpha\beta\gamma}+\frac{n\gamma'}{c\mathrm{S}\alpha\beta\gamma}\right)$$

or

$$\lambda+\mu=-\mathrm{L}\sigma^{-1} \quad . \quad . \quad . \quad . \quad (7)$$

where σ by comparison with (5) is the normal drawn from the origin to the plane whose Miller indices referred to the axes α, β, γ are (*mnp*).

The equation (7) is the vector expression of Bragg's law. It contains the following implications: (1) The vectors λ, μ, and σ are coplanar; or the incident and diffracted rays and the normal to the plane (*mnp*) lie in one plane. (2) λ, μ are equally inclined to σ and if the angle between λ and σ is $\frac{\pi}{2}-\theta$ then (3) $\mathrm{L}=2d\sin\theta$.

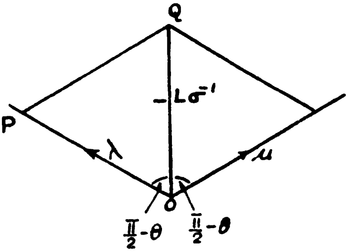


FIG. 90.

These three consequences of the condition (7) are easily verified from Fig. 90; λ and μ are vectors of unit length, $-\mathrm{L}\sigma^{-1}$ is a vector of length L/*d* in the direction σ. The results (1) and (2) above follow from the rule for the addition of vectors, and (3) from the fact that $\mathrm{OQ}=2\mathrm{OP}\sin\theta$. They may also be derived formally from the equation: multiplying by σ and taking the vector and scalar parts of the product,

$$\mathrm{V}\lambda\sigma+\mathrm{V}\mu\sigma=0 \quad . \quad . \quad . \quad . \quad (7a)$$

$$\mathrm{S}\lambda\sigma+\mathrm{S}\mu\sigma=-\mathrm{L}. \quad . \quad . \quad . \quad . \quad (7b)$$

(7*a*) means that $\mathrm{V}\lambda\sigma$ and $\mathrm{V}\mu\sigma$ are equal in magnitude and oppositely directed, and since λ and μ are unit vectors that the angle between λ and σ is equal to the angle between σ and μ. If this angle is $\frac{\pi}{2}-\theta$ then $\mathrm{S}\lambda\sigma=\mathrm{S}\mu\sigma=-d\sin\theta$ and Bragg's law follows at once from (7*b*).

It will be observed that (7*b*) can be thrown into the form $\mathrm{S}(\lambda+\mu)\sigma=-\mathrm{L}$ which expresses the condition that the path difference of scattered wavelets from atoms at the origin and the extremity of σ shall differ in phase by one wave-length. In general there are not atoms situated at the points σ, 2σ, 3σ, etc., but these vectors terminate on planes of atoms, so that the equation means that if we consider the series of planes perpendicular to σ the path difference of the scattered waves from successive planes is one wave-length. This leads to the very simple interpretation of Bragg's law illustrated in Fig. 91. The path difference between the rays diffracted at N and O is PO + OQ = 2D sin θ. For reinforcement we must therefore have

$$NL = 2D \sin \theta$$

where N is an integer—the "order" of diffraction from the plane. This expression of Bragg's law differs from that previously obtained by the appearance of the integer N. This difference is artificial, and arises from the slightly different aspect from which we are now viewing the process of diffraction. The quantity D now represents a physical entity, the distance between successive similar planes of atoms in the lattice. If we suppose the crystal to be rotated about an axis perpendicular to the plane of the paper through N, then as sin θ assumes the values $\frac{L}{2D}, \frac{2L}{2D}, \frac{3L}{2D}$, etc., a diffraction maximum will occur. These correspond to the first, second, etc., orders of diffraction by the plane (*hkl*). From the point of view previously adopted we would regard the Nth order spectrum of the lattice plane (*hkl*) as the diffraction spectrum (N*h*, N*k*, N*l*), the numbers N*h*, N*k*, N*l* being the number of whole wave-lengths in the path differences of waves scattered by successive atoms in the three crystal axes.

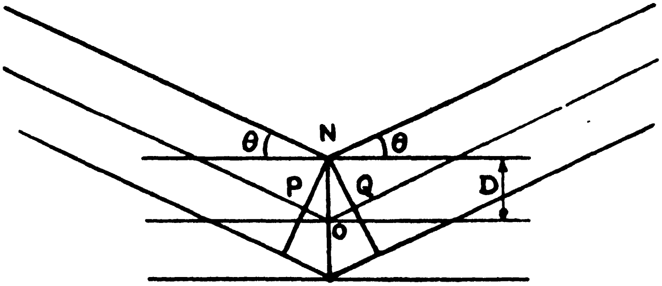


FIG. 91.—Diffraction by a series of equidistant planes.

A consideration of an optical analogy is instructive. A beam of monochromatic light from a point source is rendered parallel by a lens and after traversing a plane grating is brought to a focus on a screen. The diffraction pattern will consist of a number of bright spots on a line at right angles to the grating rulings, which we may suppose to be vertical. If the apertures of the grating are not too close to one another the separation of the bright spots will be uniform along the line OA, Fig. 92, and will be inversely proportional to the distance, *a*, between neighbouring apertures of the grating. The different spots, A_1, A_2, etc., are the different orders of diffraction;

in the Nth order the path difference of rays from neighbouring apertures of the grating is N wave-lengths, so that each order may be defined by a single integer N, the phase number. If now a second grating be interposed with its rulings horizontal, each of the spectra will be diffracted so as to produce a series of bright spots in a rectangular array. The distance between neighbouring spots on the line OB will be inversely proportional to *b*, the spacing of the second grating. Along the line OB the different orders of diffraction can be defined by the series of integers 1, 2, 3, etc. A point such as P_1, however, requires two integers to define it; we could call it the A_2B_1 spectrum, but it is evidently simpler to describe it as the (21) spectrum; the next spot, P_2, in the direction OP will be (42) and the Nth (2N, N). Moreover, OA_1 is inversely proportional to *a* and OB_1 to *b*, so that taking the constant to be unity we may write $OA_1 = \frac{1}{a}$ and $OB_1 = \frac{1}{b}$. Thus for any point Q of the pattern corresponding to the (*hk*) spectrum we will have $OQ = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2}\right)^{\frac{1}{2}}$, and if Q is the first bright spot in the row OQ, i.e. if *h* and *k* are prime to one another, the spectra in the row OQ will occur just at the points at which they would be produced by a grating in which the spacing is $c = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2}\right)^{-\frac{1}{2}}$ and whose rulings are perpendicular to OQ. This expression for *c* should be compared with those for the

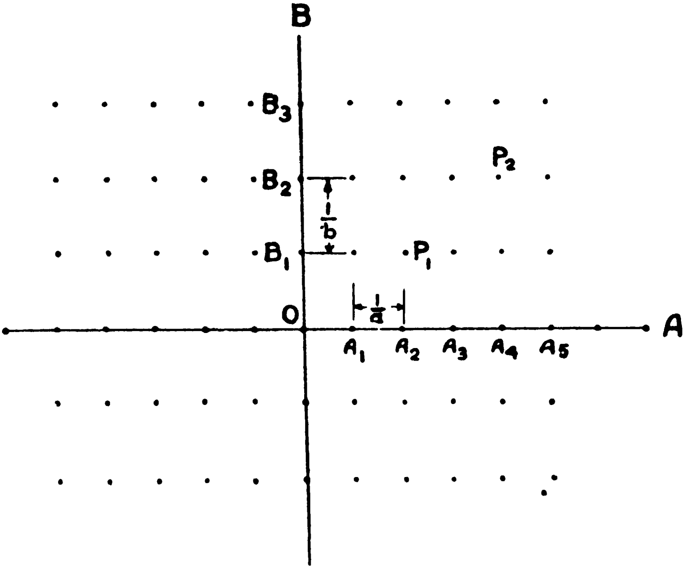


FIG. 92.—Crossed grating diffraction pattern.

spacing of an orthorhombic crystal, given in § 5, with which it is identical if the term l^2/c^2 is omitted. It will be observed that the pattern of diffraction spots of Fig. 92 is the reciprocal " lattice " of the crossed gratings.

Crossed grating spectra have not been recorded by the diffraction of X-rays by crystals, but they have been observed when a beam of electrons is diffracted by very thin sheets of mica or metal crystals.

The first two consequences of the vector equation (7) are the same as the laws governing the reflection of light at a surface. For this reason the phenomenon of X-ray diffraction in a crystal is frequently spoken of as reflection ; such terms as " the (*hkl*) reflection," " X-ray reflection spectra," etc., being commonly used. In so far as optical reflection can be considered to be a diffraction effect (as in fact it is), this extension of the terminology of optics is justified. But the two cases differ in one all-important respect which is expressed in the third condition. In the case of light, if a beam of *any* wave-length is allowed to fall on a reflecting surface at *any* given angle a reflected beam will be observed. This is not the case for the " reflection " from crystal planes. For a given wave-length and a given crystal plane there is a condition involving the angle of incidence which must be satisfied in order that the scattered waves may reinforce. If this condition is not satisfied there is no reinforcement of the scattered wavelets and the " reflected " beam does not exist. When the condition expressed by Bragg's law is satisfied reinforcement takes place, and a " reflected " beam appears in the direction in which a beam of light parallel to the incident X-ray beam would be reflected by the crystal plane.

The difference between optical reflection and X-ray " reflection " is of such importance that it is worth while to look at the matter from another point of view. We go back to the vector expression of Bragg's law and put it in the form $\sigma^{-1} = -\frac{\lambda}{L} - \frac{\mu}{L}$. In Fig. 93 the vectors λ, μ, σ, $-\frac{\lambda}{L}$, $-\frac{\mu}{L}$ and σ^{-1} are shown. The extremity of the vector σ^{-1} is a point of the reciprocal lattice. If a circle is drawn with its centre, C, at the extremity of the vector $-\frac{\lambda}{L}$ and with radius $\frac{1}{L}$ it will pass through the origin of the vectors (where we may suppose a point of the crystal and its reciprocal lattice to be situated), and through the extremity of σ^{-1} if the relation $\sigma^{-1} = -\frac{\lambda}{L} - \frac{\mu}{L}$ is satisfied. For in the isosceles triangle OCP, OP = 2OC cos COP or $\frac{1}{d} = \frac{2}{L} \sin \theta$. Now suppose the figure to be rotated about the line OC. The circle of radius $\frac{1}{L}$ becomes a sphere (the "sphere of reflection") of the same radius, the vector σ^{-1} generates a cone of semi-vertical angle $\frac{\pi}{2} - \theta$, and the reflected ray μ generates a cone of semi-angle 2θ, the "cone of reflection." The point P describes a small circle on the sphere of reflection, and for every position of P on this circle a reflected ray on the surface of the cone of reflection exists. In order that Bragg's law shall be satisfied it is necessary that P shall lie on the sphere of reflection. Now the sphere of reflection is determined by the wave-length of the incident radiation. The length of the vector σ^{-1} is determined by the parameters of the crystal lattice and the direction of σ^{-1} by the orientation of the crystal relative to the incident beam. In general there is no reason for expecting the extremity of σ^{-1} to lie on the sphere of reflection; if it does so it is a purely fortuitous accident. In order to obtain X-ray reflections the experimental arrangement has to be such that the points of the reciprocal lattice are brought on to the surface of the sphere of reflection. This can be achieved in two ways. I. The crystal can be kept fixed and the wave-length continuously altered so that the sphere of reflection sweeps out a volume of the reciprocal lattice containing some points. This is the Laue method. II. The wave-length is fixed and the orientation of the crystal changed: (*a*) By rotation or oscillation about a fixed axis, so that points of the reciprocal lattice sweep through the sphere of reflection. The reflected ray comes into existence at the instant when a point of the reciprocal lattice meets the sphere of reflection. (*b*) By placing a large number of small crystals with random orientation in the incident beam. This is the powder method. These methods will be described in greater detail below.

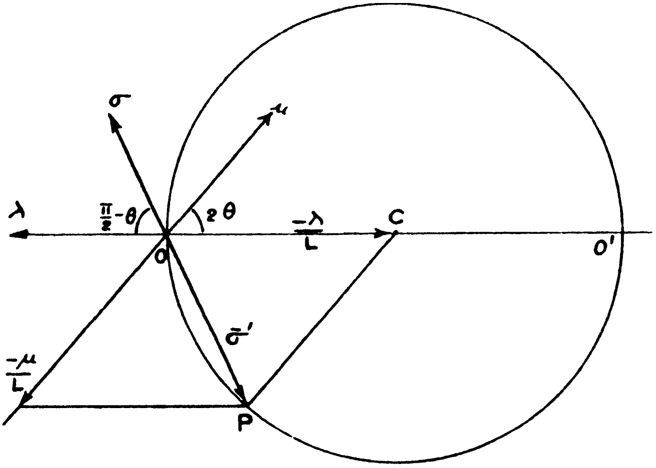


FIG. 93.—**Relations of the incident ray (— λ), reflected ray (μ), the point P of the reciprocal lattice, and the sphere of reflection.**

CHAPTER X.

X-RAYS. PART II. EXPERIMENTAL.

(By G. D. PRESTON.)

The Laue method.

IN this method, historically the first used to demonstrate the fact of diffraction of X-rays by crystals, the crystal is held stationary in a beam of " white " X-radiation, that is a beam in which the energy is distributed continuously throughout a range of wave-lengths (as in " white " light). The range of wave-lengths is generally from about 0·1 to 1·0 Å., the lower limit being fixed by the voltage applied to the X-ray tube and the upper by the absorbing quality of the glass or metal which the beam traverses in leaving the tube. The diffracted radiation is (usually) received on a photographic plate or film mounted so as to be perpendicular to the incident beam, as shown in Fig. 94. The incident beam is restricted to a narrow pencil by means of a suitable slit system, so that the resulting diffraction pattern consists of a number of spots.

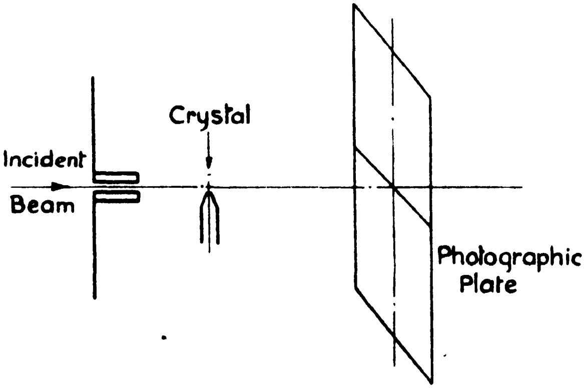
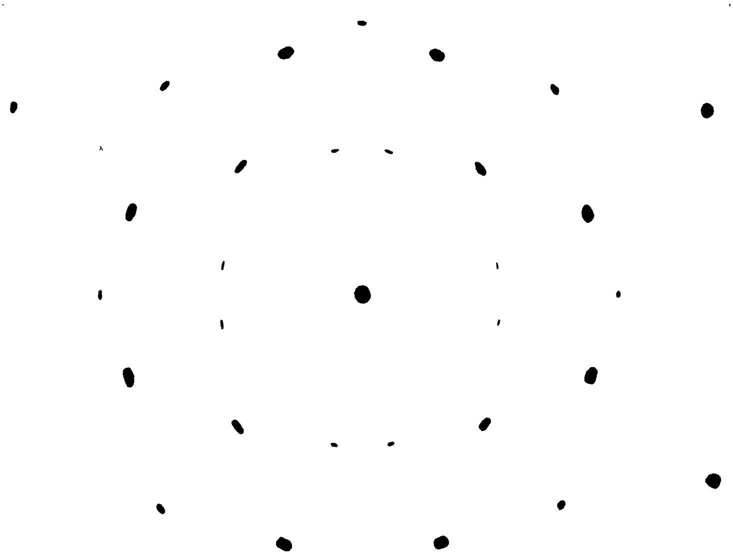
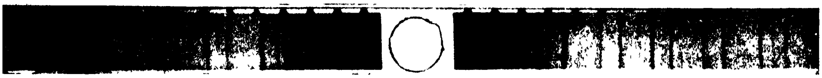


FIG. 94.—Diagram of Laue method.

Referring to Fig. 93, we imagine O to be a point of the reciprocal lattice, C to be the centre of the sphere of reflection for the longest wave-length L in the beam. The sphere of reflection for the wave-length L/2 will have a radius 2/L and its centre will be at O′. If the



A Laue photograph of aluminium crystal. X-rays parallel to [100]



B. Powder photograph of silicon. Circular camera, Copper radiation

PLATE VIII

vector σ^{-1} terminates on the first sphere the vector $2\sigma^{-1}$ will terminate on the second and both will produce a reflected ray in the same direction. If the wave-length band includes L/3 then $3\sigma^{-1}$ will also reflect to the same spot. Thus the spots on the Laue photograph do not correspond to a single wave-length. Each spot includes 1st order reflections of wave-length L, 2nd order of wave-length L/2, etc., provided the appropriate wave-length is present in the incident beam. The position of the spots is fixed by the orientation of the crystal relative to the incident beam. If a symmetry axis of the crystal lies along OC then corresponding to the vector σ^{-1} there will be a number of other vectors of equal length distributed symmetrically around the axis OC. All (or none) of these will reflect in different directions μ which are also symmetrically distributed around OC. If the diffracted radiation is received on a photographic plate perpendicular to OC the pattern of spots will reproduce the symmetry of the crystal. For this reason the method is very useful for ascertaining the system to which a crystal belongs; it can, of course, be used even when natural faces are not developed on the crystal.

Indices can be assigned to the spots of a Laue diagram indicating the crystal planes from which they arise. An account of the methods by which this is done would be outside the scope of this essay, and the interested reader must be referred to text-books.

A typical Laue photograph is reproduced in Plate VIIIA. It was obtained from single crystal of aluminium, grown in a wire by the strain-anneal method. The crystal has been orientated so that the X-ray beam is parallel to [100] direction, i.e. perpendicular to a cube face of the crystal lattice. The resulting four-fold symmetry of the diffraction pattern is clearly seen in the reproduction.

The rotating and oscillating crystal methods.

The X-ray spectrometer.—The instrument, Fig. 95, consists of a slit system S_1S_2 which allows a narrow beam of monochromatic X-rays to fall on a single crystal mounted at O the axis of the spectrometer. The crystal can be rotated about O and its orientation adjusted by means of a goniometer. The reflected radiation is detected by an ionization chamber C which can be rotated independently of the crystal about the spectrometer axis and which is shielded from all radiation except that reflected from the crystal at O. In order that the focussing condition (see below, p. 176) may be satisfied the distances OS_1 and OS_2 are made equal. The crystal holder and the mounting of the ionization chamber are provided with circular scales and verniers so that their angular displacements about the spectrometer axis can be recorded.

We suppose a crystal with naturally developed faces to be mounted at O with a zone axis parallel to the axis of the spectrometer. A face is selected and initially set parallel to the incident X-ray beam, and the ionization chamber is adjusted to receive the incident beam, the slits being set rather wide. The crystal is then rotated, say, 5°, and the chamber 10°, so that the incident beam is no longer falling into the slit S_3. The intensity of the reflected radiation is then measured at intervals of, say, 1° for the crystal and 2° for the ionization chamber, the latter by being moved through twice the angle of movement of the former being always in the correct position to receive any reflection. When a crystal setting is reached for which Bragg's law is satisfied, i.e. when $\sin \theta = NL/2d$, an intensity maximum will be observed. The slits can then be narrowed and the region examined in greater detail, say at intervals of 10′, so that position of the intensity maximum is located with greater accuracy, and its magnitude determined. A search is then made in the appropriate positions for other orders of reflection from the same plane and the intensity of each order can be measured. Attention is then given in turn to other planes in the zone and the intensities of the diffraction maxima are measured. Thus if a cubic crystal is mounted with the

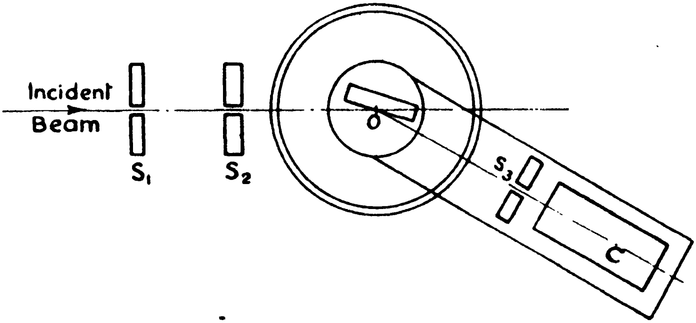


FIG. 95.—Ionization spectrometer.

normal to (001) parallel to the spectrometer axis, the intensities of reflection from planes of the type (*hko*) can be measured.

The complete examination of a crystal by this means is very laborious, even when natural faces are present on it. When the crystal exhibits no natural facets it is even more difficult. The X-ray spectrometer is, however, one of the best methods of obtaining accurate measurements of the relative intensities of the diffraction maxima.

The rotating crystal method.

This method is in some ways very similar to that described above, but the diffraction maxima are recorded photographically. For this purpose the ionization chamber is replaced by a photographic film held on a cylindrical drum, usually about 6 cm. diameter and 10 cm. high. The film holder is held so that the crystal lies at its centre, and so that the spectrometer axis coincides with the axis of the cylinder. If the crystal is mounted so that it rotates about a symmetry axis the resulting photographs are comparatively simple. For instance, let us consider a crystal of orthorhombic symmetry rotating about its c axis. The normals to all the planes (*hko*) are then perpendicular to axis of the spectrometer and all the reflections from these planes will lie in a plane perpendicular to the spectrometer axis so that, when the film is unwrapped, they form a row of spots. Reflections from planes (*hkl*) lie on the surface of a cone whose axis is parallel to the spectrometer axis and which, therefore, meets the film in a circle. After unwrapping the film this circle becomes a line of spots parallel to the line of spots (*hko*). These rows of spots are called "layer lines." If the planes (*hk*1) produce a layer line above the central line (*hko*), then ($hk\bar{1}$) will be represented by a similar line of spots below the central line. If ϕ is the angle subtended at the specimen by the vertical distance on the film separating the layer lines $l = 0$ and $l = 1$, then the parameter c of the crystal is given by $L = c \sin \phi$. The method determines this spacing uniquely. By bringing the a and b axes parallel to the spectrometer axis and taking rotation diagrams, the a and b parameters of the crystal can be similarly determined.

The separation of the reflections into classes (*hko*), (*hk*1), etc., is a very great advantage of the method. If the single crystal were replaced by a powder all the planes (*hkl*) would be represented in the central line of the film, and to assign indices to the reflections would require the solution of a number of equations of the type

$$\frac{\sin \theta}{L} = \frac{1}{d} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{\frac{1}{2}}$$

where a, b, c are unknown lengths and hkl are integers. The method supplies a direct method of measuring a, b, c by the distance between layer lines on three photographs and after that it is a comparatively simple matter to assign integral values to (*hkl*).

A further advantage is that the resolving power or ability to differentiate reflections of different indices, which fall close together, is much greater than in the powder method. For instance, in the cubic system the reflections (300) and (221) have the same $\sin \theta$, because $d = a/\sqrt{9}$ in each case. In powder photographs these reflections are therefore superimposed, but in the rotating crystal method if (001) is the axis of rotation, (300) falls on the central and (221) on the first layer line.

The oscillating crystal method.

A further improvement in the resolving power of the method can be obtained by restricting the amount of rotation. In practice this is effected by oscillating the crystal about the spectrometer axis through an angle of 10° or 15°. By taking a series of photographs all the reflections recorded on a rotation photograph are obtained; but only some of them are recorded on each oscillation diagram. The reason for this can be very easily seen in terms of the reciprocal lattice. Let us confine our attention to the (*hko*) zone and suppose the axis of oscillation to be (001) and the crystal to be orthorhombic. The reciprocal lattice is also orthorhombic and may be represented by points at the corners of a number of rectangular parallelopipeds with edges $1/a$, $1/b$, and $1/c$. The planes (*hko*) are represented by the points of the reciprocal lattice lying in a plane OAB, Fig. 96, forming a rectangular network with sides $1/a$ and $1/b$. This plane cuts the sphere of reflection in a circle through O of radius $1/L$. Instead of imagining the lattice to oscillate we can suppose the sphere of reflection to oscillate about an axis through O perpendicular to the plane of the paper. Its positions at the beginning and end of its range of oscillation are shown in the figure. During the oscillation the points of the lattice within the lunes have at some instant been on the surface of the sphere, and at these instants they will have given rise to reflected rays, those in one lune to the left and in the other to the right of the central spot where the incident ray produced cuts the photographic film. A limited number of spots will therefore be recorded on each photograph.

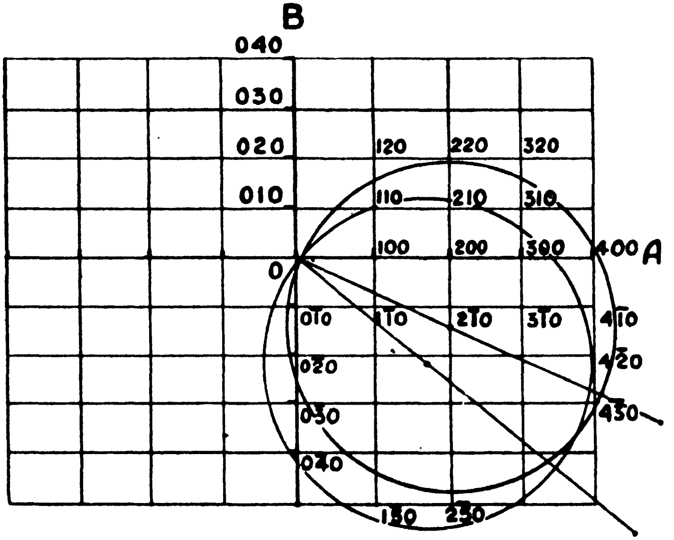


FIG. 96.—Projection of reciprocal lattice and sphere of reflection.

The "powder" method.

This method is of great importance on account of the variety of problems to which it can be applied and to the accuracy with which it enables us to measure the parameters of the crystal lattice. A "powder" is not necessary for its application; any crystal aggregate will serve, provided the grain size is sufficiently small. This condition is often satisfied by specimens of metals and alloys, which can therefore be examined in the state in which they are used technically.

The simplest form of powder camera consists of a cylindrical drum, generally between 5 and 10 cm. diameter, on the circumference of which a strip of photographic film is mounted, Fig. 97. The specimen may consist of a wire of metal or a thin hair covered with the powder to be examined. This is mounted at the centre of the film holder. The monochromatic X-ray beam, confined by a small aperture to a pencil about 1 mm. diameter, traverses a diameter of the film holder from which it emerges through a hole punched in the film. In order to increase the effective number of crystals irradiated the specimen is usually oscillated or rotated about the axis of the camera during exposure.

The principle involved in the production of powder photographs has been briefly referred to in § 7. In Fig. 93 of that section we now have the sphere of reflection fixed by the wave-length of the incident beam. The powder consists of a large number of crystals at O. Let us confine our attention to some plane (*hkl*) of the crystal. Since the crystals are oriented at random the vectors σ^{-1} corresponding to this plane of the reciprocal lattices of each crystal will form a bundle of rays emerging from the point O. Now the condition for reflection is that these vectors must terminate on the sphere of reflection. Accordingly the incident beam selects those vectors which satisfy that condition. The extremities of all these vectors lie in the small circle generated by the revolution of Fig. 93 about OC, and each of them is associated with a reflected ray μ which lies on a cone of semi-vertical angle 2θ. The rays reflected by the plane (*hkl*) therefore lie on the surface of a cone whose apex is at O (the centre of the circular camera), and whose semi-vertical angle is 2θ. This cone will cut the photographic film in a curve and the distance between the intersections on opposite sides of the incident beam is

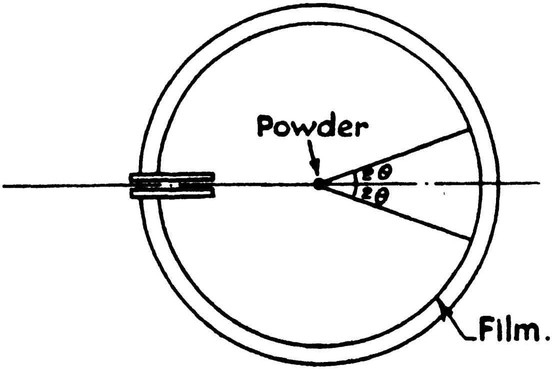


FIG. 97.—Diagram of powder method.

$4r\theta$ if r is the radius of the cylinder on which the film is held. The values of θ for the different lines of the X-ray spectrum can thus be obtained by measurement of the film, and if the wave-length of the incident ray is known the values of d can be deduced. To determine the structure it is then necessary to correlate the values of d observed with those calculated from one of the formulæ of § 5. Except for the simplest types of structure this is generally a matter of very great difficulty unless some additional information, such as that given by a Laue photograph, is available. If, however, as a result of a Laue photograph we know that the crystal is, for instance, cubic, then the solution of the problem is greatly facilitated. The values of d observed must all be expressible in terms of three integers in the form

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is the side of the cubic lattice. The quantity under the square root sign assumes a series of integral values, 1, 2, 3, etc., the only whole numbers which are missing from the series being those which cannot be expressed as the sum of the square of three integers, such as 7, 15, 23, 28, etc.

Certain integers, such as 9 and 27, can be expressed as the sum of three squares in two different ways. These integers correspond to reflections from two different types of crystallographic planes, e.g., $9 = 2^2 + 2^2 + 1^2$ or $3^2 + 0^2 + 0^2$, $27 = 3^2 + 3^2 + 3^2$ or $5^2 + 1^2 + 1^2$, so that the reflections (221) and (300) have the same values of sin θ and are superimposed in the powder photograph as are (511) and (333) also.

An example of a powder photograph is reproduced in Plate VIIIB and its analysis is given in Table I. The material which gave the photograph is the residue from the solution of an alloy of silicon and aluminium. Some of the powder attached to a hair was mounted at the centre of a circular camera as described above. The first column of the Table gives an estimate of the intensity of the reflections, s = strong, m = medium, w = weak; the second column gives the distance in millimetres between corresponding lines on opposite sides of the centre of the film where a hole is cut to allow the incident beam of X-rays to pass out of the camera without striking the film and so fogging it by scattered radiation. From these figures θ is derived from the known radius of the camera and hence the value of sin θ for each line of the spectrum. The photograph was obtained with radiation from a copper target which emits the K spectrum characteristic of copper, consisting of three wave-lengths α_1, α_2, and β. Of these α_1 and α_2 differ by so small an amount as not to be resolved except in the highest order reflection. From the known values of the wave-lengths which are given at the head of the table, the β lines can be recognized; they are always less intense than the α lines. To illustrate the way in which the list of values of sin θ

may be used to determine the structure of the material, we will suppose that we know from chemical analysis that it is silicon and that silicon is known to be a cubic crystal, either as the result of a Laue photograph or otherwise. With this information to help us we must now use Bragg's law $\lambda = 2d \sin \theta$ and the relation $d = a/\sqrt{h^2+k^2+l^2}$ to find the value of "a" the parameter of the cubic lattice. Graphical methods have been devised to facilitate this process, but in the present instance a few minutes' work with a slide rule would show that, omitting the β lines, the values of sin θ for the first three lines were very nearly in the ratio $\sqrt{3} : \sqrt{8} : \sqrt{11}$. Trial would then lead to the set of whole numbers recorded in the table under $h^2 + k^2 + l^2$. Since $\sin \theta/\sqrt{h^2 + k^2 + l^2}$ is equal to $\lambda/2a$ the value of a can be calculated for each reflection and is recorded in the table. Within the limits of error the figures are constant, and their mean may be taken as the value of the parameter of the crystal lattice.

TABLE I.—Powder Photograph of Silicon.

Copper Radiation $\lambda\beta = 1{\cdot}389$, $\lambda\alpha_1 = 1{\cdot}537$, $\lambda\alpha_2 = 1{\cdot}543$.

Camera radius $r = 29{\cdot}95$ *mm.*

I.	$4r\theta$ mm.	θ.	sin θ.	$h^2 + k^2 + l^2$.	λ.	a.	hkl.
m	26·90	12° 52′	0·2226	3	β	5·41	111
vs	29·90	14° 18′	0·2470	3	α	5·39	111
m	44·65	21° 21′	0·3541	8	β	5·40	220
vs	49·80	23° 49′	0·4038	8	α	5·39	220
m	53·00	25° 21′	0·4283	11	β	5·38	311
vs	59·05	28° 14′	0·4731	11	α	5·39	311
vw	64·75	30° 57′	0·5143	16	β	5·40	400
vw	70·30	33° 37′	0·5536	19	β	5·48	331 ?
ms	72·90	34° 52′	0·5717	16	α	5·38	400
s	80·25	38° 23′	0·6209	19	α	5·40	331
vw	81·60	39° 1′	0·6295	24	β	5·41	422
vw	87·75	41° 56′	0·6682	27	β	5·40	511, 333
vs	92·50	44° 14′	0·6976	24	α	5·40	422
vw	97·70	46° 43′	0·7280	32	β	5·40	440
s	99·70	47° 40′	0·7393	27	α	5·41	511, 333
w	103·45	49° 27′	0·7599	35	β	5·40	531
s	112·05	53° 36′	0·8049	32	α	5·41	440
w	113·65	54° 22′	0·8128	40	β	5·41	620
vs	119·65	57° 14′	0·8409	35	α	5·41	531
vs	133·70	63° 56′	0·8983	40	α	5·41	620
w	138·80	66° 21′	0·9160	51	β	5·41	711
s	143·30	68° 31′	0·9305	43	α_1	5·41	533
w	144·00	68° 52′	0·9327	43	α_2	5·42	533
ms	154·30	73° 44′	0·9600	56	β	5·42	642

Further information concerning the nature of the structure is now obtained by writing down the values of h, k, and l for each reflection as shown in the last column. It is observed that for each line the indices are either all even or all odd; no line occurs for which some indices are even and some odd. This indicates that the structure is face centred and the number of silicon atoms in the unit must be a multiple of four. If the density is known the number can be found because if it is n then nM/a^3 is the density where M is the mass of the silicon atom. The mass of the hydrogen atom is $1{\cdot}664 \times 10^{-24}$ grammes, its atomic weight (oxygen = 16) is 1·0077, the atomic weight of silicon on the same scale is 28·3, so that the mass of the silicon atom is $\frac{28{\cdot}3}{1{\cdot}0077} \times 1{\cdot}664 \times 10^{-24}$ grammes. The density of silicon is 2·5 grammes per c.c. and therefore

$$n\frac{28{\cdot}3}{1{\cdot}0077} \times 1{\cdot}664 \times 10^{-24} = 2{\cdot}5 \times (5{\cdot}40 \times 10^{-8})^3$$

$$\text{giving } n = 8{\cdot}42.$$

Now, since we know that n must be a multiple of four we may assume it to be equal to 8, and ascribe the difference to error in the assumed value of a or the density. There are four lattice points associated with a face-centred cube so the structure must consist of two face-centred lattices intermeshed. The way in which the two lattices are disposed can be found from the fact that certain reflections are not observed. Referring to the table it is seen that (200), (222), (600) are all absent. It can be shown that this is to be expected if the structure consists of two face-centred lattices, the origin of one dividing the diagonal of the other in the ratio 1 : 3. One lattice is derived from the other by a translation along the cube diagonal of an amount $a\sqrt{3}/4$. The positions of the 8 atoms in the unit are thus completely determined.

Focussing cameras.

For simple structures the experimental arrangement described above may suffice, but it is often necessary to determine the values of d with greater accuracy. To do this "focussing cameras" are frequently employed. The principle on which they depend is sketched in Fig. 98. S is a slit admitting a divergent beam of X-rays to the camera; the specimen PQ is arranged to lie on the circumference of a circle passing through S. For a particular plane the rays SP, SQ are reflected at suitably orientated crystals at P and Q, in the directions PR and QR. On account of the equality of the angles SPR and SQR, which are both equal to $\pi - 2\theta$, the reflected rays converge to a focus at R which lies on the circumference of the circle SPQ. The chord SR subtends at any point on the specimen the angle $\pi - 2\theta$, so that all suitably orientated crystals reflect to R. It is not practicable to construct a camera of this type which will record on one film all the reflections from $\theta = 0°$ to $\theta = 90°$; usually three cameras covering different ranges of θ are employed. The ranges are generally about $10° < \theta < 30°$, $25° < \theta < 60°$, and $60° < \theta < 90°$.

The employment of the focussing principle has several advantages. A divergent beam of X-rays is used, covering an area large compared with the surface of the wire or thin rod employed in the simplest type of camera, and the geometrical condition for focussing is accurately satisfied. This results in very sharp lines, so that for equivalent exposures faint reflections can be recorded. The dispersion of the spectrum is greater for the focussing type than for a camera of the same radius with the specimen mounted centrally, so that overlapping lines can be separated, and the accuracy of determination of sin θ is increased. Cameras of this type have been successfully used by Westgren and his collaborators, and are particularly useful in the examination of alloy systems.

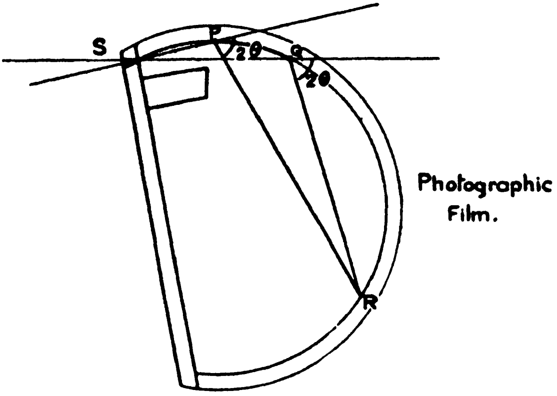


FIG. 98.—Camera of focussing type.

Precision measurements.

The powder method is capable of yielding exceedingly accurate values of the parameter of a crystal. This arises in the following way. In Bragg's law L = $2d \sin \theta$, regarding L as constant, we find by differentiation that $\delta\theta = -\frac{\delta d}{d} \tan\theta$ where $\delta\theta$ is the change of θ produced by a small change δd in d. Now $\tan\theta$ increases very rapidly as θ approaches 90° so that for a given $\frac{\delta d}{d}$, $\delta\theta$ increases rapidly for large angles of reflection and for values of θ near 90, when the reflected beam almost returns on the incident beam, changes of θ form a very sensitive test for changes of d. A number of applications of this "back reflection" method have been used successfully to demonstrate the existence of small parameter changes resulting from the solution of one metal in another. The method is capable of detecting the change in parameter associated with a rise of temperature of 10° C. and can therefore be used to measure thermal coefficients of expansion: elastic strains can also be measured. Up to the present changes in the spacing *d* of the order of one part in 10,000 are commonly measured, but the limit of accuracy attainable has probably not yet been reached.

Grain size and preferred orientation.

Two other applications of the powder method must be briefly referred to. We have supposed in the preceding section that the powder consisted of such a large number of grains oriented at random that the cone of reflected rays, Fig. 93, was uniformly filled. If the grain size is too large, an insufficient number of crystals will be irradiated and there will only be certain regions of the cone which contain reflected rays—because the vectors σ^{-1} do not now fill all the space surrounding the origin. The result is that, if the diffracted rays are recorded on a photographic plate placed perpendicular to the incident beam, instead of a series of uniform circles the diffraction pattern will consist of a number of small spots lying on circles described about the incident beam. By standardizing the method of experiment an enumeration of the spots on a particular circle will give a figure which can be correlated with the number of grains in the specimen, and thus an estimate of the number per unit volume in the specimen obtained.

There is another way in which the circles normally produced by a powder can be broken up. This is by preferred orientation resulting from cold work, such as rolling or drawing. The effect of such treatment is to produce a tendency for certain crystallographic directions to assume fixed directions in the specimen. For example in rolled magnesium the hexagonal axis tends to be perpendicular to the plane of rolling, so that the basal plane lies in the plane of rolling. If a thin sheet of rolled magnesium is mounted in a beam of X-rays which traverses it normally, and if the diffraction pattern is recorded on a photographic plate perpendicular to the beam, a series of concentric circles will be obtained, but the circle corresponding to reflection from the basal plane will be absent. If instead of having the normal to the sheet parallel to the X-ray beam the specimen is mounted so that the normal is inclined at about 75° to the incident beam, the reflection from the basal plane will appear as a very intense arc, showing that the normals to the basal planes of all the small crystals tend to lie parallel to the normal to the plane of rolling. This is an example of the simplest case of preferred orientation where one crystallographic direction only is fixed with respect to the surface of the specimen. In many cases, however, two crystallographic directions tend to lie in specified directions, so that the rings usually obtained from powders are broken up into a series of short arcs. From the position and length of these arcs it is possible to define the type of orientation and to estimate its perfection. It is clear that where two crystallographic directions are fixed with reference to the surface of a sheet all the crystals are trying to lie in a fixed orientation and it is only in the amount of deviation from this fixed orientation that the specimen differs from a single crystal.

High-voltage equipment.

The design of equipment for the production of X-rays is a branch of electrical engineering, and a complete account of such apparatus would be outside the scope of this book. The requirements of crystal analysis are fully met by a self-contained unit produced by the Metropolitan-Vickers Electrical Co., Fig. 99, and a brief description of this equipment will here be given.

The hot cathode X-ray tube, which is demountable and continually evacuated, consists of a cylindrical porcelain insulator to one end of which is attached the connections to the filament and high-voltage supply, the other end being connected to an earthed metal head-piece through the medium of a flat grease-sealed joint. A quickly detachable water-cooled target (anticathode) is located in the metal head-piece and has a removable operating face which can be changed without difficulty so as to permit the use of the characteristic X-radiation of different elements. A branch pipe leads down from the metal head-piece to the high vacuum oil condensation pump.

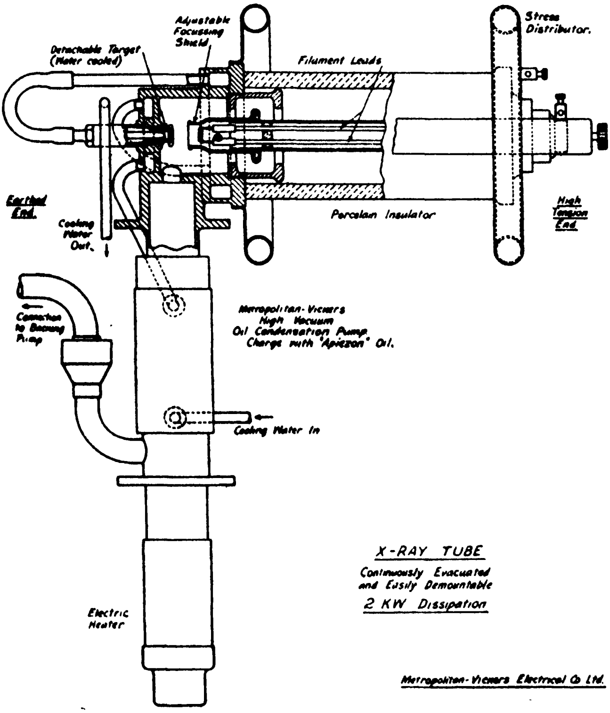


FIG. 99.—Metropolitan-Vickers X-ray apparatus.

The filament consists of a spiral of 0·3 mm. tungsten wire supported on leads carried by a steel tube fitted into the closed end of the porcelain insulating cylinder. A screwed extension to this tube acts as a focussing shield and enables a line focus to be obtained on the target. The X-rays emerge from the head-piece through two windows 3 mm. wide, sealed by 0·001 inch thick aluminium foil; the windows are provided with adjustable slits. The provision of two windows allows two X-ray cameras to be used simultaneously, each camera being held in adjustable supports so that the camera slits may be accurately directed towards the source of X-rays. A conical earthed protecting shield surrounds the high-voltage end of the tube, and enables adjustments to the cameras to be carried out in safety while the tube is running.

The pumping system consists of a Metropolitan-Vickers type 02 oil condensation pump backed by a rotary oil pump; a high vacuum tap is provided between the two pumps so that the tube can be shut down under vacuum, thus shortening the pumping time on starting up. The operation of the pumps is made automatic by a system of vacuum relays.

The high-voltage transformer is mounted on the same stand as the X-ray tube and pumps, the whole forming a compact unit occupying 6 ft. × 4 ft. floor space. The transformer tank contains both the high-voltage and filament-heating transformers. The high-voltage transformer of 5 k.v.a. rating will deliver 70 milliamps at 100 k.v. peak continuously, one end of the secondary winding being at earth potential. The filament transformer delivers 10 amps. at 15 volts and has insulation for 100 k.v. peak between primary and secondary windings.

The control equipment, which is described as " semi-automatic " is ingenious. The system of interlocking is such that it is impossible to carry out any operation in the starting sequence until the preceding operation has been correctly performed, and if the water supply should fail or the tube soften the equipment shuts down automatically and cannot be re-started until the fault has been rectified.

The permissible power dissipation on the target depends on the size of the focal spot and on the material of which the target is made; an input quite safe for a copper target would puncture an iron one.

The equipment is capable of giving a high output of X-rays. With a mean tube current of 40 milliamps at 50 k.v. peak, representing a dissipation of 1 kw. on a copper target, good photographs of copper wire may be obtained in a camera of 9 cm. radius with only five minutes' exposure.

The following works should be referred to for further information on X-ray methods of investigation :—

W. H. Bragg and W. L. Bragg, " X-Rays and Crystal Structure," London, 1924. " The Crystalline State," London, 1933. R. W. G.

Wyckoff, "The Structure of Crystals," New York, 1935. G. L. Clarke, "Applied X-Rays," New York and London, 1932. G. W. C. Kaye, "X-Rays," London, 1929. U. Dehlinger and G. Borelius, "Handbuch der Metallphysik," Vol. I, Leipzig, 1935. H. Hilton, "Mathematical Crystallography," Oxford, 1903. "International Tables for the Determination of Crystal Structures," Berlin and London, 1935.

APPENDIX I (TO CHAP. X).

THE LATTICE STRUCTURES OF THE METALS.

Most of the metals crystallize in one of three simple lattices: the face-centred cubic, body-centred cubic, and close-packed hexagonal. These are represented in Fig. 100. In the first (*a*), the atoms may be considered as occupying the corners of a cube and also positions in the centre of each face. In (*b*) each corner is occupied, and there is one atom at the centre. In (*c*) the atoms are arranged on a hexagonal prism, which may be broken up into six triangular prisms, the height of which is 1·633 times the edge of the base. In the hexagonal prism, there is an atom at each corner and one at the centre of alternate triangular prisms. In (*a*) and (*c*) each atom, regarded as a sphere, is in contact with 12 others, and both structures are equally close-packed, whilst in (*b*) an atom is only in contact with 8 others. Some metals have the hexagonal structure, but with a ratio which differs from 1·633, so that an atom has two groups of neighbours at slightly different distances, each group having 6 atoms.

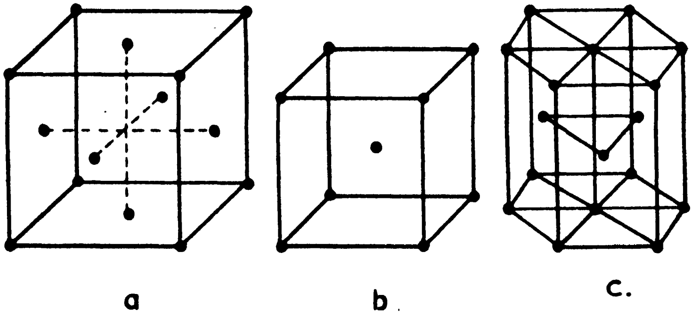


Fig. 100.—Cubic and hexagonal lattices.

The face-centred tetragonal structure (Fig. 101 (*a*)) resembles the face-centred cubic, but one axis differs in length from the other two.

Rhombohedral structures in which the atoms are arranged in double layers, so that each atom has 3 close neighbours and 3 at a slightly greater distance, are represented by Fig. 101 (*b*), and several more complex structures occur among the metals. The more important are shown in the Table, arranged according to the periodic system.

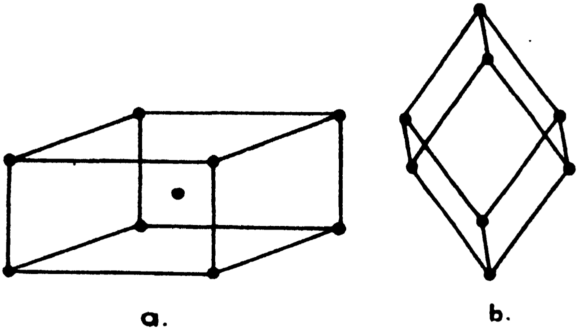


FIG. 101.—Tetragonal and rhombohedral lattices.

Group.	Metal.	Lattice.	Axial Ratio.
IA	Li, Na, K, Rb, Cs	Body-centred cubic	
IB	Cu, Ag, Au	Face-centred cubic	
IIA	Be	Close-packed hexag.	1·568
	Mg	,, ,,	1·623
	Ca (two modifs.)	F.c. cubic and C.p. hexag.	1·638
IIB	Zn	Close-packed hexag.	1·856
	Cd	,, ,,	1·885
	Hg	Rhombohedral	
IIIA	Al	Face-centred cubic	
IIIB	Tl (two modifs.)	F.c. cubic and C.p. hexag.	1·60
IVA	Th	Face-centred cubic	
IVB	Sn (white)	Face-centred tetrag.	0·546
	Sn (grey)	Non-metallic, diamond	
	Pb	Face-centred cubic	
VA	V	Body-centred cubic	
VB	As, Sb, Bi	Rhombohedral	
VIA	Cr (two modifs.)	B.c. cubic and C.p. hexag.	1·626
	Mo, W	Body-centred cubic (W also forms a modification with complex structure)	
VIIA	Mn (three modifs.)	Two have complex modifications of the cubic structure; one is face-centred tetragonal	
VIII	Fe (two modifs.)	B.c. cubic and F.c. cubic	
	Co (two modifs.)	F.c. cubic and C.p. hexag.	1·624
	Ni (two modifs.)	F.c. cubic and C.p. hexag.	1·64
	Rh, Pd, Ir, Pt	Face-centred cubic	
	Ru	Close-packed hexag.	1·585
	Os	,, ,,	1·584

APPENDIX II (TO CHAP. X).

DIFFRACTION OF ELECTRON BEAMS.

FOLLOWING on the theoretical work of de Broglie, according to which wave properties are associated with an electron, it was shown [1] that a beam of electrons could be diffracted in the same manner as X-rays. As a means of studying structure, the electron beam method resembles the use of X-rays of exceedingly short wave-length, although caution must be used in the interpretation of the patterns on account of the different degrees of interaction with atoms. The penetrating power of electrons is, however, very small compared with that of X-rays, and this makes the method particularly valuable in the study of thin films and of surface structures.[2] The practical convenience of the method is increased by the great intensity of the reflections from crystal planes as compared with X-rays, making it possible to see the pattern on a fluorescent screen, and to use photographic exposures of only a few seconds.

High voltages are necessary, the usual range being from 30,000 to 70,000 volts, and the current from the transformer may either be rectified and smoothed externally, or the discharge tube may itself serve as a rectifier.

Substances may be examined by either transmitted or reflected beams. The transmission method is suitable for thin foils or for films prepared by evaporating, sputtering, or electro-depositing metals on a non-metallic support, such as collodion or cellophane, held on a wire frame or on a small piece of wire gauze. Reflection from a solid surface must be carried out at grazing incidence (an angle of a few degrees only) so that delicate adjustment is necessary. The surface of liquid metals may be examined by using a horizontal camera, a bead of the molten metal being supported on an electrically heated stage in an intermediate furnace chamber. This method has been used in studying the surface oxidation of molten metals.[3]

The method lends itself well to the study of the structure of foils and films. Rolled or hammered foils usually have a considerable degree of orientation, and on heating this is increased, until the specimen approaches the state of a single crystal. When one metal is deposited on another, the structure of the deposit, when only a few atoms thick, may be determined by that of the underlying metal, and this gives a valuable means of studying the process of crystal growth. Thus a thin layer of aluminium deposited on crystalline

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[1] G. P. Thomson, *Proc. Roy. Soc.*, 1928, **117**, A, 600; L. H. Germer, *Z. Physik*, 1929, **54**, 408.

[2] G. P. Thomson, *Proc. Roy. Soc.*, 1928, **119**, A, 652; G. I. Finch, A. G. Quarrell, and H. Wilman, *Trans. Faraday Soc.*, 1935, **31**, 1051. This paper constitutes a monograph on the subject.

[3] G. D. Preston and L. L. Bircumshaw, *Phil. Mag.*, 1935, [vii], **19**, 160.

platinum appears to take up an orientation in which it has a tetragonal structure, the basal dimensions being those of platinum, whilst the height of each prism is that of the normal unit cube of aluminium.[1]

One of the most valuable results of electron beam experiments has been the evidence that it has given for the existence of the " Beilby layer " on polished metals which is discussed in Chapter XVI. It has also proved most useful in the study of the thin protective films of oxide on the surfaces of metals. It has been shown, for instance, that the rate of oxidation of molten tin is determined not only by the thickness but also by the orientation of the films of oxide composing it,[2] and that whilst most oxide films on solid metals are crystalline,[3] the highly protective character of the thin film formed on aluminium and some of its alloys at low temperatures is associated with its amorphous character.[4]

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[1] G. I. Finch and A. G. Quarrell, *Proc. Roy. Soc.*, 1933, **141**, A, 398.

[2] L. L. Bircumshaw and G. D. Preston, *Phil. Mag.*, 1936, [vii], **21**, 686.

[3] J. A. Darbyshire, *Trans. Faraday Soc.*, 1931, **27**, 674 ; G. D. Preston and L. L. Bircumshaw, *Phil. Mag.*, 1935, [vii], **20**, 706 ; W. G. Burgers, A. Classen, and J. Zernicke, *Z. Physik*, 1932, **74**, 593.

[4] G. D. Preston and L. L. Bircumshaw, *Phil. Mag.*, 1936, [vii], **22**, 654.

CHAPTER XI.

THE GROWTH OF METALLIC CRYSTALS.

THE general outline of the crystallization of metals having been considered in Chapter VIII, the mechanism of growth has now to be examined. Starting from a centre, a crystal must have different rates of growth in different directions; otherwise its boundary would always be spherical. In general, the rule of Bravais[1] holds good that the velocity of growth is least perpendicularly to the most closely packed planes. In the experiments of Volmer[2] on zinc and mercury deposited from a molecular stream impinging on a surface, the most densely packed plane is the basal plane of the hexagonal crystals, and atoms impinging on such a plane attach themselves to the edges rather than to the surface, so that the crystal grows into a hexagonal plate, very broad in proportion to its thickness, and it is only when the plate has grown considerably that the atoms begin to build up its thickness rather than to migrate to the edges. Volmer concluded, and experiments in which a wire is interposed so as to cast a shadow confirm,[3] that at temperatures which are not too low the impinging atoms are at first loosely adsorbed, and move in a two-dimensional layer in a Brownian movement over the face of the crystal. Nuclei are formed in this layer, and by their lateral growth the mobile layer is "frozen." The process of growth is thus essentially intermittent. It differs, however, from that of ionic crystals, in which the process has been studied quantitatively. The lattice energies of homopolar or metallic crystals cannot be calculated in the same way as heteropolar crystals, but Stranski[4] has assumed that the attraction on an atom colliding with the surface may be measured by the number of atoms in each of several shells around the point of contact, weighted according to the radius of each shell. In this way it has been shown, and confirmed by experiment, that for zinc the most probable position to be filled is that on an incompleted edge of a (0001) plane. Next follow edges of pyramidal and prismatic faces, the least probable being attachment at a new point on a basal (0001) face. Hence

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[1] A. Bravais, "Études cristallographiques," Paris, 1866, 167.

[2] M. Volmer, *Z. Physik*, 1921, **5**, 31; 1922, **9**, 193; M. Volmer and I. Estermann, *ibid.*, 1921, **7**, 13.

[3] J. D. Cockcroft, *Proc. Roy. Soc.*, 1928, **119**, A, 293.

[4] I. N. Stranski, *Z. physikal. Chem.*, 1928, **136**, 259; 1930, **11**, B, 342.

building up on that face has to await the formation of a two-dimensional nucleus in the mobile layer, a fact in accordance with observation.[1] Strictly speaking, the results only apply to the formation of crystals from neutral atoms, as by sublimation or from the melt, and when deposited from solutions containing ions, as in electrodeposition, the ionic forces alter the conditions,[2] but this fact is of less practical importance, and for metallographic purposes attention may well be concentrated on crystallization from the molten state.

In this instance also, the first process is the formation of nuclei. This may come about by chance collisions of atoms in the course of the thermal movement. In most metals this occurs readily in the neighbourhood of the freezing-point, so that undercooling does not as a rule proceed very far. The effects of undercooling are discussed in Chapter XII, and are neglected for the present purpose, except in so far as a small undercooling is essential to the growth of crystals.

The order of development of the various faces of a metallic crystal may be conveniently studied by making use of a single crystal previously prepared in the form of a sphere or hemisphere. In experiments on the growth of zinc from its vapour,[3] a single crystal was grown from the liquid by Bridgman's method and a hemispherical free end was exposed to the vapour of zinc in an evacuated vessel. Hexagonal plates were formed, lying on one another like a pack of cards, all being parallel with the (0001) plane of the crystal. By an examination of the process of building up the several faces, it was possible to verify the hypothesis of Stranski [4] as to the process of growth.

A similar method was used in the study of the growth of electrodeposited crystals of silver.[5] A spherical crystal of silver, again grown from the molten metal, was made the cathode in various solutions containing silver ions. Some solutions gave complex forms, but when the concentration of silver ions was low, as in solutions of silver chloride in ammonia, simple faces, mainly (111), were obtained.

As mentioned earlier, the crystals in an ingot have a marked tendency to grow perpendicularly to the cooling surface, at least during a large part of the process of solidification. These columnar crystals have, as a rule, one axis in common, although the direction of their other axes about that one may be random. That is, the columnar crystals form a "fibre" structure (Chap. XVII). The orientation may be determined by cutting sections and examining the etch-figures,[6] or by means of X-rays. The latter method has

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[1] P. A. Anderson, *Phys. Rev.*, 1932, [ii], **40**, 596. See also M. Straumanis, *Z. physikal. Chem.*, 1931, **13**, B, 316.

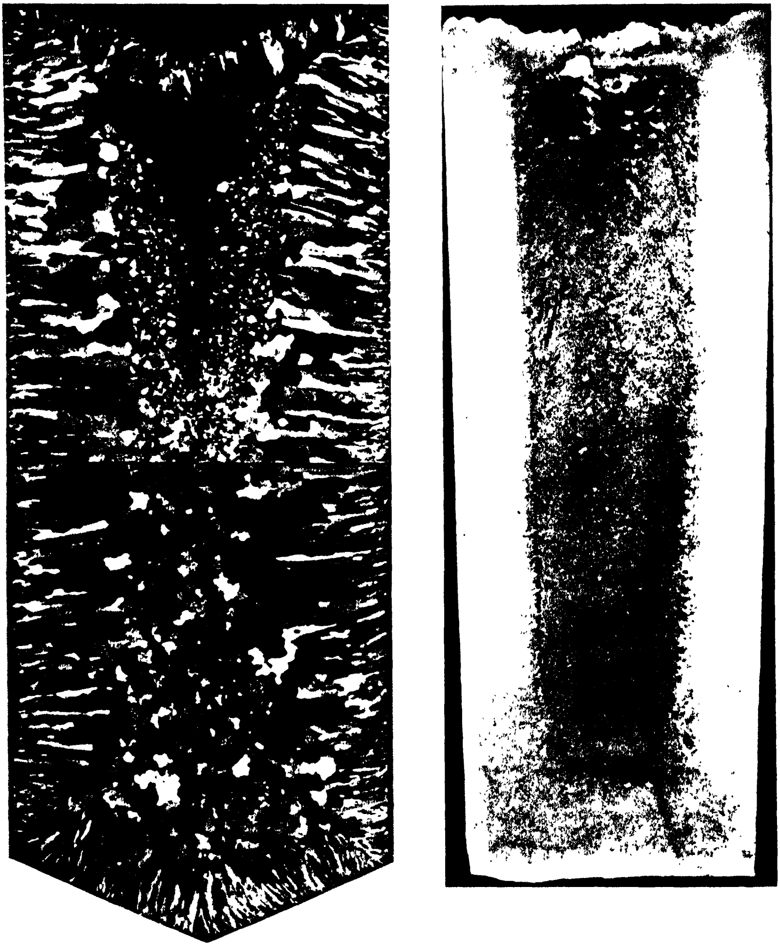
[2] I. N. Stranski, R. Kaischew, and L. Krastanow, *Z. Krist.*, 1934, **88**, 325.

[3] P. A. Anderson, *Phys. Rev.*, 1932, [ii], **40**, 596.

[4] I. N. Stranski, *Z. physikal. Chem.*, 1930, **11**, B, 342.

[5] T. Erdey-Grúz, *ibid.*, 1935, **172**, A, 157. See also I. N. Stranski, R. Kaischew, and L. Krastanow, *Z. Krist.*, 1934, **88**, 325.

[6] G. Tammann and A. Heinzel, *Z. Metallk.*, 1927, **19**, 338; F. R. Hensel, *Dissertation*, Berlin, 1929.



A. Ingot of silicon iron alloy.
Macro-etching

B. Ingot of rimming steel.
Sulphur print

PLATE IX

been most fully applied.[1] As might be expected, the face-centred cubic metals, Al, Cu, Ag, Au, Pb, behave alike, a [100] edge being parallel with the length of the columnar crystals. α-iron, in the form of a 4 per cent. silicon alloy, and β-brass, both of which have body-centred cubic lattices, have a similar orientation, but the iron shows some variation. In all these metals, then, cube faces are found perpendicular to the cooling surface. Zinc and cadmium, which crystallize in the hexagonal system, have their basal plane parallel with the axis of growth, whilst magnesium, which only differs from them in having a different axial ratio, also has a further direction fixed. White tin, which is tetragonal, has the diagonal of the base, [110], parallel with the axis of growth, whilst with bismuth the [111] axis takes that direction.

Except for tin, the direction of growth corresponds with one of the closely-packed lines in the lattice.

Nix and Schmid also examined two eutectics. In the eutectic alloy of aluminium and silicon, the aluminium was found to preserve its normal direction in the columnar crystals or colonies, whilst the silicon gave no sign of orientation. On the other hand, the eutectic of zinc and cadmium, two metals with very similar space lattices, had a common orientation; and a study of very carefully grown and isolated colonies of that eutectic showed[2] that the basal planes of both metals are parallel, and perpendicular to the cooling surface.

In a large ingot, an outer layer of "chill" crystals is found close to the wall of the mould, and the orientation of these appears to be random. The columnar crystals would seem to be the survivors, only those continuing to grow which have the favoured axis already in the right direction. The mechanism of selection, which depends on the differing velocities of growth along the several axes, has been studied in organic substances, narrow tubes being used to confine the mass as it solidifies.[3]

THE PREPARATION OF SINGLE CRYSTALS.

One of the most important steps in metallographic research in recent years has been the invention of methods for the preparation of metals and alloys in the form of single crystals of such size as to allow their physical and mechanical properties to be determined. This provides a means of studying metals in their simplest form, the influence of varying orientation and grain boundaries being eliminated, whilst the effects of anisotropy can thus be examined and measured. Four methods are available: (1) by the solidification of liquid metal, (2) by deposition from a gaseous phase, (3) by electrolysis, and (4) by recrystallization of a solid polycrystalline specimen after mechanical strain or during an allotropic change.

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[1] F. C. Nix and E. Schmid, *Z. Metallk.*, 1929, **21**, 286.

[2] M. Straumanis and N. Brakšs, *Z. physikal. Chem.*, 1935, **30**, B, 117.

[3] R. Gross and H. Möller, *Z. Physik*, 1923, **19**, 375.

(1) From the liquid. By enclosing undercooled organic liquids in narrow glass tubes, and causing crystallization to begin by further cooling the closed end, Tammann obtained single crystals, and in the same way crystals of bismuth up to 20 cm. in length were prepared.[1] This method was improved to allow of much larger crystals being obtained, the cooling being made to proceed regularly along the length of the containing tube by the use of a gradient furnace.[2] Crystals of copper even several kilograms in weight may be prepared in this way.[3] It is important to avoid agitation of the liquid during cooling, and in the writer's experience a liquid metal which is cooled with precautions against agitation or convection currents is most likely to solidify as a single crystal or as a few parallel crystals, even in large masses of one or more kilograms,[4] without any special gradient furnace. The surface of the moulds should be smooth. Glass serves well for the more fusible metals, being preferably smoked inside. For higher temperatures silica, sillimanite, or graphite should be used. The removal of the crystal from the mould requires great care, as single crystals are readily distorted by very small forces.

The orientation of crystals thus grown in tubes is largely a matter of chance, although when there is a marked difference in the velocity of growth along different axes this will naturally exert an influence. Thus zinc crystals tend to have their basal plane nearly parallel with the length of the tube, the rate of growth perpendicularly to that plane being a minimum. The use of a capillary inclined at any desired angle to the axis of the tube, crystallization being caused to begin in that capillary, gives satisfactory results with zinc and cadmium.[5] For bismuth, the device of melting a rod lying horizontally in a groove in a uniformly heated copper block has been successful.[6] Surface tension and a thin film of oxide retain the rod in its original shape, and by pressing a fragment with the desired orientation against the end crystallization may be set up.

A method which has been used by a number of experimenters consists in touching the surface of a molten metal with a solid point, and raising this mechanically at a rate corresponding with the velocity of crystallization.[7] A wire with a rather irregular surface is obtained.

(2) From the vapour phase. Those metals, like zinc, cadmium, and mercury, which have a marked minimum rate of growth normal

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[1] G. Tammann, "Lehrbuch der Metallographie," Leipzig, 1921, p. 12; I. Obreimow and L. Schubnikow, *Z. Physik*, 1924, **25**, 31.

[2] P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1925, **60**, 305. An improved vacuum apparatus is described by G. Sachs and J. Weerts, *Z. Physik*, 1930, **62**, 473.

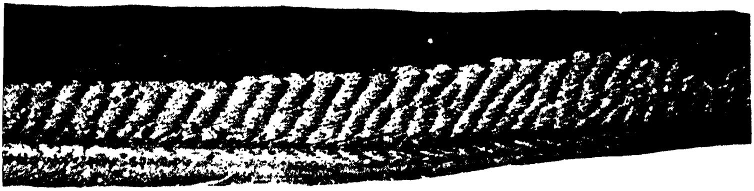
[3] K. W. Hausser and P. Scholz, *Wiss. Veröff. Siemens-Konzern*, 1927, **5**, iii, 144.

[4] R. G. Heggie, *Trans. Faraday Soc.*, 1933, **29**, 707.

[5] A. Palibin and A. I. Froiman, *Z. Krist.*, 1933, **85**, 322.

[6] P. Kapitza, *Proc. Roy. Soc.*, 1928, **119**, A, 358; A. Goetz, *Phys. Rev.*, 1930, [ii], **35**, 193; M. F. Hasler, *Rev. Sci. Instr.*, 1933, **4**, 656.

[7] J. Czochralski, *Z. physikal. Chem.*, 1917, **92**, 219. The method was improved by E. von Gomperz, *Z. Physik*, 1922, **8**, 184.



A. Dendritic pattern in tin crystal. × 5

B. Etch-figures in copper. × 200

PLATE X

to one plane, give single crystals, although of irregular outline, when a molecular stream of the metallic vapour impinges on a solid surface. A more usual method consists in starting with a single crystal wire of tungsten, prepared in another way, and heating it in the vapour of a halogen compound of the metal required.[1] In this way large and regular crystals of tungsten, molybdenum, titanium, zirconium, and other elements of high melting-point have been prepared, as well as various carbides, nitrides, and borides.

(3) By electrolytic deposition. Single-crystal wires of tungsten have been built up to thick crystals by making them the cathode in a bath of fused sodium tungstate.[2] At lower temperatures a similar method has been used for the preparation of single crystals of silver.[3]

(4) By recrystallization. Aluminium and iron have been mainly examined in this form, and it was with such crystals that the study of the properties of metallic single crystals first began. It had long been known that annealing a metal after it had been deformed beyond its elastic limit led to grain growth, and it had been noted that a certain critical strain gave a maximum amount of growth.[4] By a careful choice of conditions it was found possible[5] to obtain such growth in aluminium as to convert tensile test pieces into single crystals, the mechanical tests on which are described in Chapter XVI. It is necessary to bring the metal into a condition of uniform grain size by a preliminary annealing, and then to produce a critical amount of strain, usually amounting to an extension of 1·6 to 1·7 per cent., followed by an annealing process in which the temperature is gradually raised at the rate of 10° a day to 550°, and finally raised to 600°. A large proportion of the specimens so treated become single crystals. The material used was in the form of sheet, and when cylindrical bars are required it is advisable to obtain a more uniform condition throughout the bar by giving a preliminary deformation amounting to an extension of 15 per cent., then annealing at 500°, following this by a critical deformation and gradual annealing as before, completing the operation by keeping the specimens at 640° for a few days, in order to absorb the few small crystals which may remain.[6] With this treatment nearly all the specimens become single crystals. The method of critical strain is also used[7] to produce single crystals of iron. It is necessary to remove impurities as far as possible by

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[1] A. E. van Arkel, *Physica*, 1922, **2**, 56; *Chem. Weekblad*, 1927, **24**, 90; F. Koref and H. Fischvoigt, *Z. techn. Physik*, 1925, **6**, 296.

[2] J. A. M. van Liempt, *Z. Elektrochem.*, 1925, **31**, 249.

[3] V. Kohlschütter and A. Torricelli, *ibid.*, 1932, **38**, 213; T. Erdey-Grúz, *Z. physikal. Chem.*, 1935, **172**, A, 157.

[4] A. Sauveur, *Proc. Intern. Ass. Test. Mat.*, *VI Congr.*, 1912, ii, Sect. 1; C. Chappell, *J. Iron Steel Inst.*, 1914, i, 460; F. Robin, *Rev. Métall.*, 1914, **11**, 489.

[5] H. C. H. Carpenter and C. F. Elam, *Proc. Roy. Soc.*, 1921, **100**, A, 329; H. C. H. Carpenter, *J. Iron Steel Inst.*, 1923, i, 175.

[6] V. H. Stott, *Trans. Faraday Soc.*, 1935, **31**, 998.

[7] C. A. Edwards and L. B. Pfeil, *J. Iron Steel Inst.*, 1924, i, 129.

annealing in hydrogen before straining. When highly purified iron is made, there is a great tendency for very large crystals to be obtained even under ordinary mechanical and thermal treatment,[1] and in general it may be said that the preparation of single crystals becomes easier as the purity of the metal is improved.

In the Pintsch process for making single-crystal wires of tungsten, the microcrystalline mass is drawn through a furnace at 2500° at such a rate (about 1 mm./sec.) as just to keep pace with the growth of the grains. Iron strips yield single crystals on drawing through a region heated to 900° (the temperature of the γ-α change), the allotropic change to the α-phase causing new crystals to form, the rate of travel being adjusted to the rate of growth.[2]

INTERGRANULAR BOUNDARIES.

In a mass of metal consisting of many crystal grains of varying orientation, the nature of the boundary is likely to play an important part in determining the properties of the metal as a whole. The lattices of adjoining grains cannot fit perfectly, and there must be a region of misfit, which if of appreciable thickness would differ from the neighbouring crystals in both physical and chemical properties. It has been supposed [3] that the attraction of two crystals on the still molten metal lying between them will bring about a condition in which growth will cease when they approach within a certain distance, so that the metal still liquid will cool without taking up a definite geometrical arrangement. This "amorphous" intercrystalline layer has been invoked to account for a great variety of properties of metallic aggregates.[4] Being an undercooled liquid, it might be expected to have the property of viscous flow, and to differ from the crystal in the effect of temperature on its mechanical strength.[5] It should have a higher vapour pressure than the crystal, and some experiments have been taken to indicate that this is so. Further, it should be chemically more active than the remainder of the metal, and therefore should be more readily attacked by reagents. The fact that grain boundaries are often attacked rapidly in the process of etching has been held to support the hypothesis, as well as the frequent occurrence of intergranular corrosion in technical practice. In spite of these facts, the balance of evidence is strongly against there being a layer more than a few atoms thick having random orientation between the crystal grains. The attractive forces between atoms become negligible at a very short distance, and a layer hundreds of atoms thick, such as is called for by the hypothesis, would certainly

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[1] F. Adcock and C. A. Bristow, *Proc. Roy. Soc.*, 1935, **153**, A, 172.

[2] L. W. McKeehan, *Nature*, 1927, **119**, 705; *Phys. Rev.*, 1927, [ii], **29**, 920.

[3] W. Rosenhain and D. Ewen, *J. Inst. Metals*, 1912, **8**, 149; and many later papers by Rosenhain, to whom the development of this idea is due.

[4] See W. Rosenhain, *Intern. Z. Metallogr.*, 1913, **5**, 65.

[5] G. D. Bengough, *J. Inst. Metals*, 1912, **7**, 123; W. Rosenhain and D. Ewen, *ibid.*, 1913, **10**, 119.

crystallize. Decisive experiments are difficult on account of the influence of even very minute traces of impurities on the properties of metals. Many of the forms of intergranular weakness are caused by thin layers of impurities—solid or gaseous—at the boundaries. The form of the grains seems to be determined in part by an interfacial tension (p. 139) and residual stresses are often present, small in amount, but enough to produce a difference between the boundary and the mass of the crystal. It must be admitted that the nature of the crystal boundary is imperfectly understood, and experiments with metals of the highest degree of purity obtainable are to be desired.

MOSAIC STRUCTURE.

In the course of the study of crystals, the attention of investigators has been drawn to a number of facts which seem to call for the existence within the crystal of a secondary structure, coarser than the atomic lattice, but still minute in comparison with the size of crystals as usually examined. The fact that the intensity of the reflection of X-rays from crystals is in general greater than would be expected from perfect planes led to the conclusion [1] that most crystals are made up of small blocks, each block being a perfect crystal, but neighbouring blocks being tilted slightly towards one another. These blocks cannot be more than a few thousand atomic planes in thickness.[2] They need not be regularly spaced.

Arising out of the work of Griffith,[3] which however related to non-metallic materials, an extensive field of investigation has been opened up, dealing with the discrepancies found between the cohesive strength of solids as calculated from fundamental data and the observed strengths. Griffith showed that the discrepancies could be accounted for if such substances as glass and vitreous silica contained cracks of which the spacing is of the order of 10^4 times the atomic spacing. The reasoning is not strictly applicable to metals, as the cohesive forces cannot be calculated from electrostatic theory, but the facts point to a spacing of a similar order. Smekal [4] has distinguished between two classes of properties common to solids, of which the first are nearly the same for single crystals and for aggregates, and are little affected by small quantities of impurities, whilst the second are profoundly influenced by these factors. The "structure-insensitive" properties include the content of thermal and chemical energy, the modulus of elasticity, the expansibility on heating, and the X-ray parameters. The "structure-sensitive" properties include the elastic limit, breaking stress, electrical and thermal conductivity, and properties depending on diffusion. These peculiarities are most easily

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[1] G. C. Darwin, *Phil. Mag.*, 1914, [vi], **27**, 315, 675; 1922, [vi], **43**, 800.

[2] R. W. James, *Z. Krist.*, 1934, **89**, 295.

[3] A. A. Griffith, *Phil. Trans.*, 1920, **221**, A, 163.

[4] A. Smekal, *Physikal. Z.*, 1926, **27**, 837; *Z. Physik*, 1929, **55**, 289, and many later papers.

accounted for by supposing that solids contain cracks or loosened regions with a spacing of the order indicated above.

Metallographic observations point in the same direction. In the process of mechanical deformation (see Chap. XVI) all the parallel planes in a perfect crystal may be supposed to be similar, and slip should occur as freely on one as on another, but in fact a crystal is deformed in blocks, on planes separated from one another by many thousands of atomic distances, and in any given metal the average spacing is about the same under similar conditions of stress, temperature, and time. So, also, the attack of a chemical reagent on the surface of a crystal is not uniform, but is local, producing etch-figures, and it has been found in some instances that indications of a definite unit may be traced, as of a triangular mesh of 1·4 μ on the cleavage planes of bismuth,[1] of a cubic unit of 0·25 μ in α-iron,[2] of steps 2 μ apart on the dodecahedral faces of tin,[3] etc.

The literature of the subject is very extensive.[4] Many attempts have been made to prove that such a mosaic structure must arise in the formation of a crystal, and even that a mosaic crystal is more stable than a perfect crystal,[5] but none of the theoretical derivations of a secondary or mosaic structure are satisfactory.[6] It may be accepted that the properties of metallic crystals are such as to make it probable that there exists some kind of rough periodicity, of a coarser order than the units of the atomic lattice, and the possibility of several such periods, standing to one another in an approximately harmonic relation, should not be excluded.

A secondary structure, which is not necessarily periodic, may be accounted for by the nature of the processes of growth of crystals.[7] The tendency of metals to grow as dendrites has already been mentioned. If the branches of the dendrite were strictly parallel to definite crystal planes, the repeated branching would fill up the gaps between them, and when complete there would be nothing left to indicate the course of growth. It is more likely, however, that some slight divergences will be found. Minute variations in conditions during growth, or local distortion caused by foreign atoms in solid solution, will cause the branches to become inclined to one another, however slightly. Buerger has called these branches "lineages," so that a crystal is in general made up of a number of lineages originating from the nucleus. A rough two-dimensional sketch is shown in Fig. 102. The pattern of the lineages is often made evident by traces of impurities, which accumulate between the branches, in the

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[1] A. Goetz, *Proc. Nat. Acad. Sci.*, 1930, **16**, 99.

[2] N. T. Belaiew, *Proc. Roy. Soc.*, 1925, **108**, A, 295.

[3] Desch, "Chemistry of Solids," p. 80.

[4] See "The Solid State of Matter," being vol. ii of the *Proceedings of the Internat. Conf. on Physics*, London, 1935, containing the views of Smekal, Goetz, Ewald, Joffe, Orowan, Burgers, Bragg, and others, with discussion.

[5] F. Zwicky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 816; 1931, **17**, 524.

[6] E. Orowan, *Z. Physik*, 1932, **79**, 573; *Z. Krist.*, 1934, **89**, 327

[7] M. J. Buerger, *ibid.*, 1934, **89**, A, 195.

last portions to solidify. For this reason a structure is usually to be seen on etching a single crystal, even of relatively high purity. Plate XA shows a single crystal of tin, containing only 0·01 per cent. of impurity, and the lineage structure is evident. Pure tin to which 0·004 per cent. of bismuth has been added gives a structure which is deceptively like a eutectic, although the quantity of foreign metal is far below the limit of solid solubility,[1] the apparent lines of the eutectic being the boundaries of lineages.

A perfect periodicity is not to be expected from such a structure, but it may well be that such a statistical regularity as would account for slip-bands and etch-figures may originate in this way. In addition to etching, the structure may frequently be detected on a cleavage face of a crystal, when this is illuminated very obliquely, rounded elevations becoming visible. Buerger has obtained this effect with many kinds of crystals, ionic as well as metallic, a particularly beautiful example being the surface of a crystal of spectroscopically pure zinc, grown from vapour.[2] It is probable that many of the phenomena, to explain which a mosaic or secondary structure has been invoked, may be accounted for by the existence of lineages, with the advantage that no new hypothesis as to the stability of crystal lattices, perfect or imperfect, is required.

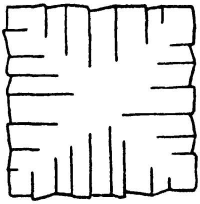

FIG. 102.—Lineages.

An application of the crack theory of Griffith to the problem of the deformation of metals is discussed later (Chapter XVII).

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[1] C. W. Mason and W. D. Forgeng, *Metals and Alloys*, 1935, **6**, 87.
[2] *Loc. cit.*, Fig. 17.

CHAPTER XII.

UNDERCOOLING AND THE METASTABLE AND LABILE STATES.

HITHERTO only systems in a state of stable equilibrium have been considered, the assumption being made that each new phase makes its appearance at the temperature at which it is theoretically formed. This condition is by no means always fulfilled in practice. Inertia often causes a body to remain in a condition differing from that of maximum stability, until some external circumstance causes rearrangement to take place. The simplest instance is the formation of the solid phase in a cooling homogeneous liquid. When pure water is cooled below its freezing-point in a clean vessel, ice does not separate when the temperature reaches 0°. On further cooling, a point is reached at which crystallization suddenly sets in, and the temperature rises rapidly to 0°, freezing then proceeding steadily. This fact was observed by Fahrenheit in the eighteenth century. Fused metals behave in the same way, and the phenomenon is a general one, the terms *undercooling* or *superfusion* being applied to it.[1]

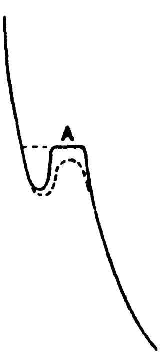

FIG. 103.—Effect of undercooling on cooling curve.

The effect is shown in the cooling curve, which assumes the form shown in Fig. 103, the normal curve, in the absence of undercooling, being indicated by the dotted straight line. When the undercooling is considerable, and the mass is losing heat rapidly to its environment, the latent heat liberated may be insufficient to raise the temperature to the true freezing-point A, and the summit of the curve will therefore indicate too low a freezing-point. For this reason, undercooling is to be avoided in the taking of cooling curves.

In the operation of cupelling gold, the globule of molten gold under certain conditions emits a brilliant light at the moment of solidification. The development of heat at this point was at first[2] attributed to a chemical reaction between dissolved oxygen and metals present as impurities. A careful study of this "flashing"

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[1] The term "undercooling" (Germ. *Unterkühlung*) will be employed in what follows, since, as will be shown, the phenomenon occurs at other changes of state besides that of freezing, to which alone the term "superfusion" Fr. *surfusion*) is applicable.

[2] A. Levol, *Ann. Chim. Phys.*, 1845, [iii], **15**, 55.

or "éclair," proved, however, that the phenomenon is due to undercooling.[1] The gold must be in a clean state to show the effect, and must not be shaken during cooling. Its temperature falls below the freezing-point until crystallization sets in, and the development of heat causes the glow. If the globule is touched with a gold wire when it has cooled to the freezing-point, freezing takes place normally without any flashing.

Soon after the first observation of undercooling by Fahrenheit, it was observed [2] that saturated salt solutions behave in a similar manner, it being possible to cool them below the point at which crystallization should take place, the separation of crystals setting in suddenly when further cooled, the temperature at the same time rising to the crystallizing point. What has been said of pure substances therefore also applies to the separation of one component from a mixture. Solutions cooled in this way below their proper crystallizing points are said to be supersaturated, and the sudden crystallization of a supersaturated solution of sodium thiosulphate in water is a common lecture experiment.

If the viscosity of the liquid is high, the undercooling may be carried very far. Many organic substances—for instance, papaverine—become very viscous in the undercooled state, and on reaching the ordinary temperature consist of a glassy mass, which may be preserved indefinitely without crystallization taking place. Ordinary glasses are mixtures, chiefly of silicates, the viscosity of which in the undercooled state is so great that crystallization entirely fails to occur during cooling in the ordinary process of manufacture. If subsequently treated in such a way as to facilitate crystallization, as by prolonged heating at a temperature sufficient to lessen the viscosity to a marked degree, "devitrification" takes place, crystals corresponding with the stable solid phases making their appearance. Glassy volcanic rocks, such as obsidian, are also formed from an undercooled magma, and all stages of their devitrification are found in nature.

The formation of glasses, that is, of rigid non-crystalline masses, by undercooling, has not been observed in metals or alloys, the viscosity of which is in fact low, being comparable with that of water.[3] In the cooling of an alloy, the formation of a crystalline phase always takes place, although the temperature may be considerably below that corresponding with the true freezing-point.

Investigations of undercooled liquids have shown that the region

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[1] A. D. van Riemsdyk, *Ann. Chim. Phys.*, 1880, [v], **20**, 66; *Chem. News*, 1880, **41**, 126, 266.

[2] J. T. Lowitz, *Crell's chem. Ann.*, 1795, **1**, 3. A full history of the subject of undercooling and supersaturation is given by W. Ostwald, *Lehrb.*, II., 2, i, 704 ff. Accurate measurements of the extent of undercooling in various metals and alloys were made by W. C. Roberts-Austen, *Proc. Roy. Soc.*, 1898, **63**, 447.

[3] It is a familiar fact that metals, even of high melting-point, form mobile liquids, which may be poured like water if free from dross.

below the solubility curve should be divided into two parts. In the first, immediately below the curve representing the equilibrium of the solid and liquid phases, crystallization does not take place spontaneously, but only when a crystal of the solid substance (or of a solid isomorphous with it) is introduced. At a lower temperature, crystallization begins spontaneously, shaking or other mechanical disturbance being sufficient to initiate it. On the suggestion of Ostwald, these regions have been termed *metastable* and *labile* respectively. It was long a matter of doubt whether there was any true boundary between the metastable and labile regions, it having been argued that the apparent existence of a region in which crystallization would not occur spontaneously was only due to the small number of crystal centres, corresponding with a small undercooling.[1] This has been disproved by the exhaustive investigations of Miers and his collaborators.[2] It has now been shown that spontaneous crystallization, that is, the appearance of the solid phase without the previous introduction of a particle of the solid (" inoculation ") does not take place above a certain definite temperature, which is characteristic of each substance. The same holds good of mixtures. Below the solubility curve, and approximately parallel with it, lies a curve representing the temperature at which each solution begins to deposit crystals spontaneously, without inoculation with a crystal. To this curve the name of *supersolubility curve* has been given.

Most supersolubility measurements have been made with aqueous solutions of salts. The mixtures of two organic substances, betol and salol, have been fully investigated,[3] and the diagram constructed from the data thus obtained is typical of the conditions which must prevail in alloys. The diagram is reproduced (Fig. 104). The two compounds form a simple eutectiferous series. The freezing-point curve consists of two branches, AC and BC, intersecting at the eutectic point C. The two supersolubility curves, DF and EF, also intersect at a point, F, to which the name *hypertectic point* has been given. It will be noticed that the abscissæ of these two points are not necessarily the same, so that the eutectic and hypertectic mixtures need not have the same composition.

The area ACBEFD is the metastable region. Mixtures represented by points falling within its limits are liquid, and only deposit crystals if the appropriate solid phase is introduced. Below the line DFE is the labile region, in which crystallization can occur spontaneously, although it may sometimes fail to occur when either of the supersolubility curves is crossed. The significance of the four curves may now be illustrated by the consideration of a few possibilities.

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[1] G. Tammann, *Z. physikal. Chem.*, 1898, **25**, 442.

[2] H. A. Miers and F. Isaac, *Trans. Chem. Soc.*, 1906, **89**, 413 ; H. Hartley and N. G. Thomas, *ibid.*, 1906, **89**, 1013 ; H. Hartley, B. M. Jones, and G. A. Hutchinson, *ibid.*, 1908, **93**, 825.

[3] H. A. Miers and F. Isaac, *Proc. Roy. Soc.*, 1907, **79**, A, 322 ; F. Isaac, *ibid.*, 1910, **81**, A, 344.

A mixture represented by the point *o* is cooled, the access of solid matter being prevented. When the point *p* is reached, the solid phase being absent, crystallization does not take place, and the mixture remains liquid until the temperature has fallen to *q*. The supersolubility curve of betol, or more generally of the substance M, has now been cut, and crystallization takes place spontaneously if the mixture is shaken. The composition of the part remaining liquid is now represented by a point travelling down DF, until F, the hypertectic point, is reached. This being the point of intersection with the second supersolubility curve, the second solid, N, begins to separate and the whole of the mother-liquor solidifies at the constant temperature of the point F.

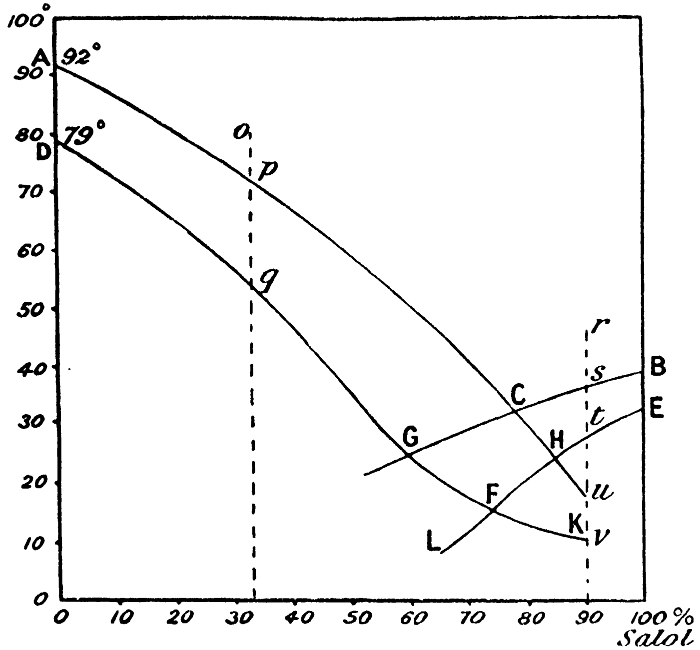

FIG. 104.—Betol and salol.

Taking the same mixture *o*, we may now assume that on reaching the temperature *p*, a crystal of M is introduced. This crystal grows, and the point representing the composition of the liquid moves along *p*C. When the eutectic point C is reached, however, the eutectic mixture does not solidify as a whole, as it is metastable as regards the substance N, the separation of M therefore continues in the direction CH. The temperature then falls until the curve EF is cut, crystallization of N begins, and continues until the hypertectic point is reached. The curve BC may similarly be prolonged into the metastable region, as shown by CG.

In the absence of mechanical disturbance, mixtures may even be cooled below the temperatures indicated by the curves DF and EF without crystallizing. Thus the mixture *o* may be cooled, under favourable conditions, below *q*, but crystallization is sure to begin before the undercooling has proceeded very far into the labile region, unless prevented by increasing viscosity. The heat developed causes the temperature to rise to *q*, and freezing then proceeds. Under similar conditions, however, the phase N may also fail to appear when F is reached, so that the labile prolongation FK may be experimentally realized. The curve EF may be similarly prolonged as at FL.

The formation of crystals on the upper curves takes place with comparative slowness, and the temperature may therefore fall low enough for the supersolubility curve to be intersected before the separation of solid is complete. In that case a further crystallization of the same solid phase, but now proceeding rapidly from a large number of centres, may take place. Miers and Isaac found it easy to distinguish by inspection alone the crystals formed in the metastable region from the shower deposited on reaching the supersolubility curve.

It is clear from this description that the eutectic point C may entirely fail to appear on the cooling curve of a mixture. In one case, that of a mixture containing 90 per cent. salol and 10 per cent. betol, Miers and Isaac were even able to observe four freezing-points, none of which was the eutectic point. Representing such a mixture by *r*, the upper salol curve is crossed at *s*, at which point salol crystals may be obtained by inoculation. Crystals of betol are obtained at *u* by inoculation with that compound, whilst labile showers of the two components may be obtained spontaneously by cooling to *t* and *v* respectively.

When one or more of the components is capable of existing in polymorphic forms, the conditions become yet more complicated, since a metastable modification may crystallize from the liquid. This has been observed in mixtures of naphthalene and chloroacetic acid, the latter of which may crystallize in three modifications, each of which has its own supersolubility curve.[1]

The high thermal conductivity of metals in comparison with that of organic compounds introduces an important difference, but it has been possible to apply the principle to a few metallic systems. A good example is that of the alloys of aluminium and silicon, which are largely used on account of their good casting qualities. The alloys form a simple eutectiferous series with very limited solid solubility, the eutectic point being at 11·6 per cent. Si and 577°.[2] The silicon, however, forms large crystals, and the alloys are brittle. On adding to the liquid metal a small quantity of a "modifying

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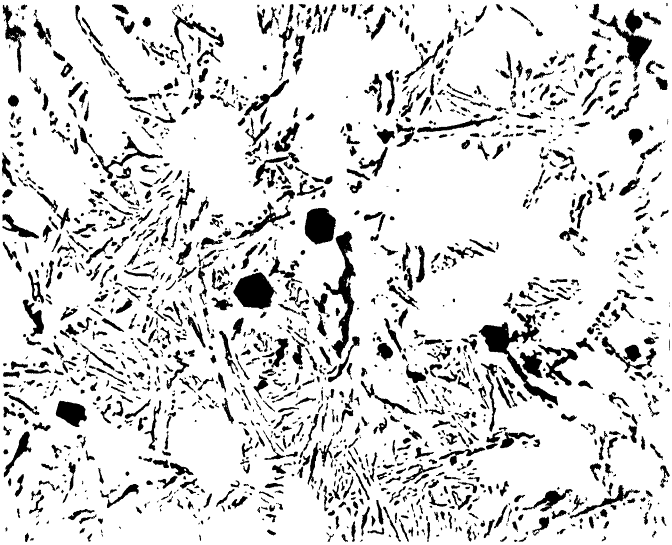
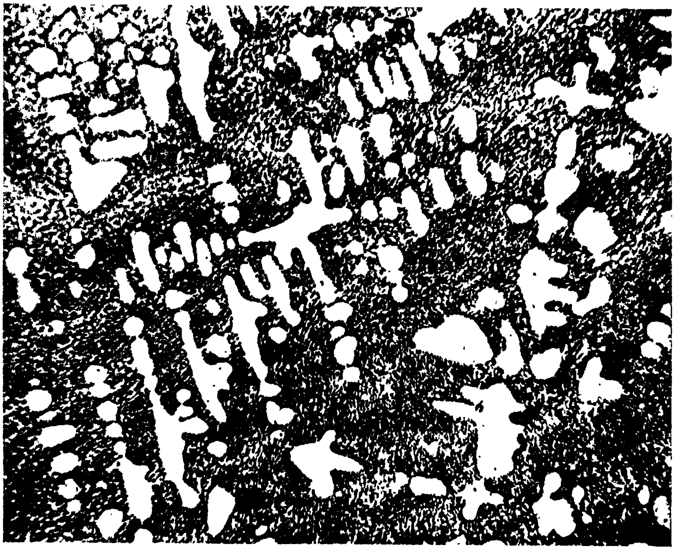
[1] H. A. Miers and F. Isaac, *Phil. Trans.*, 1909, **209**, A, 337.

[2] J. D. Edwards, *Chem. Met. Eng.*, 1923, **28**, 165; A. G. C. Gwyer and H. W. L. Phillips, *J. Inst. Metals*, 1926, **36**, 283.



A. Aluminium-silicon alloy. Unmodified. × 350



B. Aluminium-silicon alloy. Modified. × 350

PLATE XI

agent" (for instance, 0·1 per cent. or less of sodium, or larger quantities of certain alkali salts), the structure is completely changed, and the castings obtained are tough. The same solid phases are present, as is confirmed by X-ray methods,[1] but the crystals are fine, the difference being shown in Plate XI. It was a suggestive fact that the eutectic freezing-point (but not the melting-point) of the modified alloys was found to be lower than that of the normal alloys, and that the eutectic composition was evidently shifted towards the silicon end of the system.

Modification has been explained in various ways. It has been regarded as the introduction of a protective colloid, which causes the crystals to remain very fine, the eutectic in some castings needing a high magnification to resolve it, but the quantity of foreign matter introduced seems insufficient for the purpose. Drastic quenching, however, will produce the fine structure, although with slight differences in texture, and this fact, together with the thermal results, suggests that undercooling is responsible. The alloys in the normal condition, with a definite rate of chilling, give thermal arrests which seem to represent points on the supersolubility curve.[2] The hypertectic point is at 12·9 per cent. Si and 564°. On the other hand, the modified alloys show little undercooling, and the solubility curves appear to coincide with the supersolubility curves of the normal alloys. With highly purified materials, the modified structure can only be obtained with very drastic chilling, by pouring into a massive copper mould. The analogy with the systems described by Miers, although not completely proved, is suggestive.

A second example is the formation of the eutectoid, pearlite, in steel, by the breaking-up of a solid solution, austenite (see p. 349). The curves representing the deposition of ferrite and of cementite from austenite intersect at the eutectoid point at about 700° and 0·81 per cent. of carbon (Fig. 141, p. 346). Some degree of undercooling is necessary, and the texture of the pearlite, that is, the spacing of the alternating lamellæ of ferrite and cementite, may be linked up with its amount.[3] The actual determination of the supersolubility curve was attempted, but more recent work on the highly undercooled decomposition of austenite to form martensite (p. 357) has altered the situation, and the conditions need re-examination.

The prolongation of a freezing-point curve into the metastable region, as at CG, Fig. 104, is very frequently observed. The effect on the cooling curve is to cause the eutectic arrest to come too late. To prevent this undercooling of the eutectic the liquid is inoculated with the second component, N, when the temperature corresponding with C is reached. The effect on the microscopic structure is to cause the crystals of M to occupy too large an area, the area of eutectic being correspondingly lessened. Undercooling may even proceed

[1] H. Kotô, *Mem. Coll. Sci. Kyoto*, 1935, 18, A, 17.
[2] M. L. V. Gayler, *J. Inst. Metals*, 1927, 38, 157.
[3] A. F. Hallimond, *J. Iron Steel Inst.*, 1922, i, 359.

so far that the eutectic structure is absent from the section of the solidified alloy, especially when the constituent which crystallizes first is in large excess. As an example, the solutions of cuprous oxide in copper, which behave as true alloys, may be taken. The freezing-point curve, up to 9 per cent. Cu_2O, is shown in Fig. 105.[1] When the copper is in excess of the eutectic proportion, the freezing usually takes place normally, and the sections obtained show areas of copper and of the Cu—Cu_2O eutectic.[2] The case is different, however, when the mixture is richer in oxygen, so that crystallization begins on the second branch of the curve. If slowly cooled, the crystals of Cu_2O continue to grow after the eutectic point is reached, and this process continues until nearly all the oxide has been removed from the liquid alloy. At this point the supersolubility curve of copper is probably intersected, and practically pure copper solidifies around the skeletons of oxide.

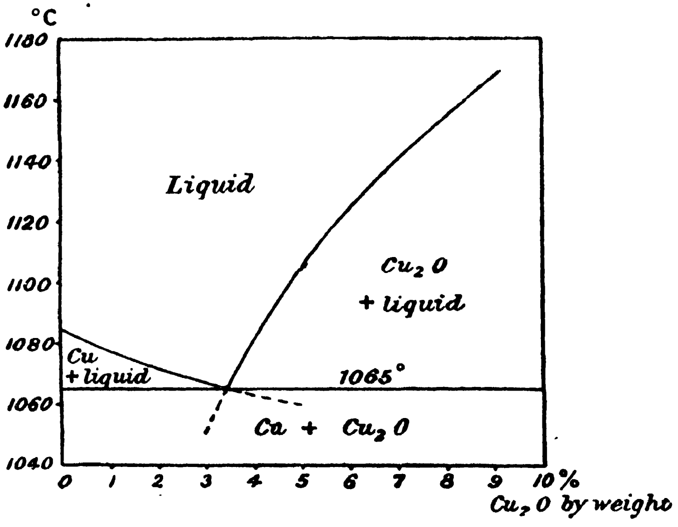


FIG. 105.—Copper and cuprous oxide.

An effect which is seen in the microscopic sections of many alloys has often been attributed to the same cause. This is the appearance of a band of the constituent N surrounding the crystals of M which had originally solidified, and separating them from the banded areas of eutectic. This is particularly well seen in alloys of copper with cuprous phosphide, and of copper with silver, containing copper in excess of the eutectic proportion.[3] The envelope is due to segregation

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[1] E. Heyn, *Z. anorg. Chem.*, 1904, **39**, 1.

[2] Giraud, *Rev. Métall.*, 1905, **2**, 297.

[3] A. K. Huntington and C. H. Desch, *Trans. Faraday Soc.*, 1908, **4**, 51. A similar band is seen surrounding the skeletons of iron in iron-phosphorus

at the moment of solidification of the eutectic. This continues until a layer of the second constituent has been formed, completely coating the skeletons, and the eutectic is then free to assume the banded structure, with a general parallelism determined by the previous orientation. Later experiments confirmed this view, and showed that the envelope is not due to undercooling.[1]

The occurrence of undercooling may result in an entire alteration of the form of the freezing-point curve of a system of alloys. Such a condition has been observed in the alloys of antimony and cadmium.[2] In the diagram, Fig. 106, the full curve corresponds with the condition of stable equilibrium, and is only obtained after inoculation with crystals of the compound CdSb, the dotted curve representing a metastable condition realized in alloys cooled without stirring or inoculation. The stable curve has a maximum at 50 atomic per

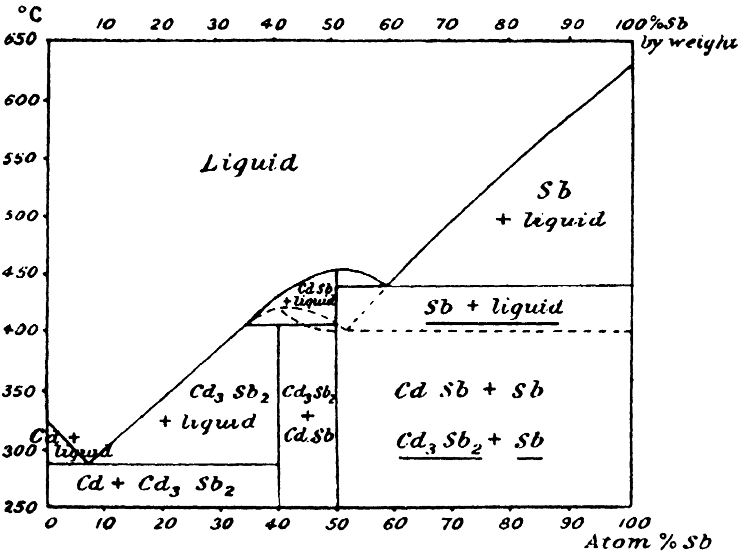

FIG. 106.—Cadmium and antimony.

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alloys, but not in those richer in phosphorus, in which the primary crystals are isolated rhombs of Fe_2P (J. E. Stead, *J. Iron Steel Inst.*, 1900, ii, 60). Segregated bands also surround the crystals of copper in alloys of copper and silver, as is seen in Plate IIIA.

[1] F. E. E. Lamplough and J. T. Scott, *Proc. Roy. Soc.*, 1914, **90**, A, 600.

[2] W. Treitschke, *Z. anorg. Chem.*, 1906, **50**, 217; N. S. Kurnakow and N. S. Konstantinow, *ibid.*, 1908, **58**, 1. The diagram was not completed by these observers, and X-ray and other evidence shows that both the stable and the metastable compounds form solid solutions over a small range, whilst the two freezing-point curves do not quite coincide (T. Murakami and T. Shinagawa, *Kinzoku no Kenkyu*, 1928, **5**, 283; F. Halla and J. Adler, *Z. anorg. Chem.*, 1929, **185**, 184). The approximate diagram shows the essential facts.

cent. Sb, with a eutectic point, CdSb-Sb, at 58·4 atomic per cent. Sb. In the absence of inoculation, however, the curve corresponding with the separation of free antimony is prolonged downwards, and when separation of a second solid phase does take place, it is not the stable compound, CdSb, that crystallizes, but the metastable compound, Cd_3Sb_2, which has its own solubility curve, with a maximum at 40 atomic per cent. Sb and 423°, 32° lower than the maximum on the stable curve. This is in accordance with the general rule that metastable modifications melt (or freeze) at a lower temperature than stable modifications.

Consider now an alloy containing 53 atomic per cent. Sb. If slowly cooled and inoculated it deposits crystals of CdSb, and shows a eutectic point at 445°. If cooled without inoculation, crystallization does not set in until later, when antimony separates, and there is a eutectic arrest at 402°, corresponding with the simultaneous separation of Sb and Cd_3Sb_2. On further cooling, the reaction

$$Cd_3Sb_2 + Sb = 3CdSb$$

occurs with considerable development of heat, and the solid alloy passes, more or less completely, into the stable condition. To the left of the vertical line at 50 atomic per cent. Sb, the compound Cd_3Sb_2 appears to be stable at low temperatures, although this is not quite certain. The development of heat is observed in metastable alloys, containing between 40 and 50 atomic per cent. Sb, owing to the transformation of their excess Cd_3Sb_2. To the left of the line at 40 atomic per cent. Sb, again, Cd_3Sb_2 is alone stable.

Peritectic reactions are particularly liable to undercooling, as one of the reacting substances is solid as well as the product so that the velocity of the reaction is limited by the solution and re-deposition of the solid phase, or by the velocity of diffusion in the solid solution. Both of these processes are slow in comparison with that of crystallization. Very slow cooling and thorough agitation are therefore necessary if the reaction is to proceed to completion.

The possibility of undercooling is not confined to the passage from the liquid to the solid state, but is also associated with the physical and chemical changes after solidification. A typical example is that of a solid solution breaking up into two constituents when cooled to a certain temperature. It has been mentioned on p. 42 that iron containing 0·81 per cent. of carbon is, at temperatures above 700°, a homogeneous solid solution. At 690° this solution resolves itself into a conglomerate, or eutectoid, of iron and iron carbide, Fe_3C, the process of resolution being completed at constant temperature under conditions favouring equilibrium. In the ordinary cooling of a bar of steel, as an iron-carbon alloy of such a composition is called, the temperature falls below that at which the change should take place, then rises to 690°, and continues at that temperature, the course of events bearing a complete resemblance to that already described in the freezing of an undercooled liquid. The amount of heat developed by the transformation is large, and when a bar of steel of the stated composition is cooled in air, the rise of temperature due to the change is sufficient to cause a visible brightening of the red glow emitted by the metal, if observed in a darkened room. The phenomenon, which was first observed by Barrett,[1] is due to the breaking up of the solid solution, austenite, into a mechanical mixture of pure iron (ferrite) and iron carbide (cementite). It has received the name of "recalescence," and the term has since been applied more generally to those developments of heat which occur during the cooling of many solid alloys. Very marked instances are observed in the ternary alloys used as fusible metals, which often show a sudden rapid rise of temperature during cooling, accompanied by a change of volume sufficient to cause the alloy to fly to pieces.[2]

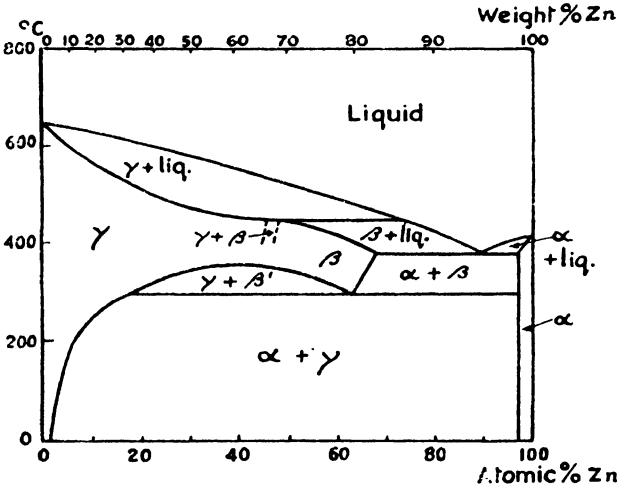

FIG. 107.—Aluminium and zinc.

A striking instance of the occurrence of a change in an undercooled solid solution is that of the decomposition of the β phase in the alloys of aluminium and zinc. The equilibrium diagram is given in Fig. 107.[3] At 256° the β phase breaks up into a eutectoid of α and γ. Previously polished specimens of an alloy containing 77 per cent. of zinc

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[1] W. F. Barrett, *Phil. Mag.*, 1873, [iv], **46**, 472. The momentary elongation of a stretched steel wire on cooling to this temperature was observed by G. Gore, *Proc. Roy. Soc.*, 1869, **17**, 260, and it was while investigating this volume change that Barrett observed the glow. The effect is easily shown as a lecture experiment.

[2] Erman, *Ann. Physik*, 1827, [ii], **9**, 557; R. Warington, *Mem. Chem. Soc. Lond.*, 1843, **1**, 77; Person, *Compt. rend.*, 1847, **25**, 444; W. Spring, *Ann. Chim. Phys.*, 1876, [v], **7**, 178.

[3] D. Hanson and M. L. V. Gayler, *J. Inst. Metals*, 1922, **27**, 267; modified on the side of solid solubility by W. Fraenkel and E. Scheuer, *Z. Metallk.*, 1922, **14**, 49; W. L. Fink and K. R. Van Horn, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 132; E. A. Owen and L. Pickup, *Phil. Mag.*, 1935, [vii], **20**, 761.

were heated to 370° and quenched in ice-water. On leaving the specimens untouched, a spontaneous rise of temperature of as much as 50° was noticed, whilst on repolishing and examining after intervals of a few minutes the gradual development of the eutectoid structure could be seen.[1] The transformation started from nuclei, so that dark spots first appeared on etching, gradually running together until a dark etching structure, too fine to be resolved, covered the whole surface. A calorimetric study showed the reaction to be unimolecular.[2]

The process of "quenching," so often applied to alloys both in metallographic investigations and in technical practice, consists in cooling a solid alloy through a critical range so rapidly that the transformation which takes place on slow cooling is either entirely or partly suppressed, so that a phase which is stable only at some higher temperature is retained in the cooled alloy in a metastable or labile condition. To take an instance of the technical application first, the well-known hardening of steel by quenching depends on the suppression of the recalescence point by rapid cooling through the critical range. The transformation of the solid solution of carbon in iron, which exists at high temperatures, into a mechanical mixture of pure iron and iron carbide, is thus hindered. This checked transformation results in a hard product the nature of which is discussed in Chapter XXI. Here it is enough to say that the metastable structure, whatever its true nature may be, is much harder than the stable alloy. Many copper alloys, especially those containing certain proportions of zinc, tin, or aluminium, may also be hardened by quenching, although not to so great an extent as steel.

Quenching is resorted to in metallographic researches as a means of investigating the nature of the phases existing at high temperatures.

In technical and ordinary laboratory practice, the metal or alloy is heated to the required temperature in a muffle or electric furnace and held long enough to reach equilibrium. It is then seized with heated tongs, and rapidly plunged into cold water. As a method of research, such a procedure is quite insufficient. Cooling to an unknown and inestimable extent takes place during the opening of the furnace and the transfer of the specimen, so that the actual temperature of quenching is quite unknown. Better results are obtained by heating the specimen in a bath of fused salts, such as the alkali chlorides, borates, or silicates, or mixtures of these. Hardening furnaces of this type are in use for technical purposes. On removing the specimen, a film of salt, of low conducting power, remains adherent to the metal, and hinders the fall of temperature during the transfer to the cooling bath. This plan was adopted by Le Chatelier in his researches on the quenching of tool steel.[3] Benedicks, in a thorough investigation of the quenching process,[4] used a horizontal electric furnace having a longitudinal slot in the under side for one-half of

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[1] Hanson and Gayler, *loc. cit.*

[2] W. Fraenkel and W. Goez, *Z. anorg. Chem.*, 1925, **17**, 12.

[3] *Rev. Métall.*, 1904, **1**, 184.

[4] *J. Iron Steel Inst.*, 1908, ii, 152.

its length. The specimen, with a thermo-couple attached, was mounted on a pivoted arm. During heating it occupied the centre of the furnace, and when the quenching temperature was reached, the arm was released electrically and swung by a spring through a quarter-circle, passing through the slot and carrying the specimen downwards into the quenching vessel. This arrangement provides for a very rapid transfer of the specimen.

In ordinary practice small specimens may be quenched satisfactorily by employing a tube extending beyond the limits of the horizontal furnace, and provided with a T-piece directed downwards. The object is rapidly drawn by a platinum or nichrome wire, or pushed by a quartz or porcelain rod along the tube, until it falls into the quenching liquid through the T-piece. As the tube may be closed with stoppers at both ends, the wire passing through a fine perforation, it is possible to work in an indifferent atmosphere. The specimen may also be suspended in a vertical furnace, and quickly dropped into the quenching liquid. Wires, such as are convenient for X-ray or electrical conductivity determinations, may be enclosed in thin closely-fitting sealed glass tubes for temperatures up to 550°, and withdrawn and plunged into water. The tube breaks at once, and does not delay the quenching.

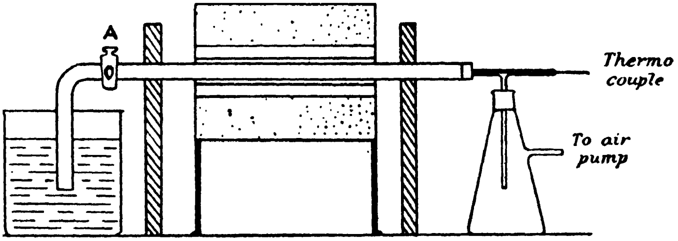

FIG. 108.—Rosenhain's quenching apparatus.

Instead of removing the specimen from the furnace and transferring it to the cooling bath, we may admit the quenching liquid to the heated space. This method has been adopted by Rosenhain,[1] whose apparatus is illustrated diagrammatically in Fig. 108. A wide silica tube passes through a horizontal resistance furnace, and is fitted at one end with a large tap, A, and an arm bent at right angles. The other end is connected with a suction flask by means of a T-piece, through which the thermo-couple passes. The specimen, previously polished if necessary, is placed in the silica tube, and the stopcock is closed. The bent arm dips into a vessel of water. When heating begins, the flask and tube are exhausted by means of a Fleuss pump. When the pyrometer indicates that the desired temperature, which should not exceed 600°, has been reached, the stopcock A is suddenly opened, when water rushes in to fill the exhausted space. The silica

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[1] *J. Iron Steel Inst.*, 1908, i, 87.

tube withstands the sudden cooling, and the specimen is driven by the inrush of water to the farther end of the tube, where it is cooled very rapidly. Quenching takes place quietly, without explosive violence, and all exposure to the atmosphere is avoided, so that the surface of the alloy is perfectly protected from oxidation.

The taking of a cooling curve during quenching is difficult. It was first attempted by Le Chatelier,[1] and later by Benedicks (*loc. cit.*). The galvanometer employed by Le Chatelier was insufficiently sensitive, and a great improvement was introduced by Benedicks, who used a sensitive string galvanometer of high resistance. In this form of instrument [2] a silvered quartz fibre carries the current to be measured and is placed in a strong magnetic field and its lateral displacement magnified by means of a mirror, and recorded photographically. The resistance of such an instrument is so high that its readings are quite independent of changes in the resistance of the thermo-couple, and it responds with great rapidity to changes of temperature.

Liquids differ in their cooling effect, and this is taken advantage of in hardening steel, water being used for rapid quenching and oil for a more gradual quenching. It was formerly thought that the thermal conductivity was the determining factor, but a little consideration will show that much turbulence must be produced on plunging a heated mass of metal into a liquid, so that the effect of conduction will be small compared with that of convection. Benedicks (*loc. cit.*) and others have laid stress on the influence of viscosity and of the latent heat of vaporization, as it is known that a layer of vapour forms around the metal at an early stage, later collapsing and again allowing contact with the liquid. When a mass of simple form is taken, such as a sphere or a cylinder, and its temperature is recorded by a thermo-couple, a typical curve is of the form shown in Fig. 109. The initial gradual fall occurs while the specimen is surrounded by vapour, the second, steep, portion corresponds with the collapse of this layer, and the last, gently sloping portion represents the final exchange of heat.

Observations in which copper spheres at 800° were lowered into the liquid and photographs taken of the region surrounding the sphere,[3] showed that in liquids of low viscosity the turbulence is great, and exchange of heat takes place readily, but that in more viscous liquids the region of turbulence is confined to a narrow zone, and in a very viscous oil only streamline flow, in a layer surrounding the layer of vapour, occurs. Calculations of the quantity of vapour formed showed that the latent heat of volatilization only plays a very small part, by far the greater part of the vapour condensing again and giving up its heat. Distilled water is much " milder " in its action than tap water, whilst the addition of 0·2 per cent. of sodium chloride

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[1] *Rev. Métall.*, 1904, **1**, 473.

[2] M. Edelmann, jun., *Physikal. Z.*, 1906, **7**, 115.

[3] K. G. Speith, *Mitt. K.W. Inst. Eisenforsch.*, 1935, **17**, 175.

hastens the cooling, the effect being greatest on distilled water. The action of salts appears to consist not in altering the viscosity, conductivity, or latent heat, but rather in influencing the duration of existence of a jacket of vapour (Leidenfrost phenomenon). This is probably the ground for the traditional belief among steel tool hardeners that some waters are better than others for quenching. In oil, some formation of permanent gas by chemical decomposition usually occurs. A 6 to 7 per cent. solution of pectin (colloidal organic material extracted from fruits) has been used to give a quenching effect similar to that of oil, although its viscosity hardly differs from that of water, but it has the disadvantage of chemical instability.

In Fig. 109 curves are shown representing the fall in temperature at the centre of a silver sphere, 2 cm. diameter, quenched from 800° in distilled water at 20° and at 60°, and in tap water and in oil at 20°.

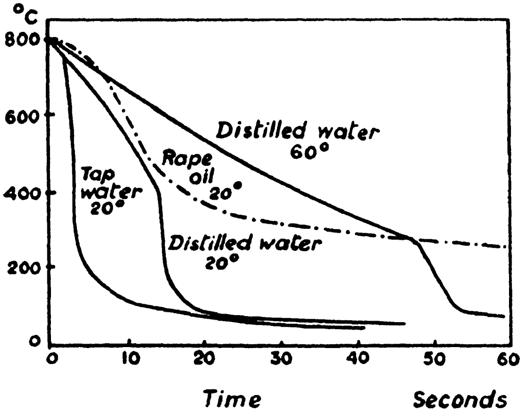

FIG. 109.—Temperature changes during quenching (Speith).

A liquid such as oil may be used for quenching in place of water for two reasons: either in order to retard a phase change without suppressing it completely, or with the object of avoiding the severe thermal stresses which may be set up and are the cause of quenching cracks in tool steels and other hard materials.

A difficulty in determining the changes which occur during quenching arises from the fact, already noticed by Benedicks, that contact with the cooling liquid forms a jacket of vapour which acts for a time as a heat insulator. On the collapse of this jacket the rate of cooling is again quickened, and in this way false arrests may be observed. The difficulty may be overcome by using a blast of a cold gas as the quenching agent. In a series of experiments on the quenching of steel, using a thread galvanometer,[1] the specimens to be quenched were discs, only 2 mm. diam. and 0·2 to 1·0 mm. thick, and the two wires of the thermo-couple were welded to the opposite

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[1] H. Esser and W. Eilender, *Arch. Eisenhüttenw.*, 1930, 4, 113.

faces. The wire-wound furnace was arranged for rapid heating, and a blast of compressed hydrogen was used for quenching, giving initial cooling rates up to several thousand degrees a second. In a parallel series of experiments,[1] using an electro-cardiograph in place of a thread galvanometer, the specimens were rods 0·25 mm. diam., again with the couple welded on. The electro-cardiograph gives a spot on the photographic paper used for recording, the lines so obtained being sharper than the shadows given by the thread. In a still further elaboration of the method,[2] the apparatus was so arranged that both thermal and magnetic records of the changes during quenching at these high rates could be made. When this system of quenching is used, with hydrogen under high pressure, the false arrests are completely eliminated, and a very simple form of cooling curve is obtained.

A dilatometer which is capable of recording mechanically the changes of length of a specimen during quenching has been described by Sato.[3] A comparison rod of some material similar in specific heat and density to the alloy under examination is used. It must have no transformation point within the range of temperature considered, and its known coefficient of expansion is used as a means of measuring the temperature. The two rods are so held as to actuate a pantagraph, by means of which an enlarged diagram is traced by a pencil on a flat sheet of paper. The rods are heated in an electric tube furnace, which can be rapidly withdrawn, and the apparatus rotated through a right angle so as to bring the specimens into the quenching liquid.

The phases retained by quenching are commonly spoken of as metastable, but, although experimental proof has not been produced, we are bound to assume that the metastable limit has been passed, and that the systems are correctly described as labile. Quenched specimens therefore tend spontaneously to assume an equilibrium condition by undergoing the transformation which was suppressed by quenching. How far the spontaneous change can proceed at ordinary temperatures will depend on the possibility of atomic interchange, a subject which is touched on in Chapter XX. White tin, which is only stable above 18°, does not change into grey tin at 0° unless brought into contact with the new phase. Below 0° the change may occur spontaneously, although even at low temperatures it may fail to occur when the tin is kept for long periods.[4] The maximum velocity of transformation is near — 45°.

Hardened steel is in the strict sense labile at the ordinary temperature ; the presence of the stable phase is not necessary to initiate change. But there is little evidence that softening of the steel takes

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[1] F. Wever and N. Engel, *Mitt. K.W. Inst. Eisenforsch.*, 1930, **12**, 93.

[2] H. Esser, W. Eilender and E. Spenle, *Arch. Eisenhüttenw.*, 1933, **6**, 389.

[3] S. Sato, *Sci. Rep. Tôhoku Univ.*, 1931, **20**, 260.

[4] E. Cohen and C. van Eyck, *Z. physikal. Chem.*, 1899, **30**, 601 ; E. Cohen, *ibid.*, 1900, **33**, 59 ; **35**, 588 ; 1901, **36**, 513.

place spontaneously unless the temperature is raised. Japanese swords of the fifteenth century, if carefully preserved, are found to be as hard at the edge as if newly hardened; it would therefore seem that no appreciable return to the stable state takes place in the course of several centuries at atmospheric temperatures. On the other hand, prolonged heating of hardened steel even to 100° produces an appreciable softening, and heating to 150°, in a few minutes. Some of the harder steels after quenching continue to generate heat spontaneously for several weeks at a diminishing rate.[1] This indicates a partial reversion to a more stable condition. A quenched steel heated to 98° in a steam-jacketed space shows a spontaneous rise of temperature, the maximum effect (0·55°) being obtained with a steel of 1·2 per cent. carbon.[2] The electrical resistance of hardened steels also undergoes small changes in the course of several years.[3]

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[1] C. F. Brush, *Proc. Amer. Phil. Soc.*, 1915, **54**, 154; C. F. Brush and R. A. Hadfield, *Proc. Roy. Soc.*, 1917, **93**, A, 188.

[2] H. Schottky, *Ferrum*, 1912-13, **10**, 274.

[3] L. C. Brant, *Phys. Rev.*, 1909, **29**, 485.

CHAPTER XIII.

DIFFUSION IN THE SOLID STATE.

THE possibility of diffusion in the solid state has already been assumed in previous chapters. Many facts known to the technical metallurgist, and many isolated laboratory observations, point to the existence of such a process, but the earliest systematic and quantitative investigation bearing on the question is that described in the Bakerian lecture of Roberts-Austen for 1896.[1] An example taken from this research will indicate the nature of the process.

An alloy of lead and gold containing 5 per cent. Au is pressed tightly against one end of a cylinder of pure lead, the two surfaces in contact being accurately plane, and the cylinder is then heated at 165° for thirty days, after which it is sawn into sections, and the gold is estimated in each section by the ordinary methods of assaying. Such a cylinder, 0·64 cm. high, placed vertically with the gold alloy downwards, gave the following figures on assaying:

No. of Section from Base.	Weight of Section.	Per Cent. Au	Diffusivity.
	grammes		
1	0·64	0·039	
2	2·33	0·030	0·005
3	2·02	0·015	

The number in the last column represents the diffusivity expressed in sq. cm. per day, calculated by means of Fick's theory of diffusion. The diffusion is still measurable at so low a temperature as 100°. At higher temperatures the process is much more rapid, so that gold is able to rise against gravity to a height of 7 cm. in lead at 250° in less than a month.

The experiments have since been repeated with greater precautions,

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[1] W. C. Roberts-Austen, *Phil. Trans.*, 1896, 187, A, 383. A summary and bibliography of the early work on diffusion in solids and glasses was given by the author, *Brit. Assoc. Rep.*, 1912, 348.

the values found at 150° and upwards being almost the same, but at 100° a higher result than that of Roberts-Austen was obtained.[1]

Temp.	*Diffusivity.*
197°	$6{\cdot}0 \times 10^{-3}$ sq. cm./day.
150°	$4{\cdot}3 \times 10^{-3}$,,
100°	$2{\cdot}0 \times 10^{-4}$,,

This system has the disadvantage that gold and lead form compounds with one another, so that it is better to consider first a system free from complications. Since the process of diffusion in a crystalline solid must consist in the movement of atoms through a lattice, the simplest possible condition is that of " self-diffusion " ; the migration of atoms in a solid composed only of atoms of the same kind as themselves by simple exchange of position. It might seem impossible to determine this, but Hevesy has ingeniously solved the problem by using atoms of a radioactive isotope of the metal being studied ; a plan equivalent to attaching labels to the atoms at the start of their journey for identification on arrival. In this way the diffusion of thorium B, a radioactive isotope of lead, through ordinary lead has been studied.[2] The interesting result was found that diffusion was more rapid the finer the grain of the lead, and that diffusion through a single crystal was imperceptible. Polonium, having a different atomic volume from lead, can diffuse even through a single crystal. A similar result has been obtained from experiments with metals of high melting-point. Tungsten and molybdenum can inter-diffuse readily in fine-grained aggregates,[3] but when molybdenum is deposited from a vapour on a single-crystal wire of tungsten, the rate of diffusion is reduced to one-tenth.[4] Normally, diffusion through a lattice implies that the diffusing element can enter into solid solution in the metal which forms the mass, even if only to a minute extent. In the absence of solid solubility, diffusion seems to be confined to the grain boundaries, as in the migration of thorium through tungsten.[5] This suggests some disturbance of the lattice in the neighbourhood of the boundaries. There is evidence from work on non-metallic substances [6] that diffusion is favoured by disturbances of the lattice, the so-called " Lockerstellen " or loosened regions, and in accordance with this is the fact that cold-working an alloy hastens diffusion, as discussed below.

Self-diffusion in lead is hastened by adding an impurity which lowers the melting-point, such as bismuth, but not by thallium, which raises it.[7]

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[1] C. E. Van Ostrand and F. P. Dewey, *U.S. Geol. Survey Prof. Paper* 95G, 1915.

[2] J. Groh and G. von Hevesy, *Ann. Physik*, 1920, [iv], **63**, 85 ; G. von Hevesy and A. Obrutsheva, *Nature*, 1925, **115**, 674.

[3] W. Geiss and J. A.-M. van Liempt, *Z. Metallk.*, 1924, **16**, 317.

[4] J. A. M. van Liempt, *Rec. trav. chim.*, 1932, **51**, 114.

[5] P. Clausing, *Physica*, 1927, **7**, 193.

[6] G. von Hevesy, *Z. physikal. Chem.*, 1922, **101**, 337.

[7] W. Seith and A. Keil, *Z. Metallk.*, 1935, **27**, 213.

In the diffusion of one metal through another the process is usually like that of self-diffusion, in that neighbouring atoms in the lattice interchange their position, a process which naturally takes place more readily the higher the temperature. Atoms which occupy interstitial spaces in the lattice, as those of carbon and nitrogen in iron, can migrate more easily, and in general their rates of diffusion at comparable temperatures are greater than those of atoms which occupy points on the lattice. The effect of temperature has been examined quantitatively in several instances, and it is found that the diffusivity increases rapidly with the temperature, approximately doubling itself for each 10° rise, a rate of increase which is familiar in connection with chemical reactions. It has been verified for a number of systems that a linear relation between log D and 1/T, where D is the diffusivity and T the absolute temperature, well represents the experimental data.[1] This applies also to the diffusion outwards of zinc from brass, the zinc escaping at the surface.[2]

From the slope of such curves the heat of solution may be calculated. Thus Dushman and Langmuir found 94,000 cal./g. atom for the diffusion of thorium through tungsten at 2000°, and Dunn 12,800 cal./g. atom for the diffusion of zinc in copper.

When a single metal is taken as the solvent, and the rates of diffusion of different metals in it are determined, diffusivity is greater the more widely separated the metals in the periodic system. Fig. 110 shows this for a number of metals diffusing in lead.[3] The logarithmic law of dependence on temperature is followed, and the effect of divergence of chemical character is well seen.

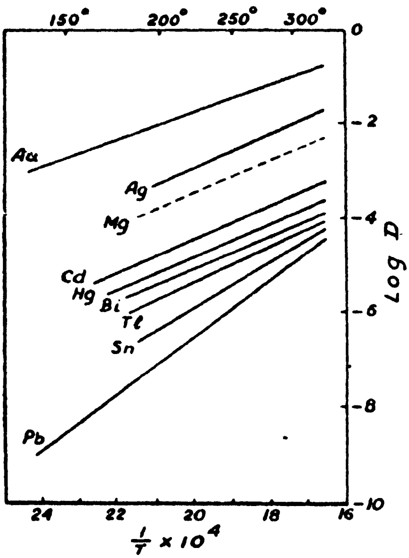

FIG. 110.—Diffusion of metals in lead.

The diffusivity at a given temperature is not actually a constant, but varies with the concentration of the dissolved element already existing in the region into which diffusion is taking place. The values usually quoted are for dilute solid solutions, and they diminish with increased concentration. The few instances which have been ex-

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[1] S. Dushman and I. Langmuir, *Phys. Rev.*, 1922, [ii], **20**, 113.

[2] J. S. Dunn, *J. Chem. Soc.*, 1926, 2973.

[3] Seith and Keil, *loc. cit.* See also H. Braune, *Z. physikal. Chem.*, 1924, **110**, 147.

A. Diffusion of zinc into copper. × 30

B. Diffusion of zinc into copper. × 30

PLATE XII

amined quantitatively suggest that the falling off is approximately linear.[1]

The analytical method used by Roberts-Austen is not often a convenient one for purposes of measurement, as the distances traversed in a reasonable time are small. The process may be conveniently followed in a system in which several solid phases, distinguishable by the microscope, may be formed. Such a system is found in the alloys of copper and zinc. On immersing a rod of copper for a short time in molten zinc, an adherent coating is formed, consisting of a brittle silvery-white alloy rich in zinc. A section cut through the rod shows that within this layer is a layer of a yellow alloy, the β solid solution, which appears, under a low magnification, to be separated from the unaltered copper of the interior of the rod by a sharp boundary. This structure is shown in the photo-micrograph, Plate XIIA, in which the upper band represents the outer layer, which consists, at least near its contact with the inner layer, of the γ solid solution. Next to it, and sharply divided from it, is a band of the β phase, and next to it again, separated by a very narrow dark band, is the core of unchanged copper.

If the rod is now heated for several hours at a temperature of about 700° C. and then slowly cooled, diffusion is found to have occurred when the specimen is again examined, zinc diffusing inwards from regions of high to those of low concentration, that is, from the outer zone to the inner core. The γ zone gradually disappears, whilst the β zone undergoes a great extension of breadth, and also loses its original homogeneity, showing isolated γ crystals near its outer margin and α crystals towards the inner margin, the latter becoming more and more closely grouped until a zone of the α solid solution is formed. This constituent being isomorphous with copper, it passes insensibly into the central mass, the transitional zone exhibiting a continuous change of colour from yellow to red. After further heating, the γ crystals disappear, and a broad band of β containing numerous α crystals forms the outer layer. This condition is seen in Plate XIIB, where the upper band consists of $\alpha + \beta$, the intermediate zone of pure α, and the lowest of copper.

When the diffusion is not accompanied by a change of phases as with copper and nickel, the boundary does not remain sharp. Diffusion takes place in both directions, but with unequal velocities,[2] and may be followed by careful etching with a reagent which attacks one metal more rapidly than the other. For quantitative purposes it is better to follow the change of some other property, such as the

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[1] For a formula connecting the coefficient with the concentration, see C. Matano, *Japan. J. Phys.*, 1932-3, **8**, 109.

[2] When the metals differ widely in properties, diffusion is almost entirely in one direction, but as they approach one another in character the diffusion tends to become reciprocal. (G. von Hevesy and W. Seith, *Z. Elektrochem.*, 1931, **37**, 528.)

electrical conductivity. In one series of experiments[1] a nickel wire, 0·5 mm. diam., was coated electrolytically with copper until the composite wire contained 59 per cent. of copper and 41 per cent. of nickel. On heating to 1000° in hydrogen and determining the conductivity from time to time, the process of diffusion could be followed, and a minimum value, corresponding with that for a homogeneous alloy of the above composition, was reached after 140 hours. Rapid diffusion was obtained by depositing successive thin alternate layers of nickel and copper, so as to present a large surface of contact.

The process may also be followed by means of X-ray measurements. Thus, using the same plan of depositing alternate layers of the two metals electrolytically, the inter-diffusion of gold and copper has been studied over a range of temperature.[2] The lines of the two metals were at first separate, but somewhat broadened owing to internal stress. They became sharp at 200°, showing that the stress was relieved, and at 300° the gold lines began to move nearer to the copper lines, at the same time becoming more diffuse. The copper lines did not change until about 400°, and at 500° the two sets of lines coincided and were quite sharp. It follows from this that copper diffuses into gold more readily than gold into copper, and the method provides a means of determining the velocities of diffusion in other systems where there is an extensive range of solid solubility.

The diffusion of interstitial atoms through a lattice is of importance in many technical processes, the most familiar of these being the cementation of iron by carbon, which was found to follow the law of diffusion.[3] In the process of case-hardening only the outer portion is penetrated, and the concentration of carbon diminishes inwards in accordance with normal diffusion. Atomic nitrogen resulting from the thermal decomposition of ammonia gas in contact with iron at 550° is caused to penetrate in the process of nitriding,[4] iron nitride being formed. Boron diffuses into iron in the same way at 900° from boron chloride, also forming a hard superficial layer,[5] as does chromium.[6]

A fact of metallographic interest in this connection is that in many instances of the penetration of an element into a metal by diffusion, grain growth occurs, producing large columnar grains with their length parallel with the direction of diffusion. This is seen

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[1] G. Bruni and D. Meneghini, *Atti. R. Accad. Lincei*, 1911, [v], **20**, i, 671, 927 ; *Intern. Z. Metallogr.*, 1912, **2**, 26.

[2] V. G. Mooradian and J. T. Norton, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **117**, 89.

[3] R. Mannesmann, *Verh. Ver. Beförd. Gewerbefl.*, 1879, **58**, 31 ; W. C. Roberts-Austen, *J. Iron Steel Inst.*, 1896, i, 139.

[4] A. Fry, *Krupp. Monatsh.*, 1923, **4**, 137 ; *Stahl u. Eisen*, 1923, **43**, 1271.

[5] N. Parravano and C. Mazzetti, *Atti. R. Accad. Lincei*, 1922, [v], **31**, ii, 424.

[6] F. C. Kelley, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 351 ; G. Grube and W. v. Fleischbein, *Z. anorg. Chem.*, 1926, **154**, 314.

in Plate XII, and is especially noticeable in processes which involve the removal of a dissolved element by diffusion outwards, as in the decarburization of iron by oxygen[1] or by moist hydrogen[2] and in cementation by chromium.[3] In the diffusion of elements into iron, the formation of columnar grains has been explained[4] by the effect of the diffusing element on the transformation point of iron, and it is probable that the production of this structure only occurs when a new phase is formed, as in the instance of the copper-zinc alloys already mentioned (p. 213).

SEGREGATION IN THE SOLID STATE

When, as the result of processes of crystallization, one solid phase is distributed through another in the form of lamellæ or of rounded particles, complete stability may not be reached even when the two phases have reached equilibrium in the sense of the phase rule. The condition of complete physical equilibrium may require that the smaller particles should aggregate to form larger, until a condition is reached in which surface forces become negligible. This effect may be regarded as one of surface tension. That very small crystals of a substance are labile in presence of larger crystals of the same substance and of a solvent is a thermodynamical necessity, and has been proved experimentally for calcium sulphate in water,[5] and in other instances. The effect is of great importance in the metallurgical treatment of steel. The eutectoid of iron and iron carbide, known as pearlite from its lamellar structure (see p. 353), undergoes a change when heated between 600° and 700°, the carbide gradually segregating into small globules, and ultimately into comparatively large masses.[6] This process, awkwardly called "spheroidization," must involve the passage of carbon into solid solution, although the solubility is very small, being only 0·035 per cent. at 700°, and falling rapidly with falling temperature.[7] That the process is essentially one of diffusion is shown by the fact that plotting the logarithm of the rate of spheroidization against the reciprocal of the absolute temperature gives a straight line.[8] In a similar way, eutectic structures may be coarsened by prolonged heating below the melting-point,

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[1] J. E. Stead, *J. Iron Steel Inst.*, 1898, i, 145.

[2] C. R. Austin, *ibid.*, 1922, i, 93.

[3] F. C. Kelley, *Trans. Amer. Inst. Min. Met. Eng.*, 1928, **78**, 390.

[4] C. Benedicks, *ibid.*, 402 ; C. O. Bannister and W. D. Jones, *J. Iron Steel Inst.*, 1931, ii, 71 ; A. Hultgren, *Trans. Amer. Inst. Min. Met. Eng.*, 1929, **78**, 591. The peculiarities of the columnar zone produced by diffusion are fully discussed by P. Bardenheuer and R. Müller, *Mitt. K.W. Inst. Eisenforsch.*, 1932, **14**, 295.

[5] G. A. Hulett, *Z. physikal. Chem.*, 1901, **37**, 385.

[6] J. E. Stead, *J. Soc. Chem. Ind.*, 1903, **22**, 340 ; J. H. Whiteley, *J. Iron Steel Inst.*, 1922, i, 339. The later literature is extensive. See, for a discussion of the conditions, F. Körber and W. Köster, *Mitt. K.W. Inst. Eisenforsch.*, 1924, **5**, 145.

[7] H. Scott, *Chem. Met. Eng.*, 1922, **27**, 1156.

[8] R. W. Bailey and A. M. Roberts, *Proc. Inst. Mech. Eng.*, 1932, 209.

even although the solid solubility may be so small as to be undetectable by other means. An instance is the eutectic of copper and cuprous oxide, which is coarsened at 1000°, even to the extent of forming well-defined crystals.[1] Electrolytically deposited nickel commonly contains hydroxide dispersed through it in fine particles. These are converted into oxide by heating, and at 1000° the oxide migrates, forming relatively large aggregates.[2] Like other processes depending on diffusion, spheroidization is greatly hastened by mechanical deformation.

The rate at which such particles will re-dissolve to form a solid solution will depend on the ratio of their surface to their mass. Calculation shows that the rate of solution of globular cementite may be either greater or less than that of lamellæ, according to dimensions, but on carrying out experiments with a 0·9 per cent. carbon steel it was found that other factors intervene, the process in the lamellar structure beginning at a grain boundary and proceeding inwards, whilst each globule dissolves in the iron immediately surrounding it.[3]

A solid solution which has solidified in such a way that the adjustment between the composition of the solid and liquid phases has not had time to complete itself has a structure in which the composition of each crystal changes from the core to the boundary, as explained in Chapter II. On annealing at a temperature below the solidus diffusion takes place, and after a time the alloy becomes homogeneous. The time needed varies greatly for different alloys, and little quantitative work has been done on the subject. Brasses, although showing a pronounced "coreing" effect under the microscope, become homogeneous after a short time at any temperature above 600°,[4] whilst alloys containing nickel, such as cupro-nickel and (especially) nickel-iron alloys, require very prolonged annealing. In a simple instance, that of the alloys of bismuth and antimony, although homogeneous crystals may be obtained by very slow cooling from the liquid, cored crystals do not lose their structure on heating even for long periods just below the solidus.[5] Whilst an uneven distribution of carbon in γ-iron is quickly removed by annealing, phosphorus diffuses far more slowly, and the "banded" structure in steel produced by phosphorus which had segregated during the

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[1] P. Siebe, *Z. anorg. Chem.*, 1926, **154**, 126.

[2] G. E. Gardam and D. J. Macnaughtan, *Trans. Faraday Soc.*, 1933, **29**, 755.

[3] A. Pomp and R. Wijkander, *Mitt. K.W. Inst. Eisenforsch.*, 1926, **8**, 55. See also A. Portevin and V. Bernard, *J. Iron Steel Inst.*, 1914, ii, 204; 1921, ii, 145; C. H. Desch and A. T. Roberts, *ibid.*, 1923, i, 249.

[4] M. Cook, *Trans. Faraday Soc.*, 1922, **17**, 522. For an approximate study of the rate of diffusion in cored alloys of copper and tin, see C. H. Mathewson and P. Davidson, *Intern. Z. Metallogr.*, 1916, **8**, 181; and H. Weiss, *Ann. Chim.*, 1923, [ix], **20**, 131.

[5] M. Cook, *J. Inst. Metals*, 1923, **28**, 421. (But compare G. Masing and M. Overlach, *Wiss. Veröff. Siemens-Konz.*, 1930, **9**, 331.)

freezing of the ingot,[1] persists even after long annealing. A part of the banded effect has also been attributed to oxygen.[2]

When it is desired to obtain a cast alloy, subject to coreing, in a homogeneous condition, it is advisable to cast under such conditions as to give a fine grain. On subsequent annealing, the distances over which migration has to take place are kept small, and the time of annealing is reduced. Chill castings of small diameter are, therefore, to be preferred, whenever the study of the structure involves bringing the alloy into a state of equilibrium. When the alloy is ductile, much time may be saved by rolling or drawing until the section has been reduced by 75 per cent. or more, after which annealing will cause diffusion to occur much more rapidly than in an unworked metal.

In the diffusion of gases through solid metals, a subject first studied in the classical discovery by Graham of the passage of hydrogen through platinum, the theoretical conclusion was reached[3] that the rate of diffusion is inversely proportional to the thickness of the metal and directly proportional to the square root of the gas pressure and to an exponential function of the temperature. The pressure relation has been verified for the diffusion of oxygen through silver,[4] but is not always strictly true in actual instances, and a careful examination of the diffusion of hydrogen through a number of metals and of nitrogen through molybdenum[5] showed that a deviation from the square root law is found at low pressures, and may be accounted for by the occurrence of activated adsorption as a necessary preliminary to diffusion. The diffusion of hydrogen through iron was found to be the same for a single crystal as for an aggregate. The evidence goes to show that gases, such as hydrogen, dissociate into atoms on entering the metal, and the small size of the hydrogen atom would account for its ready passage. Even so, its presence has a small but distinct effect on the dimensions of the lattice, the parameter of α-iron being increased from 2·8609 Å. to 2·8614 Å. when fully charged with hydrogen.[6]

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[1] J. E. Stead, *J. Soc. Chem. Ind.*, 1914, **33**, 173; J. H. Whiteley, *J. Iron Steel Inst.*, 1920, i, 359; ii, 143; 1921, i, 277; 1926, i, 213.

[2] H. Le Chatelier and B. Bogitch, *Rev. Métall.*, 1919, **16**, 129.

[3] O. W. Richardson, J. Nicol and T. Parnell, *Phil. Mag.*, 1904, [vii], **8**, 1.

[4] F. M. G. Johnson and P. Larose, *J. Amer. Chem. Soc.*, 1924, **46**, 1377.

[5] C. J. Smithells and C. E. Ransley, *Proc. Roy. Soc.*, 1935, **150**, A, 172; **152**, A, 706; 1936, **155**, A, 195. The first paper contains references to previous experimental work.

[6] F. Wever and B. Pfarr, *Mitt. K.W. Inst. Eisenforsch.*, 1933, **15**, 147.

CHAPTER XIV.

THE PHYSICAL PROPERTIES OF ALLOYS.

THE determination of the physical properties of metals and alloys falls partly outside of the scope of metallography, but it is frequently necessary to determine certain properties in the course of a study of the constitution of a system of alloys. The absolute values of physical constants may be of less importance for this purpose than the change of a property with variation of temperature or of composition. The properties which have been brought into closest relation with the constitution are: (1) density; (2) thermal expansibility; (3) hardness; (4) electrical conductivity; (5) thermo-electric power; (6) magnetic properties; (7) colour; and (8) electrolytic potential. Of these, (2) has been partly considered when discussing dilatometric methods of determining transformation points, and (8), on account of its connection with chemical corrosion, will be considered separately. The remaining properties will now be briefly considered in order.

DENSITY AND SPECIFIC VOLUME.

The density of a metal or alloy, that is, the mass of unit volume, is dependent on the temperature and also on the mechanical condition of the body, a rolled or hammered metal, for instance, having a different density from one cast or annealed. The first effect of applying a pressure exceeding a certain limit is often to produce an increase of density, which persists after the load is removed. This increase is only apparent, and is merely due to the closing up of previously existing pores and cavities, which are usually present to an unexpected extent, even in apparently homogeneous materials. A pressure of 10,000 atmospheres has been found sufficient to produce this effect, the compressed substances behaving as perfectly elastic bodies towards any further increase of pressure, however long continued.[1] This is only true if polymorphic change, which is brought about in many substances by the application of pressure, is absent. Further, it only holds good of pressure applied equally in all directions. When a solid is subjected to rolling, drawing, or hammering, the compression is accompanied by change of form, and by an actual diminution of density. This fact is known in workshops where wire

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[1] W. Spring, *Bull. Acad. Roy. Belg.*, 1883, [iii], 6, 507.

is drawn, and it has been accurately studied in some instances.[1] The meaning of the phenomenon will be discussed subsequently in connection with the plasticity of metals. When a diminution of density is produced by deformation, annealing at a temperature well below the melting-point causes a return to the maximum density. A metal or alloy which has been thoroughly compressed by drawing or hammering, and subsequently annealed, is therefore likely to approach the true density. It must be noted that even this precaution does not exclude every source of error, as the original metal may contain bubbles of gas, which will be compressed to very small dimensions, but may recover their original volume on annealing, causing the observed density to be too low.

Although the density of a body is properly the mass of unit volume, and the specific gravity is the ratio of the mass of the body to that of an equal volume of water, the two magnitudes are expressed by the same number when metric units are employed, and the Archimedean method, which consists in comparing the weight of the specimen with that of the water which it displaces, is therefore the best adapted to the study of the density of alloys. The principal error in this method is due to the suspending hair or wire. It is advisable to use a fine wire of silver or platinum, and to perform a blank experiment, in which the suspending wire is immersed to exactly the same depth as when carrying the specimen Errors caused by surface tension are thus eliminated. The specific gravity referred to water at the same temperature (say 15°) is then given by the formula

$$S_{15^\circ}^{15^\circ} = \frac{w}{w - w_1}$$

in which w and w_1 are the weights of the specimen in air and in water respectively. Corrections for the density of the air, and for reference to water at temperatures other than atmospheric, may be made by the usual methods.

The accuracy is increased by using a liquid heavier than water, such as carbon tetrachloride, with a sp. gr. of 1·6, which has also the advantage of wetting solids easily. Liquid amalgams are weighed in a pyknometer.

The density of an element or of a homogeneous solid phase may be determined from its X-ray parameters, when the structure of the unit cell is known, and this method is independent of porosity (compare p. 176). V being the volume of the unit cell ($= a^3$ for a cubic crystal, a being the edge of the cube, as determined by X-ray measurements),

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[1] This observation has usually been attributed to Spring (1891) and later writers. An account of earlier statements of the same fact is given by H. O'Neill, *J. Inst. Metals*, 1928, **39**, 63. The earliest detailed study appears to be by C. O'Neill (*Mem. Lit. Phil. Soc. Manchester*, 1861, [iii], **1**, 243). See G. W. A. Kahlbaum, K. Roth, and P. Siedler, *Z. anorg. Chem.*, 1902, **29**, 277; J. Johnston and L. H. Adams, *J. Amer. Chem. Soc.*, 1912, **34**, 563; and, for single crystals, M. Masima and G. Sachs, *Z. Physik*, 1929, **54**, 666.

A the atomic weight, m the mass of a single atom of hydrogen, and n the number of atoms in the unit cell, the density ρ is given by

$$\rho = \frac{nAm}{V};$$

m is taken as $1{\cdot}662 \times 10^{-24}$. Thus for silver, which has 4 atoms in the unit cell, the atomic weight 107·88, and a lattice parameter $a = 4{\cdot}076 \times 10^{-8}$, the density is given by

$$\frac{4 \times 107{\cdot}88 \times 1{\cdot}662 \times 10^{-24}}{(4{\cdot}076 \times 10^{-8})^3} = 10{\cdot}5.$$

Should the crystal contain atoms of more than one kind, the mean atomic weight is substituted for A.

Metals.	*a*.	*b*.	$\frac{100\Delta v}{v}$.
Bi—Cd	0·10181	0·0001373	− 0·1
Bi—Sn	0·10181	0·0003530	+ 1·0
Cd—Sn	0·11554	0·0002156	+ 0·5
Pb—Cd	0·08791	0·0002763	+ 0·4
Pb—Sb	0·08791	0·0006106	+ 0·9
Pb—Sn	0·08791	0·0004919	+ 0·9
Pb—Ag	0·08791	0·0000760	+ 0·7
Ag—Bi	0·09550	0·0000630	− 0·4
Sn—Zn	0·13710	0·0000400	+ 0·5
Hg—Pb	0·07368	0·0001422	− 1·0
Hg—Sn	0·07368	0·0006345	− 0·9

When comparing the members of a series of alloys the magnitude selected is not the density, but its reciprocal, the specific volume. If a series of alloys consists, as in the simplest case, entirely of conglomerates of crystals of the two components, the specific volume of any alloy will be that calculated by the additive rule from the specific volumes of the component metals, whilst there is no such linear relation between the densities. The specific volume-concentration curve for conglomerates is therefore, when percentages by weight are taken as abscissæ, a straight line.[1] When atomic percentages are taken as abscissæ, the ordinates must represent the *atomic* volumes, but as the " atomic volume " of an alloy is a purely statistical value, and has no theoretical significance, it is preferable to use percentages by weight and specific volumes.

In the table, which has been constructed from Maey's figures,

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[1] **Many determinations were made by A. Matthiessen, *Phil. Trans.*, 1860, 150, 177, who, however, expressed his results as densities. The largest mass of data is found in a series of papers by E. Maey, *Z. physikal. Chem.*, 1899, 29, 119; 1901, 38, 289, 292; 1904, 50, 200. Maey recalculated the older figures of Matthiessen and others, expressing the results in terms of specific volume, and also made many new determinations.**

the constants of the linear equations, $v = a + bp$, are given for a number of pairs of metals, the alloys of which are known, from other evidence, to consist of conglomerates of the pure component metals, or of solid solutions of limited concentration. In the equation, v is the specific volume of an alloy and p the percentage by weight of the second metal, a being the sp. vol. of the first metal, and $b =$ the difference of the sp. vols. of the two metals $\div$ 100. The fourth column contains the values of $100\Delta v/v$, where Δv is the greatest deviation from the calculated value shown by any alloy of the series, and v is the specific volume of that alloy. $100\Delta v/v$ therefore gives the greatest percentage deviation observed.

A solid solution is formed from its components with little or no change of volume. For isomorphous salts, a strictly linear relation has been found between specific volume and composition.[1] The X-ray method lends itself well to the determination of the variation of lattice parameter throughout a range of solid solutions with a high degree of accuracy, and a comparison with the direct determination of the specific volume gives good agreement.[2] The lattice parameter is in general a strictly additive property for solid solutions,[3] but small deviations are noticeable in some instances, the alloys of copper and nickel, for instance, showing a lattice contraction which has a maximum value of 0·11 per cent. at 34 atomic per cent. of nickel, corresponding with a density 0·3 per cent. greater than that calculated from the composition.[4]

In series of alloys in which intermediate phases occur, marked deviations from a linear relation may be found. Each break in the curve was formerly taken to indicate the composition of a compound, but this does not follow, the break actually indicating the limit of a new phase. The effect may be illustrated by an example. In Fig. 111 the upper part represents the thermal diagram of a series of alloys of the metals A and B containing a compound, C, which can form solid solutions up to the limiting concentrations D and E respectively. We will assume that B has a greater specific volume than A, and that the compound C is formed with contraction. All solid alloys between A and D will consist of conglomerates of A and the saturated solution D, their specific volumes will therefore follow a linear law, as indicated in the lower half of the diagram. At D the last crystals of A disappear, and between D and E the alloys consist only of the solid solution of progressively changing concentration. As the percentage of B, the metal of greater specific volume, increases, the specific volume of the solid solution increases also. From E to B the alloys consist of conglomerates of B and the saturated solid solution E, and the specific volume consequently varies again in a

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[1] J. W. Retgers, *Z. physikal. Chem.*, 1889, **3**, 497.

[2] Z. Nishiyama, *Sci. Rep. Tôhoku Univ.*, 1929, **18**, 359.

[3] L. Vegard, *Z. Physik*, 1921, **5**, 17.

[4] E. A. Owen and L. Pickup, *Z. Krist.*, 1934, **88**, 116; W. G. Burgers and J. C. M. Basart, *ibid.*, 1930, **75**, 155.

linear manner. The two discontinuities correspond, not with the compound C, but with the limits of saturation of the solid solution.[1] From an inspection of the curve, nothing could be inferred as to the composition of the compound, except that it lies between the limits D and E. The rule that a discontinuity in a physical property indicates the appearance of a new solid phase, and does not without further evidence yield the formula of the compound present, applies to the electrical conductivity, hardness, etc., and to the electrolytic potential of alloys, as well as to their density.

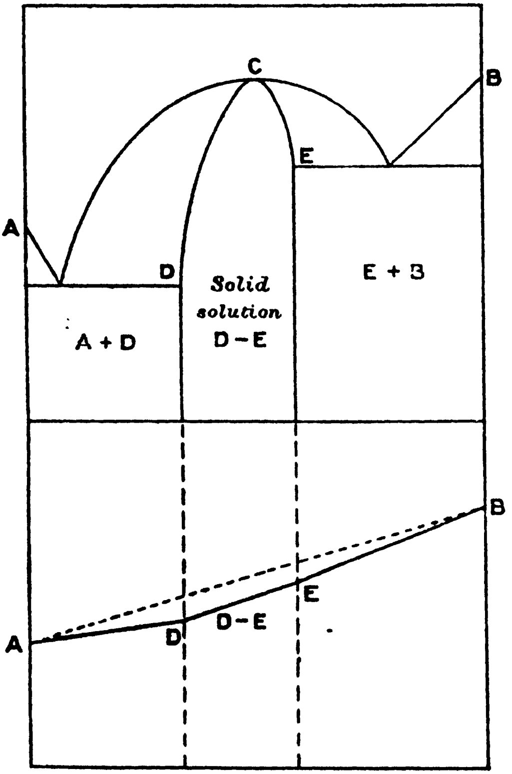

FIG. 111.—Constitution and specific volume.

To sum up, the specific volume varies with the composition within a series of alloys as follows:

1. In conglomerates of two constituents the variation is linear. The small deviations observed are probably due to want of homogeneity.
2. In a series of solid solutions the variation is almost linear, but there are small deviations.
3. In a more complex series, discontinuities occur at each point of appearance of a new solid phase. Phases containing intermetallic compounds have usually a smaller, but in a few cases a larger, specific volume than their components.

THERMAL EXPANSIBILITY.

The coefficient of thermal expansion, α, is expressed as the change of length per degree,

$$\alpha = \frac{1}{l_0} \cdot \frac{\Delta l}{\Delta t},$$

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[1] These limits may be fixed more accurately by determinations of the lattice parameter, which are equivalent to determinations of the specific volume.

and is multiplied by 10^6 to bring the value to a convenient figure. Between 0° and 100° the values for pure metals range from 4·4 for tungsten to 30 for zinc and cadmium, the alkali metals having, however, exceptionally high figures, 60 to 97. Metals which crystallize in other than the cubic system expand unequally along the different axes, and the figures given are usually averages. The coefficient increases with increasing temperature, and is least for metals of high melting-point. At low temperatures it is approximately proportional to the specific heat.[1]

The use of changes in length for the detection of phase changes has been mentioned previously (Chap. V).

The coefficients of expansion of alloys which form simple eutectiferous systems are, as might be expected, linear functions of the concentration by volume. In series of solid solutions they vary continuously, but are always smaller than would correspond with the simple linear function, so that the curve is convex downwards. Where intermetallic compounds are formed the curve may pass through a maximum.

In place of measuring the change of length of a mass of metal by using a dilatometer, the change in lattice parameter with temperature may be determined by means of X-rays. This method has the additional advantage that the expansion of non-cubic metals along their several axes may be determined directly.[2] The results are identical with those found by direct measurement.[3]

THE DENSITY OF LIQUID METALS AND ALLOYS.

The density of liquid metals and alloys of low melting-point may be determined by enclosing them in a glass or silica dilatometer, and the specific volume of alloys is then found to be very closely an additive property.[4] For work at higher temperatures, the plan has been used of suspending the molten metal in a crucible, immersed in a molten salt, from one end of a balance, and measuring its displacement, the density of the liquid salt being determined by calibration with a sinker of silica.[5] Alternatively, a sinker may be suspended in the molten metal, its displacement being determined by direct weighing, either in a vacuum or in an inert gas. This method has proved suitable for temperatures as high as that of liquid iron.[6] The sinker may be of hard refractory material, a weight being attached

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[1] E. Gruneisen, *Ann. Physik*, 1908, [iv], **26**, 211.

[2] E. A. Owen and E. L. Yates, *Phil. Mag.*, 1934, [vii], **17**, 113.

[3] A. H. Jay, *Proc. Roy. Soc.*, 1933, **142**, A, 237.

[4] R. Arpi, *Intern. Z. Metallogr.*, 1914, **5**, 142.

[5] K. Bornemann and F. Sauerwald, *Z. Metallk.*, 1922, **14**, 145; F. Sauerwald, *Z. anorg. Chem.*, 1926, **153**, 319.

[6] C. H. Desch and B. S. Smith, *J. Iron Steel Inst.*, 1929, i, 358; E. Widawski and F. Sauerwald, *Z. anorg. Chem.*, 1930, **192**, 145; F. Sauerwald and F. Fleischer, *Arch. Eisenhüttenw.*, 1933, **7**, 219.

to the upper part of the suspending rod, or of tungsten coated with a refractory layer.

The change of volume of metals and alloys on passing from the liquid to the solid state, a magnitude of importance in determining casting qualities, has been measured by the method described for liquids, but it is difficult to reach thermal equilibrium between the metal and salt, so that there is a lag which causes the freezing, even of a pure metal, to appear to extend over a wide range of temperature.[1] To overcome this a differential dilatometer was devised,[2] in which two bulbs of equal capacity immersed in a thermostat are used, in one of which the metal is enclosed, the apparatus being filled with an inert gas, and the differences of pressure measured by a manometer. Time may be allowed for equilibrium to be reached before each reading, and the densities of the solid and of the liquid have been determined at temperatures differing only by 0·5° or less. The variation of the contraction on freezing with the composition is given for several series of alloys by Goodrich, and the following figures are selected from his determinations :—

	Percentage contraction of volume on freezing.
Sn . . .	2·97
Pb . . .	3·85
Bi . . .	− 3·47 (expansion)
Zn . . .	4·48
Pb—Sn eutectic	2·40
Bi—Sn „	0·77

This method cannot well be applied to aluminium, on account of the action of the molten metal on glass or silica. A dilatometer of refractory alumina has been used,[3] the level of the surface being determined by an electrical contact. The following values were obtained :

Al . .	6·7 per cent. contraction
Al—Si eutectic	3·5 „ „ „

Light alloys of aluminium with copper and zinc gave values differing little from that for the pure metal.

HARDNESS.[4]

Although the hardness of a solid is in practice one of the most frequently determined properties, it is one to which it is difficult to

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[1] See, for instance, H. Endo, *J. Inst. Metals*, 1923, **30**, 121.

[2] C. J. Smith, *Proc. Roy. Soc.*, 1927, **115**, A, 554 ; improved by W. E. Goodrich, *Trans. Faraday Soc.*, 1929, **25**, 531.

[3] V. H. Stott, *J. Inst. Metals*, 1936, **59**, 73.

[4] A complete review of the principles and methods of hardness testing is given by H. O'Neill, " The Hardness of Metals and its Measurement," London, 1934.

assign a definite scientific meaning, and several quite distinct magnitudes are in fact comprehended under the same general term. It has not been found possible to express hardness in any scientific unit, and the numbers used to describe the hardness of a substance are therefore purely empirical, and refer only to one particular method of testing. These methods may be classified according to the kind of resistance they measure :

1. Resistance to scratching or cutting. This is hardness in the mineralogical sense.
2. Resistance to indentation. Technical hardness is usually thus determined.
3. Rebound after indentation.

1. *Sclerometric Methods.*—The mineralogist uses an arbitrary scale of standard minerals, so chosen that each member of the series is scratched by all those minerals above it, and scratches all those below it. Mohs' scale ranges in this way from 1 (talc) to 10 (diamond), but is of no value for metallurgical purposes. A more exact measure of the mineralogical hardness is obtained by scratching with a hardened point (diamond or glass-hard steel) under a fixed load, and measuring either the width or the depth of the scratch. The sclerometer takes many forms, of which that devised by T. Turner[1] has been much used. A diamond point attached to a lever arm is loaded with a variable load, and is drawn across the polished surface of the specimen, the " hardness number " being the number of grams required to press the point so heavily as to produce a " normal scratch," defined as a scratch which is just visible as a dark line on a bright surface. There is naturally considerable room for error in judging the proper depth of scratch, and the method is mainly useful in comparing samples of similar materials, such as steels. It gives concordant results in practised hands.

Martens' form of sclerometer[2] is more generally useful. The loaded point is stationary, whilst the specimen, with its polished surface horizontal, is drawn to and fro by a traversing table. The breadth of the scratch is measured, either by means of a microscope with micrometer eyepiece, or by photographing the scratch under a known magnification, and measuring the photographic image.[3] When the alloy consists of a conglomerate of two solid phases, it is still possible to obtain useful results as to the hardness, provided that the grain of the mixture is fine. The breadth of the scratch observed is then actually an average value, the microscope showing that the scratch is made up of wide and narrow portions, but a consistent reading is obtained without difficulty if the grain of the alloy

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[1] *Proc. Birmingham Phil. Soc.*, 1886, **5**, 291.

[2] A. Martens, *Mitt. k. techn. Versuchs-Anst.*, 1890, **8**, 236 ; improved by G. A. Hankins, *Proc. Inst. Mech. Eng.*, 1923, i, 423.

[3] N. S. Kurnakow and S. F. Schemtschuschny, *Z. anorg. Chem.*, 1908, **60**, 1.

is not too coarse. An improved form of Martens' sclerometer, mounted on the stage of a microscope, is described by V. Pöschl.[1]

A pointed scratching tool produces scratches of different form in materials which vary in hardness and toughness, and individual opinions may differ as to the width of the impressions. This difficulty is partly overcome by using a 1 mm. or 0·5 mm. hemisphere of diamond in place of a sharp point. An instrument of this kind, having a mechanical stage so that a series of parallel scratches may be made, has given good results with single crystals, and has also been adapted to the measurement of hardness at high temperatures.[2] It is also suitable for determining the hardness of thin electrolytic deposits. Jaggar's microsclerometer, a very delicate instrument designed for mineralogical purposes,[3] uses a minute drill, mounted as an attachment to a microscope. The point, a cleavage tetrahedron of diamond, is rotated by hand or by clockwork at constant speed under a constant load. The depth is measured by a micrometric device, and drilling is continued until a depth of 0·01 mm. is indicated. The hardness number is the number of revolutions, as recorded on a dial counter, required to drill to that depth under a load of 10 g. This instrument has the advantage of operating on an exceedingly small area, so that the individual constituents of an alloy may be separately examined if visible in the same microsection.[4]

2. *Indentation Method.*—Brinell's test,[5] which is the basis of the tests mainly used in technical practice, consists in pressing a hardened steel sphere on to the surface of the metal to be tested, and measuring the size of the circular indentation. The theory of this form of test has been discussed by Auerbach.[6]

In the practical application of the test, a hardened steel bearing ball is pressed on the surface of the metal under a known load by means of a loaded lever or of a small hydraulic press, the cylinder of which is filled with oil. Pressure is applied by a pump, and is measured by a separate cylinder, the piston of which is loaded by a lever carrying a sliding weight.[7] The load being increased to a fixed amount, depending on the nature of the metal or alloy to be examined, the diameter of the circular indentation produced is measured under a microscope with eyepiece scale.

It is not practicable to use a 10 mm. ball when testing thin sheets of metal. A small machine, employing balls of as little as 1 mm.

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[1] "Die Härte der festen Körper," Dresden, 1909.

[2] H. O'Neill, *Iron Steel Inst. Carnegie Schol. Mem.*, 1928, **17**, 109.

[3] T. A. Jaggar, *Amer. J. Sci.*, 1897, [iv], **4**, 399.

[4] Thus H. C. Boynton, *J. Iron Steel Inst.*, 1906, ii, 287; 1908, ii, 133, examined the constituents of steel with this instrument, obtaining numbers ranging from 460 for electrolytic iron to 125,480 for cementite Fe_3C.

[5] *Rapp. Congr. intern. Méthodes d'Essai*, Paris, 1900.

[6] F. Auerbach, *Ann. Phys.*, 1891, [iii], **43**, 60; 1892, [iii], **45**, 262, 277; 1900, [iv], **3**, 108.

[7] E. Preuss, *Baumaterialenkunde*, 1907, 295; A. Wahlberg, *J. Iron Steel Inst.*, 1901, i, 243.

diameter, with a dead load of from 5 kg. upwards, has been devised by H. Moore,[1] and is a useful laboratory instrument.

The Brinell hardness number is the ratio of the load in kilogrammes to the contact area of the indentation in sq. mm., using a ball 10 mm. diameter with a load of 3000 kg. or one of 5 mm., with a load of 750 kg. With different balls, the loads applied should be proportional to the square of the diameter of the ball. The hardness numbers are usually read off from a table after measuring the diameter of the impression. As, owing to differences of hardness in different directions, the impressions are often not quite circular, two diameters should be measured. The load is left on for a definite time, usually 30 seconds, and is removed before taking the reading.[2]

To ensure geometrical similarity a steel cone with an angle of 90° has been used.[3] The blunting of the cone is overcome by truncating it slightly.

When the Brinell hardness of the metal being tested is over 500, the deformation of the steel ball becomes appreciable, and the result obtained is low. This difficulty, however, is avoided by using a diamond indenting tool, preferably in the form of a pyramid, so that indentations of whatever depth remain geometrically similar. In the Vickers machine, which for scientific purposes is to be preferred to any form of Brinell testing machine, a polished diamond having the form of a square pyramid with an angle of 136° between opposite faces is employed, and the load is applied by means of levers, controlled by a cam with oil damping.[4] After the load has remained on for a fixed time, the stage carrying the specimen is lowered, and a microscope is swung into place, centring itself automatically. Two diameters of the square impression are measured by means of an eyepiece micrometer, and the hardness, on the Brinell scale, is read from a table. This instrument, by varying the weights, may be used over the whole scale up to the hardest steels. The Firth Hardometer is a rather simpler instrument on the same principle for bench use, the load being applied by a spring.[5]

The Rockwell machine, generally employed in the United States and largely also on the Continent, uses a 120° cone with a slightly rounded point, and measures the depth of the indentation directly on a dial, thus avoiding the use of a microscope and of tables.[6] Unfortunately, its arbitrary scale is different from the Brinell scale, which is used to express the hardness as measured by the machines described above, so that two entirely distinct scales are in common use.

The Vickers principle has been applied to attachments for the

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[1] *Proc. Inst. Mech. Eng.*, 1921, 51 ; *J. Inst. Metals*, 1921, **25**, 35.

[2] H. Moore, *loc. cit.*; R. G. Batson, *Proc. Inst. Mech. Eng.*, 1923, i, 401.

[3] P. Ludwik, *Baumaterialenkunde*, 1907, **12**, 147.

[4] R. Smith and G. Sandland, *J. Iron Steel Inst.*, 1925, i, 285.

[5] *Machinery*, 1926, **28**, 51.

[6] S. P. Rockwell, *Trans. Amer. Soc. Steel Treat.*, 1922, **2**, 1013 ; J. E. Malam, *J. Inst. Metals*, 1928, **40**, 375.

microscope, which makes it possible to determine the hardness of individual micrographic constituents in selected fields. A small diamond is mounted on the centre of the external lens of an 8 mm. objective which is supported by springs. The load can be varied from 0·5 to 100 grams, and a special device is provided for reading the diameter of the impression.[1] A more convenient apparatus[2] uses a diamond so ground as to give a rhombic impression with one axis seven times as long as the other. Recovery takes place transversely, so that the long dimension gives the unrecovered value of the indentation. A sharp impression is obtained even on glass. Martensite in hardened steel gave a Vickers figure of 720 and massive carbide in tool steel one of 1430.

Further information may be obtained from the Brinell test by making a series of impressions on the same specimen with different loads, and measuring the diameters. It was shown by Meyer[3] that

$$\mathrm{L} = ad^n$$

or

$$\log \mathrm{L} = \log a + n \log d$$

holds good, where L is the load, d the diameter of the impression, and a and n are constants. Three impressions may be made with different loads, and plotted on logarithmic paper, when a straight line should be obtained, the slope of which gives the value of n. This is known as "Meyer analysis," and a device for reading the value of n directly has been described.[4]

As the value of n represents the capacity of the metal for becoming hardened by cold work, its determination gives an insight into the mechanical properties of the material (see Chap. XVI).

An unusual type of instrument, which uses an indentation in an entirely different way to measure the hardness, is the Herbert pendulum tester.[5] A 1 mm. diamond ball is held in a chuck, and loaded by a casting weighing 4 kg., in such a way that the centre of gravity of the system is 0·1 mm. below the centre of the ball. When resting on the specimen and set swinging, the period of swing of the instrument depends on the hardness. The amplitude is read on a curved spirit level on the top of the pendulum. It may be used in one of two ways. In the scale test, the pendulum is tilted until the bubble stands at 0, and then released, and the figure on the scale is noted to which it returns, the swing being small for a soft metal and large for a hard one. Or it may be gently swung, and the time for ten

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[1] H. Hanemann and E. O. Bernhardt, *Z. Metallk.*, 1940, **32**, 36.

[2] F. Knoop, C. G. Peters and W. B. Emerson, *U.S. Bur. Stand. J. Res.*, 1939, **23**, 39.

[3] E. Meyer, *Z. Ver. deut. Ing.*, 1908, **52**, 645.

[4] H. O'Neill, *Iron Steel Inst. Carnegie Schol. Mem.* 1930, **19**, 19.

[5] E. G. Herbert, *Engineer*, 1923, **135**, 686; *Trans. Amer. Soc. Mech. Eng.*,

single oscillations noted with a stop watch. A further use of the instrument is mentioned in Chapter XVI. Some skill is needed to obtain consistent results, as the adjustment of the instrument must be very perfect.

A somewhat different form of pendulum, having a small knife-edge loaded by weights which hang below the specimen, has been used to determine the hardness of minerals, and also in the examination of allotropy in metals.[1]

3. *Rebound after indentation*—An instrument based on the rebound of a hard body from the surface was devised by Shore,[2] and known as the scleroscope. The specimen being placed horizontally, a vertical glass tube with a ground lower edge is applied closely to the specimen. A small steel hammer with rounded diamond point at the lower end is raised to the top of the tube by air suction with a rubber ball and then released, falling from a height of exactly 25 cm. on to the specimen. The height of the rebound is measured on the graduated scale of the tube (Fig. 112).

Several other types of instrument depending on rebound have been devised.[3] Variations of hardness over a surface, such as that of a hardened steel plate, may be detected by the "cloudburst" method, according to which several thousands of 3 mm. balls are allowed to fall in a shower on to the specimen, being continually lifted and again allowed to fall. Areas which are softer than the standard to which the apparatus has been set are indented, and a distinct pattern is produced. The method is also used to produce superficial work hardening.

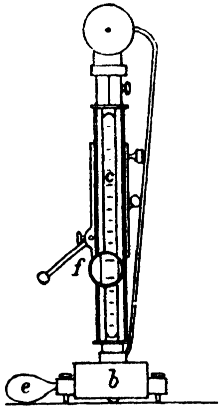

FIG. 112.—Shore scleroscope.

Different as these methods of determining hardness are from one another, the relative order of hardness revealed by them when different metals and alloys are compared is strikingly similar, if a few exceptional cases are excluded. The nature of these exceptions may be gathered from the behaviour of certain non-metallic substances. A soft but resilient substance like indiarubber, offering an insignificant resistance to the Brinell test and readily cut by a point, gives a higher result with the scleroscope than a mild steel.

It has long been known that the hardness of a metal bears an intimate relation to its atomic volume, the softest metals being those

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[1] W. D. Kusnetzov and E. W. Lawrentjewa, *Zeitsch. Krist.*, 1931, **80**, 54.

[2] A. F. Shore, *American Machinist*, 1907, **30**, ii, 747; see also E. Meyer, *Physikal. Z.*, 1908, **9**, 66; R. de Fréminville, *Rev. Métall.*, 1908, **5**, 329.

[3] E. G. Herbert, *J. Iron Steel Inst.*, 1927, ii, 265.

of greatest atomic volume.[1] The rule is an approximate one only, as data as to the hardness of pure elements, determined under strictly comparable conditions, are not forthcoming in sufficient quantity to establish an exact quantitative relation. Consideration of the "internal pressure" of metals has led to the conclusion that the hardness should be proportional to the quantity $\frac{a}{v^2}$ where v is the atomic volume, and a is van der Waals's constant.[2] The curve showing the periodic variation of hardness with atomic number closely resembles the corresponding curves of atomic volume and melting-point.

The hardness of a metal may be very greatly altered by alloying with another metal. This is, for instance, the object of alloying gold and silver for coinage purposes, the hardness, and therefore the resistance to abrasion in wear, being thereby increased. The way in which the hardness is changed will depend on the nature of the alloy formed, thus :

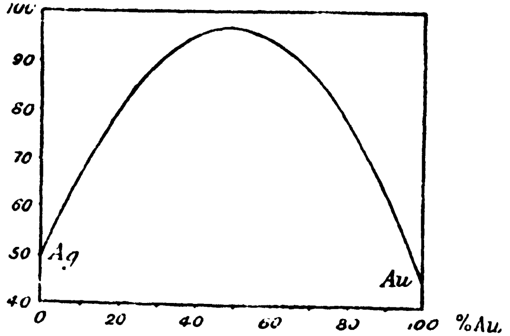

FIG. 113.—Hardness of silver-gold alloys.

1. The two metals are mutually insoluble in the solid state, all their alloys being conglomerates of the pure components. The hardness is then nearly a linear function of the composition. It is not exactly so, since a fine-grained eutectic, composed of a soft and a brittle metal, has a hardness in excess of that calculated from its composition, on account of the mutual support offered by the constituents.

2. The metals form a continuous series of solid solutions. The variation of hardness is expressed by a smooth curve having a pronounced maximum at a composition not far from that corresponding with equal weights of the component metals. A typical example is furnished by the alloys of silver and gold, shown in Fig. 113. The

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[1] S. Bottone, *Chem. News*, 1873, **27**, 215.

[2] I. Traube, *Z. anorg. Chem.*, 1903, **34**, 413 ; 1904, **40**, 377 ; *Ber.*, 1909, **42**, 1594 ; C. Benedicks, *Z. physikal. Chem.*, 1901, **36**, 529 ; G. A. Tomlinson, *Phil. Mag.*, 1931, [vii], **11**, 1009.

ordinates are sclerometric hardness numbers. An alloy composed of equal weights of gold and silver has a hardness which is practically twice as great as that of either of the pure metals.[1] Alloys of copper and nickel present a similar maximum.

If the two metals form two series of solid solutions separated by a gap, the hardness curve must present a change of slope at each limit of saturation, being rectilinear between them. This is true of the alloys of silver and copper.[2]

3. An intermediate phase is formed. As a general rule, intermetallic compounds are harder than their constituents. A familiar example is the compound Cu_3Sn, which is exceedingly hard and brittle, although its components are soft.

A series of alloys containing only a single compound, such as the alloys of magnesium with lead, tin, or silicon, from which solid solutions are absent, has a simple hardness diagram, consisting of two straight lines intersecting at the composition of the compound. The series, in fact, comprises two distinct series of conglomerates, within each of which the variation of hardness is linear. But should solid solutions occur amongst either series, the curve in that region deviates from a straight line. The copper-tin alloys were found by Martens to present a maximum hardness corresponding with the compound Cu_3Sn, the curve having a sharp peak at this point.

The hardness of a metal normally diminishes with increasing temperature, and for measurements at different temperatures a form of dynamic Brinell or Ludwik test is suitable.[3] The hardness-temperature curves of different metals are usually linear but often cross one another.[4] The hardness of lead, for example, diminishes very slowly, and that of antimony very rapidly, with rising temperature. All the metals examined still have an appreciable hardness at their melting-point.

The hardness of an alloy is a property which responds in a very sensitive way to changes taking place in a solid solution. Thus the processes of age-hardening and of change from a disordered to an ordered structure, discussed in Chapter XX, are easily followed by determinations of hardness, the Vickers diamond indenter being the most useful instrument for the purpose.

ABRASION.

Resistance to abrasion or wear is one of the meanings usually attached to the term hardness, but it proves to have no direct relation to the hardness as measured by any of the above methods. For practical purposes, resistance to wear is tested by machines in which

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[1] N. S. Kurnakow and S. F. Schemtschuschny, *Z. anorg. Chem.*, 1908, **60**, 1.

[2] N. S. Kurnakow, N. B. Pushin, and N. Senkowsky, *ibid.*, 1910, **68**, 123.

[3] C. A. Edwards, *J. Inst. Metals*, 1918, **20**, 61 ; C. A. Edwards and A. M. Herbert, *ibid.*, 1921, **25**, 175.

[4] P. Ludwik, *Z. physikal. Chem.*, 1916, **91**, 232 ; F. Sauerwald and K. Knehans, *Z. anorg. Chem.*, 1924, **140**, 231.

a specimen of the material is pressed against another solid body in relative motion. The second body may be of an abrasive character, or may be merely a hard material against which the specimen is pressed during its rotation, in such a way that the contact may be varied from pure rolling to any desired degree of slip. The special metallurgical interest of the study of wear lies in the fact that the process proves to be largely chemical in character. It was shown [1] that pure rolling, even with very high pressures, did not produce oxidation on hard steel, but even a very minute amount of slip caused the formation of a thin layer of oxide. Work on the testing of rail steel showed that when oxidation was prevented by conducting the test in a vacuum or in an inert gas, wear no longer occurred, the surfaces in contact merely polishing one another.[2] The gradual increase in friction of steel pivots running in bearings of hard material, such as sapphire, is due to the formation of oxide [3] and bearings running in an evacuated container have much lower friction, and do not undergo change.[4]

MACHINING QUALITY.

Another property associated with hardness is the ease with which operations such as turning, drilling or milling may be carried out on a material. Actually, the hardness is only one of the factors which determine ease of machining, and much depends on the texture.[5] Empirical tests are used to determine machining quality. The microscopic structure is often a good guide, and in a series of experiments on $\alpha\beta$-brasses [6] it was found that bars in which the two phases were arranged in parallel bands were most easily machined, the relative order of a number of brasses bearing little relation to their hardness, and in a similar way a banded structure in steel was found to favour easy machining.[7] In the so-called " free-cutting " steels such a texture is obtained by the deliberate introduction of fibres of sulphides, which play the same part as the lines of slag in wrought iron, a material famous for its machinability. Stainless alloy steels are difficult to machine, but they have also been improved for the rapid production of screws, etc., by the introduction of sulphide or selenide. Lead is added to brass for machining purposes, the particles of lead causing the turnings, etc., to break up into short chips rather than to form

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[1] G. A. Tomlinson, *Proc. Roy. Soc.*, 1927, **115**, A, 472.

[2] M. Fink, *Organ. Fortschr. Eisenbahnwesen*, 1929, **84**, 405 ; *Trans. Amer. Soc. Steel Treat.*, 1930, **18**, 204 ; M. Fink and U. Hofmann, *Arch. Eisenhüttenw.*, 1932, **6**, 161 ; F. Roll and W. Pulewka, *Z. anorg. Chem.*, 1934, **221**, 177.

[3] V. Stott, *J. Inst. Electr. Eng.*, 1931, **69**, 751 ; *Coll. Res. Nat. Phys. Lab.*, Vol. 24.

[4] G. F. Shotter, *J. Inst. Elect. Eng.*, 1934, **75**, 755.

[5] H. Tresca, *Mém. Acad. Sci. France*, 1883, [ii], **27**, 1 ; W. Rosenhain and A. C. Sturney, *Proc. Inst. Mech. Eng.*, 1925, 141 ; E. G. Herbert, *ibid.*, 1928, 775.

[6] C. H. Desch, *J. Soc. Chem. Ind.*, 1920, **39**, 216.

[7] F. Robinson and C. Nesbitt, *Proc. Inst. Mech. Eng.*, 1932, 383.

long spirals, and it is even added to aluminium with the same object.[1] In these properties the true hardness only plays a subsidiary part.

ELECTRICAL CONDUCTIVITY.

The specific electrical resistance, or resistivity, of an alloy, or its reciprocal, the specific conductivity, has long been recognized as being intimately connected with the internal constitution. The extensive researches of Matthiessen[2] were, in fact, earlier than the introduction of the thermal method, and played an important part in the theoretical development of the subject.[3]

The principal difficulty which confronts the metallographist who wishes to examine the conductivity of a series of alloys is that of obtaining suitably homogeneous specimens for measurement. Alloys which it is possible to draw into wire are examined with ease, and there is also little difficulty in forging small rods of malleable alloys, but many specimens are necessarily examined in the cast state, and are often so brittle that it is not possible to reduce them to accurate form by cutting or filing. Hard metals, if not too brittle, may be ground to shape on a wet emery wheel with light pressure. Very brittle alloys will not bear this treatment, and the experimenter must be content with cast rods. When the melting-point is not too high, smooth rods of uniform diameter may be obtained by the device of drawing the molten metal with the aid of a pump into previously heated glass tubes, coated internally with lamp-black. The glass is afterwards carefully broken away from the rod.[4] Cast specimens should always be examined microscopically for homogeneity, since gas-cavities lead to errors of the same nature as in determinations of density.

For metallographic work, the resistivity is most conveniently determined by the potential drop method, a constant current being sent through the specimen and the drop of voltage over a given length being measured. A convenient apparatus, which may be used to examine a metal or alloy over a range of temperature, makes use of thread recorders.[5] A resistance-temperature curve is thus obtained, and a time-temperature curve is traced at the same time. By a mechanical device described in the paper, these are combined to form a resistance-temperature curve.

When only small surfaces are available for examination, it is possible to use an arrangement of four point contacts, the two outer

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[1] L. W. Kempf and W. A. Dean, *Metal Progress*, 1935, July; H. Kästner, *Metallwirtsch.*, 1936, **15**, 1217.

[2] A. Matthiessen, *Phil. Trans.*, 1858, **148**, 383; 1860, **150**, 161; A. Matthiessen and C. Vogt, *ibid.*, 1864, **154**, 167; *Phil. Mag.*, 1862, [iv], **23**, 171.

[3] For a survey of the theory of conductivity, see W. Hume-Rothery, "The Metallic State," Oxford, 1931.

[4] N. J. Stepanow, *Z. anorg. Chem.*, 1908, **60**, 209.

[5] J. L. Haughton and W. T. Griffiths, *J. Sci. Instruments*, 1924, **1**, 225.

serving to lead in the current and the two inner to measure the drop of potential. All four are mounted in a single adjustable fitting, and the inner points may be as little as 1·7 mm. apart.[1]

When it is desired to express the dependence of the electrical properties on the composition of alloys, either the resistivity or its reciprocal, the conductivity, may be selected as the magnitude for comparison. The conductivity is usually to be preferred, as giving the simpler relationships.

The specific conductivity of conglomerates is very nearly proportional to their volume composition. The conductivity-concentration curve of alloys forming a simple eutectiferous series, that is to say, approximates to a straight line, if the concentration be expressed, as was done by Matthiessen, in percentages by volume.[2] This would be strictly true if the constituents were imagined as separated, drawn into wires of equal length, and placed side by side in a bundle. The conductivity of the whole bundle is then the sum of the conductivities of its constituent wires, and as the conductivity of each wire is proportional to its cross-section, and the wires are of equal length, it is the *volume* of each constituent which must be taken into account in the linear relation. Peltier effects, the production of back E.M.F., owing to heating at the contact of crystals of different kinds, are here neglected, but they may become appreciable, giving rise to deviations from the linear relation, in the sense of giving a conductivity lower than that calculated from the conductivity of the component metals and the volume composition. The small deviations observed in alloys of lead and cadmium, and of zinc and cadmium, are of the order required by this thermo-chemical explanation. The deviations are greater the greater the difference between the conductivities of the components.

A very different condition presents itself in those alloys which consist of solid solutions. The conductivity of a pure metal is lowered to a remarkable degree by the addition of small quantities of a second metal which it is capable of retaining in solid solution. In the graphical representation the conductivity curve falls very steeply for small percentages of the second metal, the slope then becoming less steep. In a similar manner the other end of the curve shows a steep fall, the intermediate portion being gently curved. The entire conductivity curve has therefore a characteristic U-shape, being continuous throughout. The curve for the alloys of gold and silver, determined by Matthiessen, is typical of this condition (Fig. 114). Alloys containing nearly equal volumes of the two metals have a conductivity which is only about one-fifth of that of gold, the less conducting of the two components.[3] The case of the alloys of

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[1] O. Gallander, *Proc. Intern. Ass. Test. Mat.*, 1912, **2**, IX., 7; C. Benedicks, *Intern. Z. Metallogr.*, 1915, **7**, 225.

[2] H. Le Chatelier, *Rev. gén. Sci.*, 1895, **6**, 529; W. Guertler, *Z. anorg. Chem.*, 1906, **51**, 397.

[3] The determinations of V. Strouhal and C. Barus, *Abh. k. böhm. Ges. Wiss.*, 1884, [v], **12**, No. 14, agree with those of Matthiessen.

copper and nickel is perhaps even more striking, on account of the very unequal conducting powers of the two metals. Although the conductivity of copper is about seven times that of nickel, the addition of copper to nickel produces a rapid diminution of the conductivity, and the curve has the typical U-form, the arms being of very unequal length. This property of solid solutions is utilized in the construction of electrical resistances, constantan, for instance, being an alloy of 60 per cent. copper and 40 per cent. nickel. The U-form is characteristic of all alloys forming an unbroken series of solid solutions, whether the freezing-point curve has a minimum, as in the alloys of copper with gold,[1] or is of the simpler type exhibited by the gold-silver series. Anomalies are found in systems containing ferro-magnetic metals.

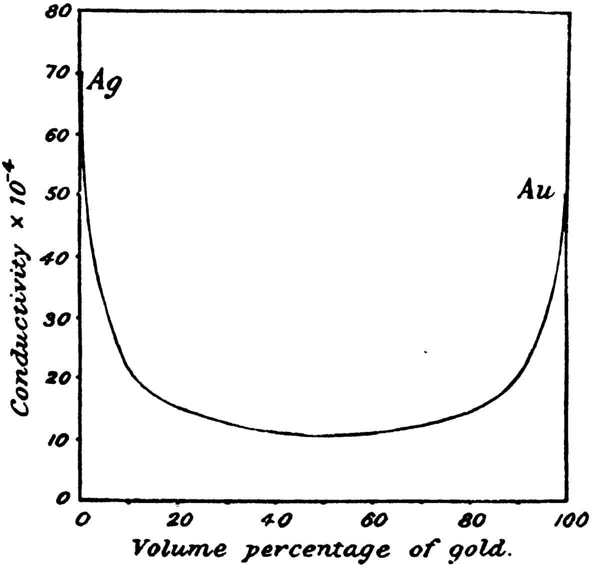

FIG. 114.—Conductivity of silver-gold alloys.

The behaviour of alloys in which two series of solid solutions are separated by a gap may now be inferred. Within the limits of formation of the solid solutions the depression of conductivity takes place, as in alloys of gold and silver, very rapidly, but between the limits of the saturated solutions the variation is linear. The entire curve therefore consists of two rapidly falling branches connected by a straight line. If this line happens to be nearly horizontal, it may be possible to mistake the entire curve for the U-form of completely isomorphous metals. Exact measurements with a sufficient

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[1] Provided that the distribution of the two kinds of atoms on the lattice is a random one (see p. 340).

number of alloys will, however, reveal the change of inclination at the junction of the branches. Curves of this kind are given by the alloys of copper and silver (Matthiessen) and of copper and cobalt,[1] the diagram of the latter being reproduced in Fig. 115.

Intermetallic compounds conduct like pure metals, although their conductivity is always less than that of the better conducting component, and in all instances hitherto observed falls below that calculated from the conductivity of the components by the rule of mixtures. What has been said as to the influence of compounds on the curve of hardness applies to a considerable extent to the conductivity also. The presence of a sharp cusp in the curve is unmistakable evidence of the existence of a compound or of an ordered lattice (p. 341), but the converse does not hold good. Should a single compound exist in the series and no solid solution be formed, the curve consists of two intersecting straight lines. A sharp cusp, the conductivity falling rapidly with departure in either direction from a simple stoichiometric formula, indicates a condition which, on the older conception of alloys, was regarded as an intermetallic compound, capable of forming solid solutions with either of its components. The depression would then be exactly parallel to the lowering of the conductivity of a pure metal by another metal entering into solid solution. This conception is not in accordance with modern views, and the alloy corresponding with the cusp is regarded merely as that solid solution in which, owing to the presence of the two metals in simple atomic ratios, the greatest degree of order can be attained. Any addition of either metal reduces the degree of order and lowers the conductivity. For most metallographic

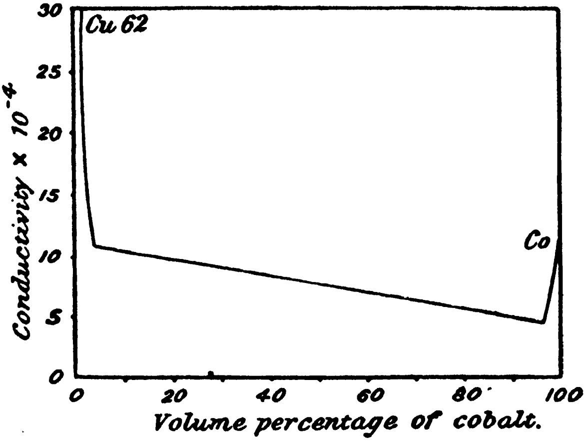

FIG. 115.—Conductivity of copper-cobalt alloys.

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[1] G. Reichardt, *Ann. Physik*, 1901, [iv], 6, 832.

purposes, the older idea of intermetallic compounds is useful in interpreting property-composition diagrams.

Dilute solid solutions of elements in metals of high conductivity, to which they have been added usually with the object of increasing the mechanical strength, are of special interest. In studying the influence of minute additions of one metal to another on its conductivity, there are advantages in plotting the resistivity, instead of its reciprocal, against the concentration by weight of the second metal. For the purposes of the electrical manufacturer, copper of the highest attainable conductivity is required, and the depreciation of its value by the presence of traces of impurities calls for chemical and physical investigation. It has been shown that the curve representing this depreciation falls very steeply at first. The actual form is that of a hyperbola for at least the initial portion of its course, and it follows that the curve of resistivity which = 1 ÷ specific conductivity, is very nearly rectilinear.

On comparing the influence of different elements on the specific resistance of iron, Benedicks [1] found that the increase of resistance is proportional to the atomic percentage of the added element, provided that the latter is present in solid solution. Hardened steels were taken for comparison.[2]

Electrolytic iron, free from carbon, melted in a magnetite crucible, gave a resistivity of 9·87 microhms per c.c. at 20°.[3] A number of specimens of highly purified iron gave 9·8.[4]

Attempts have been made to give a formula by means of which the resistance of steel may be calculated from the chemical analysis, each element being allotted a "carbon equivalent" by which its percentage may be multiplied, the sum of the products, multiplied by a factor, giving the resistivity

$$R = R_0 + A\Sigma C$$

where R_0 is the resistivity of pure iron, A a constant, and C the quantity of carbon + that of the other elements × their carbon equivalent.[5] This could only be true if all the elements were in solid solution, and the agreement is only approximate.[6]

It has been shown by Norbury [7] for alloys of copper, and by Linde [8] for alloys of copper, silver and gold, that the atomic increase

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[1] *Z. physikal. Chem.*, 1902, **40**, 545.

[2] Numerous data are found in the exhaustive researches of W. Barrett, W. Brown, and R. A. Hadfield, *Trans. Roy. Dubl. Soc.*, 1902, **8**, 1 ; *Proc. Roy. Soc.*, 1902, **69**, 480 ; *J. Inst. Elect. Eng.*, 1902, **31**, 674.

[3] E. D. Campbell, *J. Iron Steel Inst.*, 1918, ii, 428.

[4] F. Adcock and C. A. Bristow, *Proc. Roy. Soc.*, 1935, **153**, A, 172.

[5] C. Benedicks, *Thèse pour le doctorat*, Upsala, 1904 ; T. D. Yensen, *Trans. Amer. Inst. Elect. Eng.*, 1924, **43**, 145.

[6] A. L. Norbury, *J. Iron Steel Inst.*, 1920, i, 627.

[7] A. L. Norbury, *Trans. Faraday Soc.*, 1921, **16**, 570 (this paper includes a bibliography) ; *J. Inst. Metals*, 1925, **33**, 91.

[8] J. O. Linde, *Ann. Physik*, 1931, [v], **10**, 52 ; 1932, **14**, 353 ; **15**, 219.

of resistance is greater, the further apart the solvent and solute metals are in the periodic system, and although exceptions to this rule have been found, especially among ferromagnetic metals, it holds approximately and is a useful guide.

The conductivity of metals and alloys falls with increasing temperature, and the temperature-coefficient varies with the composition in almost exactly the same way as the conductivity itself. This fact has practical advantages in the study of metallography. When examining a series of binary alloys it is often difficult to obtain specimens of all the alloys in a series in such a condition that they can be drawn into wire or even cast into uniform rods, free from blowholes. The value of the temperature-coefficient is independent of the soundness or unsoundness of the specimens, and its determination, by measurements at 0° and 100°, may take the place of absolute measurements of the conductivity for constitutional purposes.[1]

For metallographic purposes it is convenient to express the temperature-coefficient as the percentage decrease of conductivity between 0° and 100°, so that

$$P = \frac{K_0 - K_{100}}{K_0} . 100.$$

For pure metals P has the value 27 — 31, and the same number is found for alloys which consist solely of conglomerates of their components. If solid solutions are formed, the value of P falls much lower. The curve representing the change of the temperature-coefficient with concentration has, in fact, a very similar form to the conductivity-concentration curve, with a deep minimum in the middle of a series of solid solutions. On this fact depends the possibility of obtaining alloys, the conductivity of which is within certain limits independent of the temperature. Thus constantan, an alloy containing 60 per cent. copper and 40 per cent. nickel, has a zero temperature-coefficient at ordinary temperatures, and the same is practically true of the alloy containing 80 per cent. copper and 20 per cent. manganese, and of platinoid (60 per cent. Cu, 24 per cent. Zn, 14 per cent. Ni and 1·2 per cent. W). Guertler has used three-dimensional diagrams to express the relations of the conductivity, temperature, and concentration of alloys.

The value of P for inter-metallic compounds is somewhat smaller than for pure metals. The presence of compounds affects the temperature-coefficient diagram in the same way as the conductivity diagram.

The conductivity of metals continues to increase when the temperature is reduced far below that of the atmosphere, and on approaching the absolute zero a new phenomenon appears, that of superconductivity. The course of the curves for some metals indicated that the resistance would become zero—or the conductivity

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[1] W. Guertler, *Z. anorg. Chem.*, 1907, **54**, 58; *J. Inst. Metals*, 1911, **6**, 135.

infinite—somewhat before reaching the absolute zero.[1] By the use of liquid helium, mercury was found to lose its resistance at 4·19° abs.,[2] and tin and lead at similar temperatures.[3] Since then many superconducting metals and alloys have been found. There is no relation between the occurrence of this property and the crystalline form. In a few instances, superconducting compounds are formed by metals which are not superconducting, such as Cu_3As [4] and Au_2Bi,[5] as well as by superconducting metals, such as $PbTl_2$.[6] The carbide, NbC, has highest superconducting temperature so far found, 10° abs., which is higher than that of pure niobium.[7] Alloys containing solid solutions, if superconducting, lose their resistance gradually over a range of temperature instead of sharply. The phenomenon is important for the theories of electrical conduction.

An abrupt change in the conductivity occurs at the melting-point. There is a remarkable similarity between the conductivity curves of liquid and solid alloys. Thus the conductivity of molten alloys of lead and tin is proportional to their composition, whilst alloys of copper and nickel give a U-shaped curve. Inter-metallic compounds which are sufficiently stable to persist in the molten state cause the appearance of a peak or kink in the curve. Examples of this are the compounds Hg_2Na, Hg_2K, and Cu_3Sb.[8]

The resistance of liquid metals just above the melting-point is most often about double that of the same metal just below its melting-point, but there are some exceptions, mercury in particular showing a much greater increase of resistance on melting. The resistance of bismuth, antimony, and gallium, which contract on melting, diminishes on passing from the solid to the molten state. Moreover, whilst the addition of a foreign metal usually increases the resistance, that of mercury is actually diminished by the addition of small quantities of gold, cadmium, tin, lead, or bismuth. The liquid probably contains regions in which the atoms have a regular arrangement, as in a crystal, these regions not being separated from one another by sharp boundaries.[9] This conclusion is in accordance with that derived from X-rays.

The thermal conductivity, λ, although of industrial importance, has been little used as a means of studying the constitution of alloys. Its ratio to the electrical conductivity, however, λ/κ, has some value

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[1] J. A. Fleming and J. Dewar, *Phil. Mag.*, 1892, [v], **34**, 326; 1893, **36**, 271.

[2] H. Kamerlingh Onnes, *Comm. Physic. Lab. Univ. Leiden*, 1911, **124** c.

[3] *Ibid.*, 1913, **133** d.

[4] P. Kapitza, *Proc. Roy. Soc.*, 1929, **123**, A, 292.

[5] W. J. De Haas and F. Jurriaanse, *Naturwiss.*, 1931, **19**, 706.

[6] W. J. De Haas, E. van Aubel and J. Voogd, *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 258.

[7] W. Meissner and H. Franz, *Z. Physik.*, 1930, **65**, 30. See also J. C. McLennan, J. F. Allen, and J. O. Wilhelm, *Trans. Roy. Soc. Canada*, 1931, [iii], **25**, 13.

[8] P. Müller, *Metallurgie*, 1910, **7**, 730, 755; K. Bornemann and G. von Rauschenplat, *ibid.*, 1912, **9**, 473, 505.

[9] N. F. Mott, *Proc. Roy. Soc.*, 1934, **146**, A, 465.

for this purpose. The values of pure metals at atmospheric temperature were found to be nearly equal, $\lambda/\kappa = 6{\cdot}3 \times 10^{10}$.[1] This value, again, was found to be proportional to the absolute temperature, so that $\lambda/\kappa T$ is sensibly constant.[2] Large deviations, however, were found at temperatures below $-100°$.[3] At high temperatures the Lorenz function for pure metals is fairly constant.[4] From an examination of over 100 alloys of copper, mostly in the α-range but including some $\alpha\beta$ alloys,[5] all fall on the same curve when the electrical is plotted against the thermal conductivity at the same temperature, independently of structure or heat treatment. Moreover, all the results at 20° and at 200° fall on a single curve when λ is plotted against κT. This is very nearly a straight line, intersecting the thermal axis at a small but definite value.

THERMO-ELECTRIC POWER.

Alloys, like pure metals, develop a thermo-electromotive force when two dissimilar specimens are connected, one junction being heated or cooled to a different temperature from that at which the other is maintained. The thermo-electric power is the temperature-coefficient of the thermo-E.M.F. In making the experiments the two specimens are only in contact with one another at a single junction, their other ends being connected with copper wires leading to the galvanometer or potentiometer employed to measure the electromotive force. When alloys are under investigation, it is usual to employ a junction consisting of the alloy and of one of its component metals, although another metal, such as copper or platinum, may also be used as a standard. The specimens are most conveniently taken in the form of rods or wires, but this is not always practicable with brittle alloys. The apparatus required is simple.[6] Experiments on crystals of bismuth [7] and on other non-cubic metals [8] indicate that the thermo-electric power varies with the orientation, so that the results obtained with cast or drawn rods or wires are average values. The specimens should be thoroughly annealed, as mechanical work has a great influence on the thermo-electric properties.

The E.M.F. developed in a thermo-electric circuit varies greatly

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[1] G. Wiedemann and R. Franz, *Ann. Physik*, 1853, [ii], **89**, 497.

[2] L. Lorenz, *ibid.*, 1881, **13**, 422. This was experimentally verified by W. Jaeger and H. Diesselhorst, *Abh. Phys.-techn. Reichs-Anst.*, 1900, **3**, 269; and for a single crystal of aluminium by E. Griffiths, *Proc. Roy. Soc.*, 1927, **115**, A, 236.

[3] C. H. Lees, *ibid.*, 1907, **80**, 143.

[4] F. H. Schofield, *ibid.*, 1925, **107**, A, 206.

[5] C. S. Smith, *Phys. Rev.*, 1935, [ii], **48**, 166; C. S. Smith and E. W. Palmer, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **117**, 225.

[6] J. L. Haughton, *J. Inst. Metals*, 1920, **23**, 499.

[7] L. Perrot, *Arch. Sci. phys. nat.*, 1898, [iv], **6**, 105, 229; 1899, [iv], **7**, 149; R. W. Boydston, *Phys. Rev.*, 1927, (ii), **30**, 911.

[8] P. W. Bridgman, *Proc. Amer. Acad. Sci.*, 1929, **13**, 351.

with the temperature, and for most pairs of metals or alloys becomes zero at a certain temperature, the neutral or inversion temperature, after passing which it changes in sign. For a large number of pairs, the relation is expressed by the formula

$$E = (t_2 - t_1)[a + c(t_2 + t_1)]\ {}^1,$$

in which t_1 and t_2 are the temperatures of the junctions, and a and c are constants. The inversion temperature is given by the formula

$$\tau = -\frac{a}{2c}.$$

The validity of Avenarius' equation has been tested for a large number of metals and alloys,[2] and more complicated expressions have been introduced to cover the observed deviations. Further deviations from the simple relation have been found at liquid air temperature.[3] There is no thermo-E.M.F. between metals in the superconducting condition.[4]

The thermo-electric properties of alloys do not follow any simple rule. Eutectiferous alloys without solid solutions do not depart greatly from a linear relation with the composition by volume, whilst with solid solutions the deviations are large.[5] The simple U-shaped curves of electrical resistance are not usually repeated, and in some instances, as in the alloys of platinum with palladium, the curvature may be in the opposite sense.[6] Intermetallic compounds are marked by singular points on the curves, but these may take different forms in different systems, and their interpretation is difficult. The very high thermo-electric power of certain compounds, especially those containing elements of low electrical conductivity, such as SbSn, SbCd,[7] $SnSe_2$, and SnSe,[8] is remarkable. As usual with electrical properties, the ferro-magnetic metals are particularly liable to show anomalies.

The measurement of the thermo-electric force when coupled with an inactive metal, such as platinum, may also be employed as a means of locating transformations in an alloy, a critical point being indicated by an abrupt discontinuity in the E.M.F. curve. This method has often been applied to steels, and has yielded results

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[1] R. Avenarius, *Ann. Physik*, 1863, **119**, 406; 1864, **122**, 193; 1873, **149**, 372.

[2] W. Jaeger and H. Diesselhorst, *Abh. phys. techn. Reichs-Anst.*, 1900, **3**, 269; L. Holborn and A. Day, *Sitzungsber. k. Akad. Wiss. Berlin*, 1899, 691.

[3] J. Dewar and J. A. Fleming, *Phil. Mag.*, 1895, [v], **40**, 95; De Metz, *Compt. rend.*, 1904, **139**, 447.

[4] G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 1365.

[5] W. Broniewski, *Ann. Chim. Phys.*, 1913, [viii], **25**, 5.

[6] W. Geibel, *Z. anorg. Chem.*, 1910, **69**, 38; 1911, **70**, 240.

[7] W. Haken, *Ann. Physik*, 1910, [iv], **32**, 291.

[8] H. Pélabon, *Compt. rend.*, 1914, **158**, 1897.

confirmatory of those obtained by other methods.[1] The use of thermo-electric measurements in detecting the effect of mechanical changes on metals and alloys will be referred to later (Chap. XVII).

MAGNETIC PROPERTIES.

Magnetic properties are exhibited by most metals and alloys in so slight a degree that their measurement is of little metallographic interest, although of great importance for physics. It has been shown[2] that the magnetic susceptibility of the elements is a periodic function of the atomic weight, but it is only in a few groups that the value exceeds a very minute amount. The group Fe, Ni, Co, of the so-called ferro-magnetic metals, is distinguished from all others by the highly magnetic character of its members, and for long the interest of the metallurgist in magnetic properties was confined to these metals and to certain of their alloys. The discovery in 1903 of a strongly magnetic alloy of copper, manganese, and aluminium,[3] gave a new stimulus to the study of the magnetic properties of alloys, since it became clear that metals, only feebly magnetic in themselves, might under certain conditions form magnetic alloys with one another.

The change of magnetic properties with temperature has great metallographic importance. The change is not continuous, but begins or ends sharply at certain critical temperatures, and it becomes of interest to correlate these critical points with the discontinuities in the thermal, microscopical, and other properties.

Single crystals, even of cubic metals, are not magnetically isotropic, and the variations of magnetic properties with orientation are theoretically important. The measurements are difficult, as it is necessary to grind the crystals to the form of discs or of ellipsoids, and any mechanical distortion affects the results A few references may be given to work on single crystals of iron.[4] The relations between magnetization and temperature are, however, the same for all orientations. Single crystals are nearly free from magnetic hysteresis.

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[1] The transformation ranges of relatively pure iron have been determined by this method, G. K. Burgess and H. Scott, *U.S. Bureau Stand., Sci. Paper*, 1916, No. 296. See also A. Goetz, *Physikal. Z.*, 1924, **25**, 562.

[2] J. Koenigsberger, *Ann. Physik*, 1898, [iii], **66**, 698; Stefan Meyer, *ibid.*, 1899, [iii], **68**, 324; *Monatsh.*, 1899, **20**, 369, 797; *Ber.*, 1900, **33**, 1918; O. Liebknecht and A. P. Wills, *Ann. Physik*, 1900, [iv], **1**, 178; H. du Bois and O. Liebknecht, *Ber.*, 1899, **32**, 3344; H. du Bois, *Rapp. Congr. intern. Phys.*, Paris, 1900, ii, 460.

[3] F. Heusler, *Verh. deut. physikal. Ges.*, 1903, 219; W. Stark and E. Haupt, *ibid.*, 222.

[4] E. Dussler and W. Gerlach, *Z. physik.*, 1927, **44**, 279; W. L. Webster, *Proc. Roy. Soc.*, 1925, **107**, A, 496; K. Honda, H. Masumoto and S. Kaya, *Sci. Rep. Tôhoku Univ.*, 1927, **16**, 235. A very full summary of existing knowledge is given by L. W. McKeehan, *Trans. Amer. Inst. Min. Met. Eng.*, 1934, **111**, 11.

Polycrystalline metals are quasi-isotropic, the various orientations being averaged. In iron, the ferro-magnetic properties virtually disappear at a definite temperature, the Curie point, A_2.[1] This temperature is independent of the strength of the field, although the course of the magnetization at lower temperatures is highly dependent on the field strength. Above the Curie point iron is paramagnetic, but measurements may be made with a torsion balance, and it is then found that the magnetization falls abruptly at the A_3 point and remains nearly constant, but increases at the A_4 point, in such a way that the curve for the δ-condition is a prolongation of that in the β (non-magnetic α) condition.[2] By such measurements of susceptibility it has even been found possible to determine the solidus curve of the iron-carbon system and the solubility line of cementite in austenite.[3]

The magnetic behaviour of the ferro-magnetic metals is very complex. The magnetic properties of iron are greatly modified by even very minute traces of impurities, in solid solution,[4] but it has not been found possible to correlate the properties of different specimens of highly purified iron with their composition. The permeability is increased and the hysteresis loss diminished in a remarkable way by heating in hydrogen,[5] and this effect is perhaps not to be attributed entirely to removal of impurities. In very strong fields the influence of small quantities of impurities is insignificant.

In alloys of paramagnetic or diamagnetic metals with one another determinations of the susceptibility show that breaks in the property-composition curve occur at the appearance of a new phase, as with other physical properties.[6] When ferro-magnetic elements are concerned the conditions are more complex. Intermetallic compounds, one component of which is ferro-magnetic, are almost always devoid of that property.[7] When solid solutions are formed the conditions may be very different.

In the study of alloys of para- or diamagnetic metals with one another, it is usual to plot the susceptibility against the atomic composition. Simple eutectiferous systems give a linear relation, whilst solid solutions give smooth curves, and the appearance of a new phase is often marked by a change of direction. The formation of an ordered structure may either increase or diminish the susceptibility, CuAu and Cu_3Au, for instance, being oppositely affected.[8]

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[1] P. Curie, *J. Phys. Radium*, 1895, **4**, 197.

[2] P. Weiss and G. Foëx, *Arch. Sci. phys. nat.*, 1911, [iv], **31**, 89; T. Ishiwara, *Sci. Rep. Tôhoku Univ.*, 1917, **6**, 133.

[3] K. Honda and H. Endo, *ibid.*, 1927, **16**, 627.

[4] T. D. Yensen, *Bull. Univ. Illinois*, 1914, **11**, No. 28; *Trans. Amer. Electrochem. Soc.*, 1929, **56**, 215; *Phys. Rev.*, 1932, [ii], **39**, 358; 1934, [ii], **45**, 742.

[5] P. P. Cioffi, *Nature*, 1930, **126**, 200; *Phys. Rev.*, 1932, [ii], **39**, 363.

[6] K. Honda, *Ann. Physik*, 1910, [iv], **32**, 1003.

[7] A preliminary list was given by G. Tammann, *Z. physikal. Chem.*, 1908, **65**, 73.

[8] H. J. Seemann and E. Vogt, *Ann. Physik*, 1929, [v], **2**, 976.

The γ-phase Cu_5Zn_8 is also marked by an exceptionally high diamagnetic susceptibility.[1]

The principal metallographic application of magnetic methods is in detecting critical or transformation points. The induction method is the simplest and most convenient, and may be used even at high temperatures. The heating coil of the furnace must be wound non-inductively, and the appearance or disappearance of magnetism may be conveniently followed by having two windings, through one of which a small high-frequency current is passed from a valve oscillator, whilst the second picks up energy from it by induction and passes it to a valve amplifier, which controls a recorder.[2] Often the change is so sharp that it is enough to bring a suspended compass needle near to the specimen, the temperature being noted at which the needle is deflected.

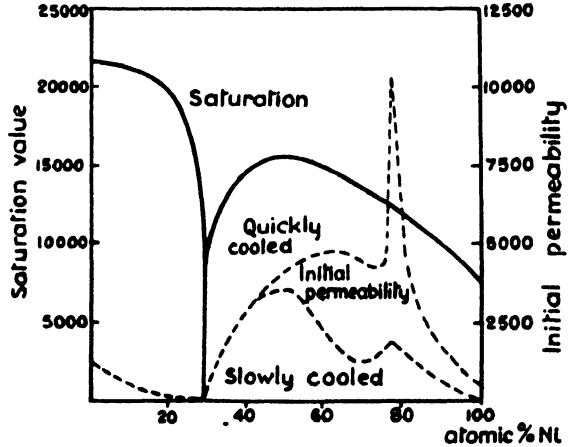

FIG. 116.—Magnetic properties of iron-nickel alloys.

For ferro-magnetic materials, the permeability μ is measured in place of the susceptibility κ, the two quantities being connected by the relation

$$\mu = 1 + 4\pi\kappa.$$

Very remarkable conditions are presented by the alloys of iron and nickel. The freezing-point curve indicates that solid solutions are formed by the γ-phases, there being a break in the liquidus at the $\delta\gamma$-peritectic.[3] The magnetic transformation temperature of iron is lowered by the addition of nickel, and that of nickel raised by the addition of iron, but the curve connecting these two points, instead

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[1] H. Endo, *Sci. Rep. Tôhoku Univ.*, 1927, **16**, 210.

[2] J. L. Haughton, *J. Sci. Instruments*, 1931, **8**, 7; F. Adcock, *J. Iron Steel Inst.*, 1931, ii, 99.

[3] D. Hanson and J. R. Freeman, *ibid.*, 1923, i, 301; R. Vogel, *Z. anorg. Chem.*, 1925, **142**, 193.

of being continuous rises to a maximum at 600° and 70 per cent. Ni, with an intermediate minimum at 25 per cent. Ni.[1] On the iron side of this point, that is to say, in alloys containing less than 25 per cent. Ni, there are two transformation curves, so that each alloy of the group has two critical temperatures, t_2 and t_1. The lower (t_1) curve falls much more steeply than the upper (t_2) curve. Between these curves each alloy is capable of existing in two conditions, a magnetic and a non-magnetic. A magnetic alloy loses its magnetism on heating at t_2, whilst an alloy cooling from a high temperature remains non-magnetic until t_1 is reached. In other words, the transformation is overstepped in both directions, the region lying between the two curves increasing in breadth with increasing nickel content, until the range within which both the magnetic and non-magnetic alloys may exist amounts to 600° when the nickel reaches 25 per cent. Beyond this limit the transformation becomes almost exactly reversible, and the curve with a maximum at 70 per cent. Ni represents the change both on heating and on cooling with fair approximation.[2]

This series of alloys presents further anomalies, even in the reversible series (Fig. 116). The alloy with 78 per cent. of nickel, known as permalloy, has an extraordinarily high permeability at low fields, and also very low hysteresis loss.[3] Similar properties, in a rather less marked degree, are shown by the 50 per cent. alloy, whilst ternary solid solutions, in which a part of the nickel is replaced by cobalt, have a permeability which is constant over a wide range.[4]

It is clearly impossible to draw general metallographic conclusions from magnetic observations of this kind, since the space lattice throughout the alloys just mentioned remains the same, and reference must be made to physical studies, such as that of McKeehan, for a discussion of the possible implications.

The fact, however, that strongly magnetic alloys have been produced from non-magnetic metals, introduces important metallographic considerations. The so-called Heusler alloys arose from a chance discovery. It was observed in 1892[5] that whilst ferro-manganese and ferro-aluminium are non-magnetic, ternary alloys containing only 10-14 per cent. of iron, the remainder being manganese and aluminium, are strongly magnetic, some members of the series being comparable with iron itself. The observation was subsequently made[6] that alloys of copper and manganese become magnetic when

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[1] F. Osmond, *Compt. rend.*, 1894, **118**, 532; F. Osmond and G. Cartaud, *Rev. Métall.*, 1904, **1**, 69; T. Kasé, *Sci. Rep. Tôhoku Univ.*, 1925, **14**, 173.

[2] For the magnetism of the nickel-iron alloys, see J. Hopkinson, *Proc. Roy. Soc.*, 1890, **47**, 23; C. E. Guillaume, *Compt. Rend.*, 1897, **124**, 176, 1515; **125**, 235; 1898, **126**, 738; W. C. Ellis and E. E. Schumacher, *Metals and Alloys*, 1934, 269; 1935, 26.

[3] H. D. Arnold and G. W. Elmen, *J. Franklin Inst.*, 1923, **195**, 621.

[4] G. W. Elmen, *ibid.*, 1929, **207**, 583.

[5] T. W. Hogg, *Chem. News*, 1892, **66**, 140.

[6] See F. Heusler, *Verh. deut. physikal Ges.*, 1903, **5**, 219; W. Stark and E. Haupt, *ibid.*, 222; E. Take, *ibid.*, 1905, **7**, 133.

aluminium, tin, antimony, bismuth, arsenic, or boron are added in certain proportions. The copper-aluminium-manganese alloys have been most fully investigated, and are found to behave in every respect as ferro-magnetic substances. Quenching from a high temperature frequently renders the alloys non-magnetic, their magnetic properties being developed by heating to 110° or 140.°

Certain binary compounds of manganese, such as Mn_4Sn, Mn_2Sb, MnSb, MnBi, Mn_3As_2, Mn_5P_2, MnP, and MnB, although not ferromagnetic, are very strongly paramagnetic.[1] The most typical of the magnetic ternary alloys are those which lie between the two compositions Cu_3Al and Mn_3Al.[2] The property proves to depend on the formation of a super-lattice. In the magnetic condition the alloys have a body-centred cubic structure,[3] and other phases which can be produced by heat treatment have not that property. In an alloy having the composition Cu_2MnAl the aluminium atoms form a super-lattice. If slowly cooled it is non-magnetic, and then gives an X-ray pattern corresponding with the compound Cu_9Al_4, manganese atoms simply replacing copper atoms at random. In the quenched condition the structure is very similar, but is now ordered, having a face-centred cubic super-lattice.[4] The magnetic properties are therefore associated with the presence of an ordered structure, and disappear when the solid solution becomes disordered.

Permanent magnets, having a high coercive force, are mostly steels containing carbide-forming elements, such as tungsten and chromium, in which diffusion takes place slowly, so that the steels may be kept in a fine-grained condition with considerable lattice distortion. By adding aluminium to a non-magnetic alloy of iron and nickel, however, an alloy is obtained [5] which with suitable heat treatment has a higher coercive force than any of the older steels, a fact which, together with the special properties of permalloy mentioned above, illustrates the great difficulty of predicting the magnetic properties of alloys from a knowledge of the equilibrium diagram.

COLOUR.

The optical properties of metals are mainly of physical interest, but certain relations between the constitution of alloys and their colour and reflecting power have been observed. The colour of different alloys may be compared by photographing the spectrum of each after repeated reflection.[6] The colour of eutectiferous series

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[1] E. Wedekind, *Ber.*, 1907, **40**, 1259 ; S. Hilpert and T. Dieckmann, *Verh. deut. physikal Ges.*, 1911, **44**, 2831.

[2] F. Heusler and F. Richarz, *Z. anorg. Chem.*, 1909, **61**, 265.

[3] E. Persson, *Naturwiss.*, 1928, **16**, 613 ; *Z. Physik*, 1929, **57**, 115 ; H. H. Potter, *Proc. Physical Soc.*, 1929, **41**, 135.

[4] A. J. Bradley and J. W. Rodgers, *Proc. Roy. Soc.*, 1934, **144**, A, 340.

[5] Known as Mishima alloys. See W. S. Messkin and B. E. Somin, *Arch. Eisenhüttenw*, 1935, **8**, 315.

[6] M. Kuroda, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **12**, 308.

is, as might be expected, an additive property, but this is not true of solid solutions, and compounds may be marked by singular points in the curves of colour and of reflectivity,[1] especially for ultra-violet light.[2] The colour of the alloys of copper and nickel has been compared by using a rotating disc of copper, which can be covered more or less completely by sectors of nickel.[3] The colour of the alloys proves not to be additive, nickel having a bleaching power which is large in proportion to the amount present, so that from 25 per cent. Ni onwards the alloys are practically white. This is attributed to deformation of the electronic shells by the mutual interference of the two kinds of atoms.

Cold working of alloys produces changes in colour which are parallel with those of electrical resistivity.[4] Cold-working silver shifts the minimum in the ultra-violet towards longer wave-lengths, and this has been connected [5] with the diminution in density produced at the same time.[6]

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[1] M. Chikashige, *Z. anorg. Chem.*, 1922, **124**, 336; 1926, **154**, 333.
[2] H. Kotô, *Mem. Coll. Sci. Kyoto Univ.*, 1929, **12**, 81.
[3] J. A. M. van Liempt, *Rec. trav. chim.*, 1927, **46**, 8.
[4] G. Tammann and C. Wilson, *Z. anorg. Chem.*, 1928, **173**, 156.
[5] H. Margenau, *Phys. Rev.*, 1932, [ii], **40**, 800.
[6] H. Honda and Y. Shimizu, *Sci. Rep. Tôhoku Univ.*, 1931, **20**, 460.

CHAPTER XV.

ELECTROLYTIC POTENTIAL AND CORROSION.

THE electrolytic potential of metals has an importance in physical chemistry, and is one of the factors determining the liability of a metal to corrosion. The potential of alloys was formerly used as one of the diagnostic characters in constructing the equilibrium diagram, but it has not realized expectations, on account of the many sources of error in the determinations. An alloy in contact with a solution of an electrolyte undergoes surface changes, so that the potential changes with time, whilst if the alloy be heterogeneous, local couples are set up between the constituents. It is therefore difficult to decide as to the value in a given experiment which is to be regarded as representing an equilibrium between the alloy and the solution.

It is usual to determine the potential of a metal in a solution of one of its salts by coupling it with a calomel electrode, that is, one of mercury in contact with mercurous chloride. Tables of single potentials are given in text-books of physical chemistry,[1] referred to the hydrogen electrode (blackened platinum saturated with hydrogen, in $N/1$ acid) as a standard. The metals have been employed in the form of a fine mass of crystals prepared by rapid electrolysis, such a mass giving more uniform results than a solid aggregate of cast or wrought metal. A single crystal might be expected to give a more reproducible potential than an aggregate, and this has been verified for zinc,[2] using a basal plane obtained by cleavage at the temperature of liquid air, followed by warming to 200°-250° under paraffin to remove strain. About 48 hours are required to reach equilibrium in zinc chloride solution, and the final value is accurately reproducible and identical with that for electrolytically prepared crystals. Etching accelerates the attainment of equilibrium, but does not alter the final value. Small quantities of impurities have little effect, which accords with the conclusions, mentioned below, which have been drawn from observations on alloys. In the cell

$$Zn/ZnCl_2\ (0{\cdot}5\ M)/HgCl/Hg$$

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[1] R. A. Lehfeldt, "Electro-Chemistry," London, 1920, p. 159; R. Kremann, in Guertler's "Metallographie," Berlin, 1921, II, i, (3), p. 21.

[2] P. A. Anderson, *J. Amer. Chem. Soc.*, 1930, **52**, 1000.

the potential difference is 1·0780 v. Using N/1 $ZnSO_4$ as the electrolyte, the value 1·077 v. was obtained for the basal plane of a single crystal, and 1·110 v. for a cast aggregate.[1] Different crystallographic planes should give different values, but the accuracy of the method does not allow of their detection.

The subject of electrolytic potential will only be considered here so far as it concerns alloys. The potential of alloys has most often been determined in a solution of the more positive[2] metal, but some investigators have used solutions containing salts of both metals. The conditions under which equilibrium can be attained with a mixed electrolyte have been much discussed,[3] but in practice the conditions are always complicated by changes in the surface of the alloy, which make it difficult to decide as to the value to be taken as representing the potential. Formulæ have been given for the calculation of the concentrations of alloy and of electrolyte, based on Nernst's formula[4] for the "solution pressure," but they have little metallographic usefulness, and the solution pressures of the more noble metals assume fantastically small values. The theoretical treatment may therefore be omitted.[5] A few of the experimental conclusions may, however, be quoted.

I. The two metals form a simple eutectiferous system, without either solid solutions or intermediate phases. This is naturally only a limiting case, but the range of solid solutions at the two ends of the series may be very small, when it is nearly approached. The electrolyte used is in most experiments a solution of an ionized salt of the more positive metal, usually of normal (N/1) concentration. The potential observed is constant throughout the whole range of composition, being always that of the more electro-positive metal.

II. The two metals form a continuous series of solid solutions. Assuming the alloys to have been made uniform by annealing, the potential is found to vary continuously from one end of the series to the other. Soon, however, changes in the composition of the surface layer take place, owing to the passage of ions into solution. The effect does not then vary continuously with the composition, but abrupt changes may be found at or near to simple atomic ratios. Such sudden jumps are called by Tammann[6] "resistance limits," and have been brought into relation with the atomic arrangement

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[1] K. H. Kreuchen, *Z. physikal. Chem.*, 1931, **155**, A, 161.

[2] The term "Positive" is here used to imply that the metal would, by sending out positive ions, become the anode, when combined with a standard, such as the hydrogen electrode. The opposite convention is also frequently used. To avoid confusion, in the discussion of corrosion, etc., the term "anodic" will be preferred.

[3] M. Herschkowitsch, *Z. physikal. Chem.*, 1898, **27**, 123; W. Reinders, *ibid.*, 1903, **42**, 225; R. Kremann, *Z. Metallk.*, 1920, **12**, 185.

[4] W. Nernst, *Z. physikal. Chem.*, 1889, **4**, 129.

[5] A modified Nernst equation, leading to more reasonable values, is given by A. W. Porter, *Trans. Faraday Soc.*, 1923-24, **19**, 817.

[6] G. Tammann, *Z. anorg. Chem.*, 1919, **107**, 1.

within solid solutions. The limits may vary according to the nature of the electrolyte, and this has also been explained by the geometrical arrangement of the lattice. The limits are not actually very sharp, and for the controversies on this subject reference should be made to the original papers.[1] It has long been known that the separation or " parting " of gold from silver in the process of assaying is only possible when at least twice as much silver as gold is present in the specimen, otherwise nitric acid only dissolves the silver incompletely. The gold atoms protect the silver in the interior unless sufficiently open channels be formed in the process of solution. In this instance only silver is dissolved, but when brass is attacked chemically both copper and zinc pass into solution, although in very different proportions, so that a sharp limit is not to be expected. The view of Tammann is of historical importance, since it led to the idea of a possible difference between metallic lattices which has since been discovered to exist, namely, that between " ordered " and " disordered " lattices, discussed in Chapter XX.

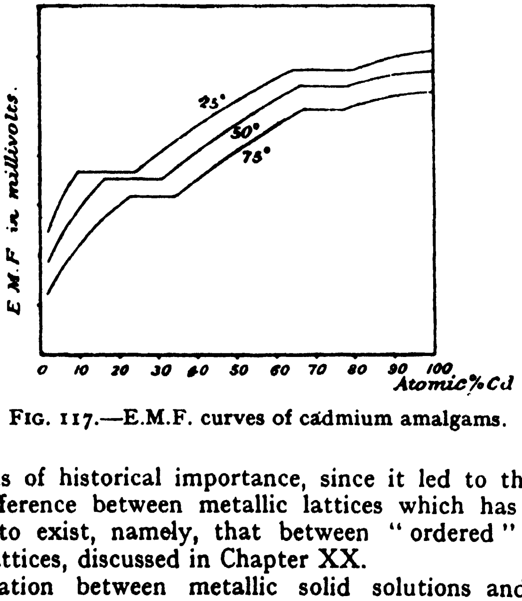

FIG. 117.—E.M.F. curves of cadmium amalgams.

The relation between metallic solid solutions and a mixed electrolyte is illustrated by qualitative experiments, in which the alloy is brought into contact with a solution containing a salt of the more positive metal. Thus zinc, or alloys containing a phase rich in zinc, will precipitate copper from its salts, even when the concentration of copper ions is very small, as in copper cyanide or cupric ammonium salts. Alloys of copper and zinc containing from 100 to 59 per cent. of zinc behave thus. With 55–40 per cent. of zinc, the β-phase being present, the alloys will precipitate copper from the ammonium compounds, but not from the cyanide, whilst the α-alloys

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[1] G. Masing, *Z. anorg. Chem.*, 1921, **118**, 293 ; M. Le Blanc, K. Richter, and E. Schiebold, *Ann. Phys.*, 1928, [iv], **86**, 929 ; 1929, [v], **1**, 318 ; G. Tammann, *ibid.*, 1929, [v], **1**, 309, 321.

will only precipitate copper when the ionic concentration is high, as in solutions of the chloride.[1]

III. The two metals form series of solid solutions separated by a gap. Within the limits represented by the gap, two phases of constant composition are present, and the condition is similar to that of simple eutectiferous alloys. The potential therefore remains constant within this range, but varies continuously within each range of solid solution. Such a condition is represented by the cadmium amalgams, the E.M.F. curves of which, for three different temperatures, are shown in Fig. 117.[2] The width of the gap diminishes with rise of temperature, and the measurements were, in fact, used to determine the slope of the lines DP and EQ in Fig. 13. On each E.M.F. curve, the first horizontal section represents the interval between the liquidus and solidus curves, and the second the gap between the solid solutions.

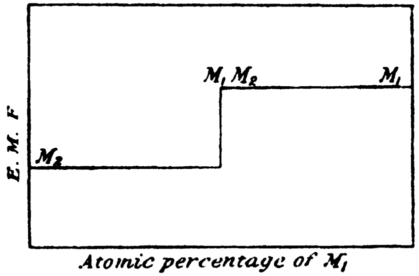

FIG. 118.—Ideal curve for system with one intermetallic compound.

IV. Intermediate phases are formed. The electrolytic potential method was formerly used very widely as a means of determining the composition of intermetallic compounds. In an ideal system, containing a single compound and with no solid solutions, the E.M.F. composition curve would have the form shown in Fig. 118. Should any range of solid solutions occur, the curve within the range of their composition would be sloping, and it should be noted that a change in direction indicates the appearance of a new phase, and not the composition of any compound which may occur within that phase. For this reason the method has lost favour as a means of fixing the composition of "intermetallic compounds," although it has recently been revived, as described below, as an auxiliary method for the determination of the phase limits in an alloy system.

A few examples of the results obtained by the older methods are shown in Fig. 119, being taken from the work of Pushin and his collaborators.[3] The antimony-bismuth curve corresponds with a continuous series of solid solutions, as found by thermal analysis.[4] The antimony-nickel curve indicates that two intermediate phases are formed. Of these, NiSb is clearly indicated by the thermal

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[1] O. Sackur, *Arb. k. Gesundheitsamt.*, 1904, **20**, 513; **22**, 187; *Ber.*, 1905, **38**, 2186; O. Sackur and H. Pick, *Z. anorg. Chem.*, 1908, **58**, 46.

[2] H. C. Bijl, *Z. physikal. Chem.*, 1902, **41**, 641.

[3] N. A. Pushin, *J. Russ. Phys. Chem. Soc.*, 1907, i, 13, 353, 528, 869; N. A. Pushin and P. Laschtschenko, *Z. anorg. Chem.*, 1909, **62**, 34.

[4] B. Obata, *Sci. Rep. Tôhoku Univ.*, 1925, **13**, 293.

method, whilst a second maximum on the liquidus corresponds rather with the composition Ni_5Sb_2.[1] The lead-tin curve shows a eutectiferous system with a range of solid solutions at the lead end. The lead-platinum curve has two breaks, which correspond with two of the intermediate phases found by thermal analysis, although the phase diagram appears to be more complex.[2]

Fused salts have been used as electrolytes in the examination of alloys with the object of determining the phases present at high temperatures. Thus, in the study of the copper-zinc alloys,[3] the difference of potential between solid or liquid zinc and the solid alloys was measured over the range 333°-626°, the electrolyte being a fused mixture of lithium and rubidium chlorides with zinc chloride. The same author has applied the method to other series of alloys, the results usually agreeing closely with those found by thermal analysis.[4] The electrolytic potential method can, however, only be regarded as of secondary importance as a means of determining constitution for reasons given above.

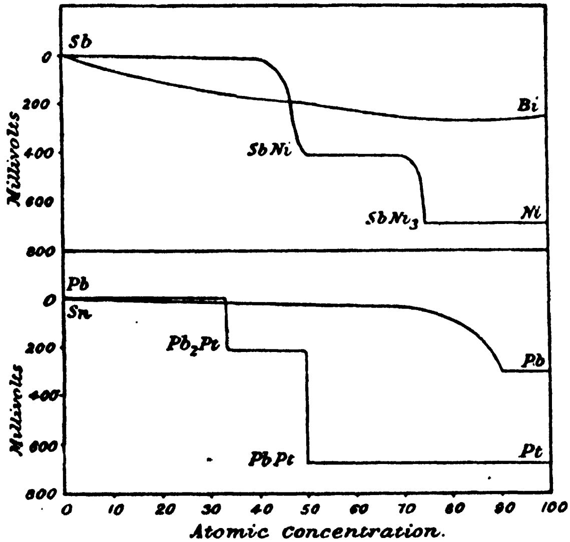

FIG. 119.—Typical E.M.F. curves of alloys.

The electrolytic potential method may also be used to study allotropic change. Since two allotropic modifications of a metal will, in general, differ in the amount of energy they contain, they

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[1] K. Lossew, *Z. anorg. Chem.*, 1906, **49**, 58.

[2] F. Doerinckel, *ibid.*, 1907, **54**, 358.

[3] A. Ölander, *Z. physikal. Chem.*, 1933, **164**, A, 428.

[4] A. Ölander, *ibid.*, 1934, **168**, A, 274 ; **169**, A, 260 ; 1935, **171**, A, 425 ; **173**, A, 284.

may be expected to assume different potentials when brought into contact with the same electrolyte. An example of such use is the study of the transformation of grey into white tin. A cell is made up, the electrodes of which are grey and white tin respectively, the electrolyte being a solution of ammonium stannichloride.[1] The E.M.F. of the cell is then determined at successive intervals of temperature from 5° upwards. At 18° the difference of potential becomes zero, proving this to be the transition temperature, above which white tin is stable, grey tin being stable below it, although as a rule the velocity of the change white → grey is very low. Some instances of allotropy among metals which have been described on the strength of measurements of this kind are, however, probably due to changes produced by cold-working, so that the electrolytic potential method must be used with caution and confirmed by other means.

A metal which has been plastically deformed will have a different potential from the same metal in the soft or annealed state. In general, the strained metal, containing stored potential energy, will be anodic to the unstrained. By using metals extruded through a narrow orifice, Spring[2] found differences of potential between the extruded and the annealed metal which were usually less than a millivolt. The existence of such a difference is of importance for the process of corrosion, as described below. It also introduces another difficulty into the measurement of electrolytic potential, as the electrolytic behaviour of a metal surface will vary according to the way in which it has been prepared: by grinding, by rubbing with emery paper, by polishing, etc.

THE PASSIVE STATE.

That iron, after heating in air or dipping in nitric acid could be made the anode in an electrolyte and allow of the production of free oxygen without itself being dissolved, was first noticed in the eighteenth century,[3] and brought to the attention of Faraday by a Swiss correspondent.[4] This "passive" state, as Schoenbein called it, was fully investigated by Faraday, who attributed it to oxidation of the surface, his conclusions being expressed cautiously, leaving it open whether the layer was one of a definite oxide, or one of oxygen atoms associated in some less definite way with the metal. More complex explanations have since been proposed,[5] but none fits the facts so completely as that of Faraday, for which direct evidence has since been obtained.

The formation of an oxidized film, highly protective against

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[1] E. Cohen and C. van Eijk, *Z. physikal. Chem.*, 1899, **30**, 601; E. Cohen, *Trans. Faraday Soc.*, 1911, **7**, 122.

[2] W. Spring, *Bull. Acad. roy. Belg.*, 1903, 1066.

[3] J. Keir, *Phil. Trans.*, 1790, 374.

[4] Letter from C. T. Schoenbein to Faraday, 17 May, 1836. See M. Faraday, *Phil. Mag.*, 1836, [iii], **9**, 122; and "Experimental Researches in Electricity."

[5] A. Smits, "The Theory of Allotropy," in this series, 1922, p. 337.

chemical attack, was an old experience of workers in steel, the colour of the film varying with its thickness, and being used as a means of determining the temperature to which the steel had been heated. By careful thinning of the film by dissolving in very dilute nitric acid [1] or by cathodic reduction [2] the succession of colours may be passed through in the reverse order, confirming the view that the tints are due to interference, a conclusion which has sometimes been disputed. The films are not always continuous, and a granular structure will give rise to tints which differ somewhat from those produced by interference. The film which is the cause of passivity is regarded as being of the same nature, but as too thin to show colour. It is resistant to oxidizing agents, and prevents the iron from displacing copper or silver from solutions of their salts, this being a simple and convenient test for passivity. Mere exposure of a clean surface of iron to air for a few minutes is enough to produce a passive film which will resist some degree of attack. A strong film, such as is formed by immersion in a dichromate solution, may be isolated by dissolving away the metal in a solution of iodine in potassium iodide,[3] leaving a transparent film which, however, is probably thicker than that which was present on the solid metal, owing to reinforcement during the process of isolation. It appears to have the properties of the oxide Fe_2O_3, and is removed by heating in nitric acid to the temperature at which freshly ignited ferric oxide is attacked.[4] Although invisible, it affects the reflectivity of the iron, the optical measurements indicating a film of mean refractive index 3·0 and a thickness of 30 Å., which would agree well enough with the supposed layer of ferric oxide.[5] Its presence also lowers the photoelectric activity of the iron.[6]

The film on aluminium may be isolated by heating in a stream of dry hydrogen chloride, which removes the metal as the volatile chloride.[7]

When the layer of oxygen on the surface is too thin to form a film with a definite refractive index, it may yet be protective, and may be detected by other means. X-rays, even at glancing incidence, penetrate too deeply, but beams of electrons reveal a structure, as described earlier (p. 184). The chemical resistance of stainless steel, containing chromium, is due to a very thin layer of this kind, which is quickly re-formed after abrasion. This fact helps to show the uselessness of the concept of "solution pressure." The addition of chromium to iron could not appreciably lessen its tendency to send out ions into solution; on the contrary, chromium is more electropositive than iron. Its effect in increasing chemical resistance is

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[1] C. W. Mason, *J. Phys. Chem.*, 1924, **28**, 1233.
[2] U. R. Evans, *Proc. Roy. Soc.*, 1925, **107**, A, 228.
[3] U. R. Evans, *J. Chem. Soc.*, 1927, 1020.
[4] E. S. Hedges, *ibid.*, 1928, 969.
[5] L. Tronstad, *Nature*, 1931, **127**, 127.
[6] H. S. Allen, *Proc. Roy. Soc.*, 1913, **88**, A, 70.
[7] W. H. Withey and H. E. Millar, *J. Soc. Chem. Ind.*, 1926, **45**, 170 T.

solely due to its power of forming a permanent film. Similarly, aluminium, which is very strongly electro-positive, is surprisingly resistant to attack by air, on account of its ready formation of a film of considerable strength, as mentioned in Chapter X (App.).

Aluminium, tantalum, and other metals which exhibit "valve action," when rendered anodic in suitable solutions, build up films of such thickness and texture as to offer a high resistance to the passage of a current, whilst when made cathodic the current passes freely, so that the plate serves as a rectifier for alternating current. Copper rapidly tarnishes in ordinary air, owing to the action of sulphur compounds, but if a clean surface be first heated to 75°-100° in pure air, a quite invisible film is produced, which serves as a protection against the atmosphere of a town.[1]

Immersed metals may become passive through the formation of layers of salts as well as of oxides.[2]

CORROSION.

The term corrosion is used to include all cases of wastage of metals and alloys by chemical action, but it is usually convenient to exclude direct solution in an acid or other reagent, when the product is removed in solution as fast as it is formed. That the mechanism of such direct solution depends on the crystal structure, resulting in etch-figures, has been shown in Chapter VIII. Atmospheric action producing a superficial coloured film, without deeper attack, is described as tarnishing, whilst the term rusting is usually confined to iron and its alloys, being associated with the formation of a spongy corrosion product. That corrosion is essentially electrochemical in its nature was maintained long ago by Faraday, and has been amply confirmed, although the idea has been often misunderstood, with the result of causing much superfluous discussion. The literature of corrosion is very voluminous, and there is a great disproportion between the mass of experimental data and the positive results. Most research in this field has consisted in exposing specimens of different metals and alloys to corroding influences, and determining the loss of weight of each specimen in a given time. Owing to the number of factors which are known to be involved, this method has been disappointing, and it is only in recent years that attention has been turned to the study of the separate factors, with the result that some insight is now being gained into the process. At the same time, there is no laboratory test which will predict with certainty the behaviour of a given material when exposed, unless the exposure be under very simple conditions, such as complete immersion in still water of known temperature and composition. In atmospheric

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[1] W. H. J. Vernon, *J. Chem. Soc.*, 1926, 2273.

[2] W. J. Müller and W. Machu, *Z. physikal. Chem.*, *Bodensteinfestband*, 1931, 687; W. J. Müller, H. K. Cameron and W. Machu, *Sitz. Akad. Wiss. Wien. Math.-naturw. Kl.*, IIb, 1931, 501, and other papers.

corrosion, the great variability of the weather is the most disturbing factor, whilst the differences between climates often outweigh any difference between materials. Thus, in one important series of experiments,[1] in which specimens have been exposed at fourteen different stations, ranging from the highly polluted atmospheres of certain industrial towns to the moist tropical atmosphere of Singapore and the dry, unpolluted atmosphere of Khartoum, in the Sudan, very wide ranges in the degree of rusting have been found, plates exposed at the last-named station having formed only a fine, even layer of rust after nearly five years' exposure, and the difference between specimens of iron and steel of different composition being small compared with the differences between stations.

Corrosion being normally electrolytic in character, it involves conditions which will allow of a voltaic circuit being set up. It is a familiar fact that metals of high purity are less readily attacked by acids than impure metals, pure tin, for instance, being hardly acted on by hydrochloric acid, so that in order to bring it into solution it is usual to add a little platinum chloride to the acid, when by precipitating spongy platinum on the surface, local couples are established. The highly purified aluminium and zinc now commercially available are also very inactive towards acids. (The term pure is, of course, only relative, as even the most highly purified metals contain large numbers of foreign atoms.) Early experiments on the rate of solution of metals indicated that the process was dependent on the formation of local circuits.[2]

The electrolytic potential of a strained metal being different from that of the same metal in an unstrained state, strained areas on the surface of a specimen may suffice to provide the necessary local couples. As it is difficult to prepare any metallic specimen free from surface strain, this cause is responsible for the initiation of corrosion in many experiments conducted with metals supposed to be pure. It may be shown that anodic and cathodic areas are formed on any piece of iron which is undergoing corrosion by the following device.[3] A dilute solution of potassium ferricyanide and phenolphthalein in water is thickened with gelatin to prevent convection currents. If a piece of iron is immersed in this reagent, blue areas appear wherever the iron is anodic, owing to the formation of ferrous ferricyanide where ferrous iron is passing into solution, and a pink area at each cathode, owing to the setting free of alkali at that point. This "ferroxyl" reagent is a sensitive means of detecting corrosion.

The factor which was formerly overlooked, but proves to be of the greatest importance, is the nature of the corrosion product. Aluminium, as mentioned above, forms a layer of oxide which is

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[1] *Reports of the Corrosion Committee* (*Iron and Steel Inst.*, 1926-36).

[2] T. Ericson-Aurén and W. Palmaer, *Z. physikal. Chem.*, 1901, **39**, 1; 1903, **45**, 182; 1906, **56**, 689.

[3] W. H. Walker, *J. Iron Steel Inst.*, 1909, i, 69; A. S. Cushman, *Trans. Amer. Electrochem. Soc.*, 1907, **12**, 403.

highly protective, but when the surface is lightly amalgamated, couples are set up, and the product is a loose, porous mass, which affords no protection, and allows the reaction to go on so fast that heat is rapidly developed. Even without an accelerating agent, in a tropical climate, the coating may be formed so fast as to be porous, when it ceases to be protective. It is well known that the addition of 1 per cent. of tin to brass greatly increases its resistance to sea water. This is not due to any alteration of potential, which would be trivial, but to the formation of a layer of basic tin chloride, which adheres like a varnish, and affords a purely mechanical protection.[1] There are three types of product: (*a*) a loose granular layer which allows the passage of gases to the metal; (*b*) a continuous film, such as that described under passivity, allowing access of gases only by diffusion; and (*c*) an impervious layer which may fail locally by cracking when thick. Under atmospheric conditions, the first is illustrated by zinc, the second by copper and silver, and the third by lead. Iron rust is a typical porous corrosion product, which does not afford protection, and by its electro-negative character provides cathodic areas which accelerate corrosion.

The most satisfactory conclusions have been reached in the study of atmospheric corrosion.[2] Exposure to natural atmospheres having given conflicting results, the plan has been adopted of using synthetic atmospheres, and of keeping all the conditions as far as possible comparable. Using square sheets of 5 cm. side, suspended from a single hole, and prepared by rubbing on fine emery paper followed by washing with carbon tetrachloride to remove grease, the change in weight may be determined with an accuracy of 0·1 mg. Experiments with copper show that in dry air the addition of sulphur dioxide is without effect, but that the addition of water vapour brings about attack, the form of the curves showing increase of weight with time indicating that the process is controlled by the catalytic oxidation of sulphur dioxide at the surface. There is a critical humidity, and the effect of sulphur dioxide is a minimum when its concentration is about 1 per cent. With such an atmosphere the product of corrosion is normal copper sulphate, whilst with more sulphur dioxide it contains an excess of sulphuric acid, and with less a basic salt is formed. Carbon dioxide has no accelerating effect, whilst hydrogen chloride attacks the metal rapidly, forming films of cuprous chloride. Arsenic in copper is known to increase the resistance to atmospheric corrosion, and this effect is shown to be due to a reduction in the hygroscopic character of the corrosion product.

The several types of corrosion product mentioned above may be distinguished by the form of the curves representing the increase of weight with time. A compact film, which grows only by diffusion

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[1] S. Whyte and C. H. Desch, *J. Inst. Metals*, 1914, **11**, 235.
[2] W. H. J. Vernon, *Trans. Faraday Soc.*, 1931, **27**, 255; 1935, **31**, 1668.

through its thickness, increases according to a parabolic law: $w^2 = Kt$.[1] On the other hand, one which is porous, so that gases can pass through it between the grains, increases in a linear manner. In oxidation at high temperatures, the nature of the film was shown by Pilling and Bedworth to depend on the change of volume produced by oxidation. W and w being the molecular weights of the oxide and the formula weight of the metal, respectively, and D and d their respective densities, a compact layer is formed if $Wd/wD > 1$, whilst if it be less than unity, shrinkage occurs and the film becomes porous. It should be added that as the thickness increases cracking frequently occurs, and fragments become detached. In the rolling of iron and steel, for instance, a thin scale may be protective, but a thicker one will flake off and expose new surfaces. Reference to the Reports of the Corrosion Committee will show the importance of this factor in the exposure of steel to the atmosphere or to sea water.

The oxidized film on iron undergoes a change of texture at so low a temperature as 200°, below which it increases according to a parabolic, and above it to a linear law. Electron diffraction assigns the structure of a cubic oxide to the low-temperature film, and of a rhombohedral oxide at the higher temperature, the latter also showing orientation,[2] and orientation is probably an important factor in determining the protective properties.

The rusting of iron differs from the production of a uniform film by being essentially local. It begins at a few spots, and spreads outwards. Since the corrosion product is in this instance very porous, its presence accelerates rusting, and it is a familiar fact that a surface of iron or steel may remain bright for a long time, but that when a few spots have appeared the attack continues rapidly. The nature of the process has been the cause of much discussion. A specimen of highly purified iron rusts with difficulty in moist air,[3] and it has usually been assumed that the presence of carbon dioxide is necessary for rusting to occur. Iron has been supposed to pass into solution as a soluble salt (in this instance a hydrogen carbonate) which then reacts with oxygen, precipitating a hydrated ferric oxide which forms the basis of rust. Some local difference of potential must exist on the surface to initiate the process. The work of Vernon,[4] however, indicates rather surprisingly that carbon dioxide will not start corrosion, and that the active constituent in ordinary air is sulphur dioxide. Particles of dust also exert an effect, so that enclosing a specimen of iron in a muslin cage will allow it to remain bright.

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[1] G. Tammann, *Nachr. k. Ges. Wiss. Göttingen*, 1919, 225; G. Tammann and W. Köster, *Z. anorg. Chem.*, 1922, **123**, 196; N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, 1923, **29**, 529; J. S. Dunn, *Proc. Roy. Soc.*, 1926, **111**, A, 203, 210.

[2] G. D. Preston and L. L. Bircumshaw, in W. H. J. Vernon, *Trans. Faraday Soc.*, 1935, **31**, 1668.

[3] B. Lambert and J. C. Thomson, *J. Chem. Soc.*, 1910, **97**, 2426.

[4] *Loc. cit.* and *Trans. Amer. Electrochem. Soc.*, 1933, **64**, 31.

Particles of ammonium sulphate are the most active. The rusting depends very greatly on the humidity.

Iron rust, which under wet conditions contains ferrous hydroxide as well as the ferric compound, contracts and loses water in time, so that ancient specimens consist mainly of hard, crystalline goethite, Fe_2O_3, H_2O.

The conditions when a metal is corroding in a liquid are somewhat different. Most of the experimental work on the subject has been based on determinations of the loss of weight of specimens immersed under given conditions, but these throw little light on the nature of the process.

When a metal or alloy is exposed to the action of an electrolyte, the products of corrosion may present themselves in five different forms, which are not distinguished from one another by any determinations of loss of weight. These are (*a*) the material actually dissolved and remaining in solution; (*b*) the loose, flocculent precipitate of basic salts which is often formed in salt solutions; (*c*) the adherent film of basic salts which in some cases has the properties and effect of a tough, protective varnish; (*d*) the metallic layers, such as the spongy layer of copper left after the removal of zinc from brass; and (*e*) crystals mechanically dislodged from the specimen by solution of the material surrounding them. All these products are removed when the specimen is brushed or scraped before re-weighing, but their relative quantity is unknown, although the power of a metal or alloy to resist corrosion depends in no small measure on the ratio between these quantities.

There are essentially two types of attack on a metal or alloy by an electrolyte. In the first, the local couples which have been set up lead to the evolution of hydrogen at the cathodic areas, and if this hydrogen can form bubbles and escape, the action can continue indefinitely. Should, however, the composition of the electrolyte and the over-potential of the cathodes be such that hydrogen bubbles cannot form, the process comes to an end, and can only continue if oxygen can reach the cathodes and cause depolarization. The attack is then controlled by the supply of oxygen by diffusion or otherwise.[1] The distinction between the "hydrogen-evolution" and "oxygen-diffusion" types of corrosion (these convenient terms are due to Evans) is important in determining the course of corrosion. The first is the simpler in character. It involves the setting up of a voltaic circuit, so that a specimen of metal of high purity is little acted on. Most commercial metals contain small particles of impurities which can serve as cathodes. Commercial zinc, for instance, contains particles of lead. On first immersing the metal in an acid, the attack may be very slight, few lead particles being exposed at the surface, but as solution progresses, more and more local couples are formed, and the reaction is accelerated. There is thus commonly

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[1] W. H. Walker, A. M. Cederholm and L. N. Bent, *J. Amer. Chem. Soc.*, 1907, **29**, 1251.

a period of induction in corrosion of this kind. In alloys which consist of two or more phases the conditions for a voltaic circuit are clearly present, and the phase which becomes anodic is attacked, the other remaining unchanged in appearance. For instance, an α-β brass, corroded naturally in sea water or by applying an external E.M.F. in a laboratory experiment, shows an attack on the β constituent, which is replaced by spongy copper, and only after this replacement is complete to some depth does an attack on the α constituent begin.[1] The final result is the production of a pseudomorph of the original object, such as a bolt, in spongy copper. The original micro-structure may sometimes be recognized, even in a completely corroded object. In an aluminium alloy containing copper, the attack is seen under the microscope to follow closely the outline of the inclusions of $CuAl_2$.[2] Local cold-working tends to produce anodic areas, so that corrosion is very liable to occur in such positions as the deformed region around a punched hole in a boiler plate, or even at a mark made by a marking punch.

For corrosion of the hydrogen evolution type [3] it is not essential that the electrolyte should be acid. Attack can take place in neutral or, with metals such as zinc, which form hydroxides soluble in alkalies, in alkaline solutions. In the examination of the alloys of aluminium, the formation of anodic and cathodic areas can be seen by covering the surface with a solution of gelatin containing a neutral salt and a " universal " indicator, which gives a range of colours, with different degrees of acidity and alkalinity. The cathodic regions become alkaline and the anodic acid, the differences mainly indicating local cold working.[4]

General corrosion, or the removal of a layer of uniform thickness from the whole surface of the metal, must be distinguished from local corrosion or " pitting," the removal of metal from small localized areas. In practice, the second is by far the more serious, as a uniform wasting, if slow, only affects the strength of the metal appreciably after a long time, whilst the formation of local pits may lead to complete perforation of a plate or similar object. Pits may arise from inclusions, forming local couples, or in other ways discussed below. A pit having once formed tends to deepen itself.

In the quantitative study of the corrosion of metals under immersed conditions, it is desirable to be able to measure the amount of hydrogen evolved and also that of oxygen absorbed. Apparatus of great precision has been devised by Bengough, the final form being somewhat elaborate.[5] The specimens are immersed horizontally at a constant depth.

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[1] S. Whyte, *J. Inst. Metals,* 1915, **13**, 80.

[2] C. H. Desch, *Trans. Faraday Soc.*, 1915, **11**, 198.

[3] This type has been very fully studied by W. Palmaer, *Ing. Vetensk. Akad. Handl.*, 1929, No. 93; 1931, No. 108.

[4] M. Prot and N. Goldowski, *Rev. Métall.*, 1934, **31**, 214.

[5] G. D. Bengough and F. Wormwell, *J. Iron Steel Inst., Corrosion Com. 3rd Rep.*, 1935, 123. A simplified form is described by the same authors in the 4th Report, 1936, 213.

In solutions of alkali chlorides of various concentrations, acid fumes being excluded, the curves showing the loss of weight with time or the absorption of oxygen with time are nearly straight lines over a considerable range, when continued for many weeks. Deviations from the linear character are shown by the authors to be characteristic, so that the course of the reaction can be inferred from a study of their form. In the later stages, the deviations are mainly caused by the accumulation of insoluble corrosion products. When this is prevented, as by the addition of sodium citrate to the solution in which iron or steel is corroding, the action goes on at an accelerated rate.

The extent of pitting is usually determined by turning or planing away the surface of the specimen until the bottom of the deepest pit is reached, and measuring the reduction in thickness.

The "electrochemical series" of the text-books, in which the metals are arranged in order of their single potentials, is of little value as an indication of their relative corrodibility, on account of this factor of the corrosion product. A metal such as aluminium, which rapidly covers itself with a protective film, is often more resistant than metals far to the negative side of it in the series. However, the series may be useful in indicating combinations of metals which should be avoided in technical practice, such as the use of bronze in contact with steel in a natural water of high conductivity, the conditions being then such that protective films are broken down by voltaic action.

The type of corrosion which is conditioned by the supply of oxygen has been the subject of much controversy. The nature of the corrosion-product becomes of the highest importance. A significant fact, on which much of the discussion has been based, is that iron rusting in water is preferentially corroded where covered with a mass of wet rust, and that even inert substances, such as filter paper or gelatin, can accelerate corrosion, the cause being the shielding of the iron at that point from access of oxygen.[1] This aspect of corrosion, known as "differential aeration," has been particularly stressed by Evans.[2] Pitting is then attributed to limitation of access of oxygen, in part by formation of "oxygen concentration cells," and as the supply of oxygen to the interior of a pit is obviously less abundant than on the free surface, a pit once formed tends to become deeper.

Bengough and his colleagues [3] lay most stress on the formation of protective films as the cause of the localization of corrosion. The product of corrosion may exert either an accelerating or a retarding effect. When the film is of a protective kind, it renders the metal on which it is formed cathodic to unprotected portions, but where

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[1] J. Aston, *Trans. Amer. Electrochem. Soc.*, 1916, **29**, 449.

[2] U. R. Evans, *J. Inst. Metals*, 1923, **30**, 239 ; U. R. Evans, L. C. Bannister and S. C. Britton, *Proc. Roy. Soc.*, 1931, **131**, A, 355 ; and many other papers.

[3] G. D. Bengough, J. M. Stuart and A. R. Lee, *ibid.*, 1927, **116**, A, 425 ; 1928, **121**, A, 88 ; and many other papers.

it is loosely adherent its effect may be the opposite. In general, a film formed immediately on a metal surface is likely to be protective, but a product of corrosion in the form of a precipitate thrown down at a distance from the cathode (as by the oxidation of a soluble ferrous salt, or by a reaction between a dissolved salt and alkali hydroxide formed at a cathodic area) is not protective, and may act as an accelerator. There is no real incompatibility between the two views. Conclusions derived on the one hand from experiments with totally immersed specimens under very strictly controlled conditions, and on the other from much shorter experiments, largely with drops, do not necessarily conflict, and for a complete theory of corrosion both must be taken into account. The work of Bengough consists in the determination of corrosion-time curves over long periods; that of Evans is largely concerned with the initial stages of corrosion.[1]

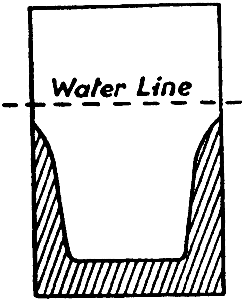

FIG. 120.—Corrosion at edges of partly immersed specimen.

When a plate of metal is only half immersed in an electrolyte, there is commonly an intense attack at or near the water line, and the specimen may be eaten through at that level before general attack has become serious. Attempts to explain this effect have been prominent in discussions on corrosion. It is well to remember that similar effects are seen in cases of simple solution.[2] A stick of sodium hydroxide, half immersed vertically in water, is quickly eaten through at the water line. This presents no difficulty; the readily soluble solid forms a heavy solution, which sinks rapidly and so sets up inward streaming at the free surface. That camphor, which is only slightly soluble and does not form a heavy solution, behaves in the same way, has been attributed to the greater activity of the superficial layer of a liquid, but this, although real, cannot account for the very marked effect in the corrosion of metals.

A plate of iron or steel immersed vertically to about half its depth in a solution of potassium chloride, normally begins to corrode at the immersed edges, as in Fig. 120,[3] the corroded areas gradually closing in until the whole of the immersed surface is attacked. This appears to be due to the condition of the cut edges, which might be expected to become relatively anodic. With thicker specimens, uniformly

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[1] Recent work of Evans and his colleagues has dealt with the "probability" of corrosion, a number of drops of the electrolyte being distributed regularly over the surface of the specimen examined, and the number of corrosion centres produced in a given time being counted. R. B. Mears and U. R. Evans, *Trans. Faraday Soc.*, 1935, **31**, 527.

[2] First studied by W. Spring, *Z. physikal. Chem.*, 1889, **4**, 658. See also L. Gurwitsch, *Z. physikal. Chem.*, 1924, **109**, 375; E. S. Hedges, *J. Chem. Soc.*, 1926, 831.

[3] U. R. Evans and T. P. Hoar, *Proc. Roy. Soc.*, 1932, **137**, A, 343.

milled, there is no such edge effect, and holes or scratches will cause local corrosion.[1] Immersing specimens of iron in air-free solutions of electrolytes, and excluding oxygen by keeping under reduced pressure, leads to the formation of a layer of ferrous hydroxide at the water-line only, whilst if totally immersed there is no action.[2] In the presence of air, the action can proceed further, and a film is formed on the surface. The attack at the water line is attributed by Evans to the partial detachment of the film from the metal under conditions which no doubt depend on the (unknown) relative interfacial tensions, causing the film to lie on the horizontal surface of the water, forming a trap into which oxygen cannot penetrate. A drop placed on the surface of a metal, allowing free access of oxygen around the edge but protecting the interior, provides a convenient means of studying the processes of film formation and detachment, and this method of experiment has been much used by Evans. Intense local corrosion may be produced by standing drops. A somewhat similar condition is presented by bubbles adhering to the inner surface of a metal vessel containing an electrolyte, and a localized form of corrosion is caused by the "hot wall effect,"[3] bubbles of dissolved air being liberated in contact with the hot surface of a boiler, for example. That such attack does not always occur is attributed to the protective action of the alkali formed at the cathodic area. Actually, the conditions at the water-gas surface are complex, and Bengough has pointed out that the distribution and adherence or detachment of the protective film depend on many factors. These may be taken to include: variations in the surface of the metal, forming local couples; density of the solutions of metallic salts and of alkali hydroxides formed during the process; interfacial tensions; convection currents in the liquid; differential aeration; stability of the films formed by exposure to air; together with the values for the electrolytic potential and overvoltage of the metal examined. It is therefore unwise to be dogmatic as to the mechanism of corrosion in general, although a clear account may often be given of the behaviour of a metal under standard conditions.[4]

In the microscopical study of corrosion, it is sometimes convenient to bring about corrosion by applying an external E.M.F., so that the conditions are easily controlled. In one method of experiment, the specimen, about 12 mm. square, was polished as for micrographic examination and placed face upwards in a cell containing a fixed volume of the electrolyte, a cathode of fine platinum gauze being fixed horizontally at a definite distance above it. The specimen could then be removed at intervals for microscopical examination. A simple apparatus was devised for the purpose.[5] Metals which

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[1] G. D. Bengough and F. Wormwell, *Proc. Roy. Soc.*, 1933, **140**, A, 399.

[2] J. E. O. Mayne, *J. Chem. Soc.*, 1936, 366.

[3] C. Benedicks, *Trans. Amer. Inst. Min. Met. Eng.*, 1925, **71**, 597.

[4] For a review of the whole subject and of the literature, see U. R. Evans, "Metallic Corrosion, Passivity and Protection," London, 1937.

[5] C. H. Desch, *J. Soc. Chem. Ind.*, 1915, **34**, 258.

have been corroded in service are often too deeply pitted to give good photographs under vertical illumination, and conical illumination, as by means of the " Ultropak " (p. 128), then gives good results, even the bases of pits being seen clearly. Information may often be obtained by embedding the specimen in bakelite, without removing the corrosion product, and cutting cross-sections.

Corrosion at a high temperature by air or superheated steam, with formation of a hard scale, is of metallographic importance. The scale is often of complex structure, showing several phases. The method of embedding in synthetic resin is again the most convenient, and the several phases may be distinguished by careful examination before and after etching with dilute hydrochloric acid.[1]

" Corrosion-fatigue," in which the effects of chemical attack are greatly modified by the application of repeated stresses, is considered later (Chap. XVI).

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[1] For a survey of this subject, with full bibliography, see " Review of Oxidation and Scaling of Heated Solid Metals " (H.M. Stationery Office, 1935).

CHAPTER XVI.

MECHANICAL DEFORMATION.

METALS and alloys are deformable solids. When such a solid is compressed, stretched, or sheared, the first effect is to produce an elastic strain, that is, the solid undergoes a change of dimensions or of form when the stress is applied, and returns to its original condition when it is removed. In a perfectly elastic solid the strain produced in this stage is strictly proportional to the stress (Hooke's law), but most metals fall short of perfect elasticity, and by using sufficiently delicate measuring instruments small deviations may be observed. The curve showing the relation between strain and stress is not exactly retraced on unloading, but a small area is enclosed (elastic hysteresis), whilst the return on unloading is often not instantaneous, but occupies a perceptible time (elastic after-working). These effects are small, although important in relation to some of the mechanical properties of metals, but they may be neglected in a first approximation, and metals may be conveniently regarded as perfectly elastic within a certain limit of stress. Under hydrostatic compression (uniform in all directions) a homogeneous solid is perfectly elastic, and returns to its original volume on unloading, however great the compression may have been. With most metals, however, deformation by tension or by shear becomes more rapid than corresponds with the elastic stage, as soon as the applied stress exceeds a certain limit. On unloading, the original form is not recovered, and there remains a certain permanent deformation. Such a solid is said to be plastic. Metals and alloys show some degree of plasticity (the term including both ductility and malleability), although it may be very small. The technical value of metals depends very largely on this property, since it makes possible such operations as rolling, pressing between dies, drawing into wire, spinning into the form of a bowl, and other ways of shaping a mass for use. There is a resemblance between the behaviour of metals in this respect and that of a soft plastic material like clay, but the mechanism of the process is different in the two materials. The essential properties of a metal depend on its crystalline character, and the behaviour of crystals on deformation is one of the most interesting problems in the modern study of the physics of solids.

The plasticity of metals is often under-estimated, and is only fully revealed by experiments designed for the purpose. That metals could be made to flow through openings by pressure was demonstrated by Tresca,[1] and even metals which cannot be drawn through dies into the form of wire may be extruded by pressure. Bismuth is an example. Although easily broken into powder, it may be extruded through a die to form a wire, which remains flexible for some time,[2] and bismuth actually proved to be the most convenient metal for a quantitative study of the extrusion process.[3]

Many crystals are capable of being deformed without losing their crystalline character, from the oleates, which are so soft that two crystals brought into contact at a point unite to form a single one,[4] or potassium manganous chloride, a crystal of which may be pressed into a lenticular shape by the fingers without being cracked or broken,[5] to the apparently rigid crystals of calcite or rock-salt. Even these may be deformed to an extraordinary extent if certain precautions are taken. If enclosed in a metal tube, tightly packed with a powder, the tube may be bent or hammered so as to produce a great plastic deformation of the enclosed crystal without inducing fracture.[6] The deformability of metals usually lies between these two extremes.

Mechanical testing, whether in tension, compression, torsion, impact, or alternating stress, does not fall within the scope of metallography, although the results of such tests are much used in the study of alloys. It is, however, sometimes convenient to have facilities in a metallographic research laboratory for testing mechanical properties on small specimens, without having to resort to the making of large test-pieces. Several instruments have been devised with this object. The tensometer [7] is a miniature testing machine, which allows of the taking of autographic load-strain diagrams during the test. It was used in the investigation of the steel specimens made by Faraday, the quantity of which was small, whilst it was desired to obtain as much information as possible as to their properties.[8] A tensile test-piece is 16 mm. long between the shoulders, and 4 mm. diameter with shoulders 6·25 mm. diameter.

Still smaller specimens are used in the delicate micro-testing machine of Chevenard,[9] the tensile test-pieces having a parallel length of only 7 mm. and a diameter of 1 to 1·5 mm. Specimens for bending and shearing tests are of about the same size. The load-strain diagram is produced optically by a moving mirror, and recorded photographically. The machine has been used for the examination

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[1] H. Tresca, *Compt. rend.*, 1864, **59**, 754; 1865, **60**, 398; 1867, **64**, 809; 1868, **66**, 263; 1869, **68**, 1197; 1870, **70**, 27, 288, 368.

[2] W. Spring, *Bull. Acad. roy. Belg.*, 1903, 1066.

[3] C. E. Pearson and J. A. Smythe, *J. Inst. Metals*, 1931, **45**, 345.

[4] O. Lehmann, " Flüssige Krystalle," Leipzig, 1904.

[5] O. Mügge, *N. Jahrb. Min.*, 1889, i, 159.

[6] G. A. Daubrée, " Géologie expérimentale," Paris, 1879; Kick, *Z. Ver. deut. Ing.*, 1890, 11; 1892, 919.

[7] L. H. Hounsfield. See *Engineering*, 1931, **131**, 104.

[8] (Sir) R. A. Hadfield, *Phil. Trans.*, 1931, **230**, A, 221.

[9] P. Chevenard, *Bull. Soc. Encouragement*, 1935, **134**, 59.

of metal cut out from welds, so that the actual properties of the weld material may be determined.[1]

Instruments of this kind lend themselves well to the study of single crystals, which are more easily grown uniformly in small sizes than in large. A delicate instrument has been constructed for such specimens in the form of thin wires.[2]

When tests of this kind are made in the course of a metallographic research, the results should be expressed in kilogrammes per square millimetre. The customary use of units other than those of the metric system survives in technical practice (tons per square inch in Great Britain ; pounds per square inch in America) but in a metallographic laboratory it is very desirable that the results should be in a form which can be correlated with the physical measurements, which in all countries are expressed in international units.

Two warnings have to be given, however, in regard to the interpretation of mechanical tests on small specimens. The test-pieces are not always geometrically similar to those used in testing laboratories, so that the figures for elongation or number of twists, although comparable amongst themselves, cannot necessarily be compared with those obtained on larger machines. Moreover, whilst single crystals will behave in the same way in the two kinds of test, specimens consisting of many crystals, if not very fine grained, will be affected by the fact that in the small test-piece the cross-section may be made up of comparatively few grains. Metallic crystals are anisotropic in their mechanical properties, the cohesion varying according to the direction in the lattice, but in masses of considerable size, with the crystal grains orientated at random, these directional qualities cancel out, and the metal is said to be "quasi-isotropic." This assumption is only justified if the number of crystal grains in the cross-section be very large.

The "maximum stress" of the engineer does not represent the true breaking stress of a ductile material, as the cross-sectional area is diminishing during the test, whilst the load is calculated on the original area. A local contraction or "necking" usually sets in before fracture. When it is possible to make measurements of the diameter at the narrowest portion of the specimen during the whole of the test, a curve may be plotted, showing the relation between the true stress and the actual area on which it is acting. Such curves, for many specimens, give an almost straight line from the point at which plastic flow sets in.[3]

The curves for compression and torsion, when plotted in the same way, are very similar to that for tension, and Ludwik has shown how a generalized "flow-curve" may be constructed from them.

Ductile metals fail by shear, so that a tensile test cannot give the

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[1] P. Chevenard, *Bull. Soc. Ing. Soudeurs*, 1935, **6**, 1760.

[2] M. Polanyi and E. Schmid, *Z. Physik*, 1925, **32**, 684.

[3] P. Ludwik, "Elemente der technologischen Mechanik," Berlin, 1909; F. Körber, *Mitt. K.W. Inst. Eisenforsch.*, 1922, **3**, ii, 1.

value of the cohesion, that is, the force required to separate two adjacent planes by pure tension. This property can only be arrived at indirectly, and with less certainty for metals than for ionic crystals. What is actually observed is a process of slip, and the study of the deformation of metals must begin with that of slip.

The mechanism of the process was first made clear by Ewing and Rosenhain.[1] If a piece of metal with a smooth, polished surface be bent or stretched, a number of fine lines make their appearance running parallel to each other over the area of a single grain, but generally varying in direction from one grain to another. The crystalline structure of the metal is in this way made evident without etching, as the boundaries of the crystal grains are revealed by the abrupt changes in direction of the fine lines. The general effect is seen in Plate XIIIA which represents a smooth surface of lead, lightly bent. The photo-micrograph shows the junction of three grains, and the lines, which are not perfectly straight, are seen to be parallel within each individual grain. By throwing oblique light on to the specimen from different directions it was shown that the lines did not represent cracks or ridges, but steps, throwing shadows in one direction only, and so alternately appearing and disappearing on rotating the stage of the microscope. The name of "slip-bands" given to them has been generally adopted. The direct height of each step is very small (about 1 μ in the soft iron examined by Ewing and Rosenhain) but a direct proof of its character was given by cutting a section perpendicularly to the strained surface, the fine detail being preserved during polishing by depositing copper before cutting the section.[2]

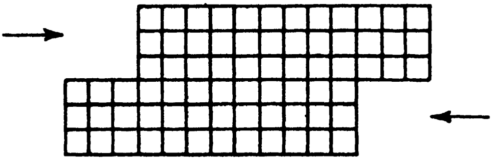

FIG. 121.—Slip on a single plane.

The mechanism of slip may be looked upon broadly as a movement of translation within a crystal along certain directions in which slip can occur more readily than in any others. The planes on which movement occurs are "slip-planes," and the slip-bands are their traces on the exposed surfaces. A movement of translation, as shown in Fig. 121, can take place without any disturbance of the crystal structure. It may be confined to a single plane, or to a number of planes parallel with one another (Fig. 122). In Fig. 123, *a* represents a polished surface before straining, portions of three grains being shown. The condition after straining is shown in *b*, inequalities of

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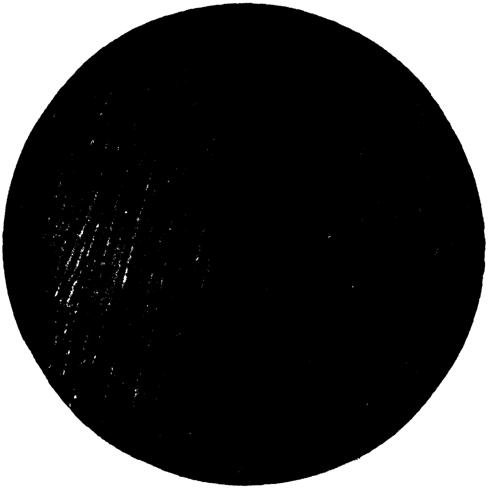
[1] J. A. Ewing and W. Rosenhain, *Phil. Trans.*, 1900, 193, A, 353.

[2] W. Rosenhain, *Proc. Roy. Soc.*, 1905, 74, 557; *J. Iron Steel Inst.*, 1906, ii, 189.



A. Strained surface of lead, showing slip-bands. × 86

B. Cupro-nickel, reduced 80 % by rolling. × 200

PLATE XIII

level having been produced by the slip. The phenomenon is exactly similar to that of repeated faults, or "step-faults," in geological strata. As many crystals have more than one set of slip-planes, slip-bands may be developed in more than one direction. With moderate straining, each grain usually shows only one set of bands, but as the deformation is increased, and redistribution of stress occurs, new systems of bands intersecting the older ones are seen. Under high magnification, the crossing of two bands is marked by a dislocation, a fact which points to their step-like character. It was shown by Rosenhain by actual measurement that the regions between the slip-bands remain undeformed.[1]

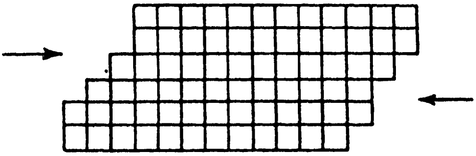


FIG. 122.—Slip on several planes.

Since movements of translation leave the internal structure of a crystal unaltered, slip-bands which have appeared on a surface are removed by polishing, and do not reappear on etching. It may happen, however, that indications of strain are seen on etching a deformed specimen, and such "strain lines" are evidence of a more profound change in the crystalline structure. They are of several kinds. Bands of localized deformation may often be seen on a large

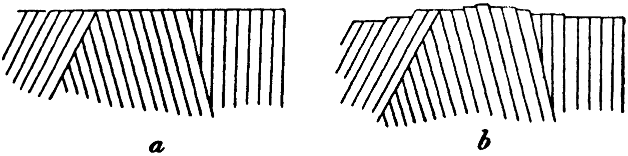


FIG. 123.—Formation of slip-bands.

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[1] The modern view as to the deformation of metals by slip is mainly based on the work of Ewing and Rosenhain. The fact had, however, been noticed in single crystals much earlier, but had not been pursued. E. Reusch, *Ann. Phys.*, 1867, [v], **132**, 441, discovered that shearing a rock-salt crystal between two plates produced slip on planes which proved to be those of the rhombic dodecahedron. O. Mügge made many observations of this kind, showing, for example, *N. Jahrb. Min.*, 1883, II, 13, that gypsum, stibnite, and other minerals could be extensively deformed by slip on parallel planes, and later, *Nachr. k. Ges. Wiss. Göttingen*, 1899, *Math.-phys. Kl.*, 56, that crystals of native gold, silver and copper exhibited superficial lines which were identified as traces of octahedral slip-planes, the direction of slip being [110]. Mügge also showed how these lines might be distinguished from twins. G. Charpy, *Compt. rend.*, 1896, **123**, 225, noticed that the surfaces of poly-crystalline metals showed a pattern when deformed, neighbouring grains being raised or depressed, making the boundaries visible.

scale, and are independent of the crystal structure, taking similar directions in metals and in amorphous materials, such as wax or solid glue. These are Osmond's "déformations banales."[1] In iron and mild steel they represent regions which have deformed suddenly at the yield point, and are separated by undeformed regions, their traces on the surface being then known as Lüders lines.[2] A similar effect may be detected on the microscopic scale in certain rolled metals. Severe deformation, as in rolling or wire-drawing, changes the shape of the crystal grains, slip occurring in such a way as to cause the mass of metal to yield under the applied force. The crystal grains become elongated and even spindle-shaped, and microscopical examination shows that the slip has not been uniformly distributed, but that bands of severe deformation (strain lines) cross the crystals in directions bearing some relation to the stress. An example is shown in Plate XIIIB which represents a section through a specimen of cupro-nickel which has been reduced 88 per cent. in thickness by rolling.[3] The dark lines are parallel with the direction of rolling in some of the elongated grains; in others they are inclined to it at an angle of about 30°.

That the process of deformation of a mass of metal is not solely one of translation, however often repeated, is shown by the well-known fact of hardening by work. As a specimen of metal is deformed, in tension or otherwise, its resistance to further deformation increases. The deformed metal is harder, and differs in many physical properties from the metal before being strained. An extreme example is that of a hard-drawn wire. Some more profound change must therefore have occurred, and the search for a satisfactory explanation of strain-hardening has formed one of the most interesting chapters of metallography. It is necessary to isolate the several factors as far as possible, and with this object many studies of single crystals have been made.

SINGLE CRYSTALS.

In experiments on single crystals of metals one disturbing influence, that of the boundary between neighbouring grains, is eliminated. In simple translation, the structure of the crystal will only be unaltered if the movement, as in Fig. 122, is an exact multiple of the unit distance of the lattice, and this is the only condition of equilibrium. The process was studied in detail in zinc, which has the advantage, as a hexagonal metal, of slipping only on a single set of planes, the basal planes, which are the most densely packed. A cylindrical cast crystal of zinc, strained in tension, develops one set of slip-bands,

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[1] F. Osmond, C. Frémont, and G. Cartaud, *Rev. Métall.*, 1904, **1**, 11.

[2] The observations of W. Lüders, *Dingl. polytech. J.*, 1860, **155**, 18, were merely incidental, as were the still earlier observations of Piobert, *Mémorial de l'Artillerie*, 1842, **5**, 502. A very detailed study was made by L. Hartmann, "Distribution des déformations dans les métaux soumis à des efforts," Paris, 1896, and in France they are commonly known as Hartmann lines. See also E. Fell, *J. Iron Steel Inst.*, 1935, ii, 75.

[3] F. Adcock, *J. Inst. Metals*, 1922, **27**, 73.

being elliptical and equally inclined to the axis.[1] These bands mark the boundaries of blocks which slip over one another, so that the cylindrical crystal becomes a narrow, flattened band. The basal planes, as the specimen is extended, are moved into positions more nearly parallel with the axis of the specimen, until the angle between them approaches 15°, when rupture occurs. At higher temperatures a still nearer approach is possible; about 2° at 200° C. The possible amount of extension thus depends on the original inclination of the basal planes to the axis of the specimen. The plasticity of a single crystal is very much greater than that of an aggregate. With favourable orientation, a crystal of zinc may be extended to 6 times its original length at 20°, or to 17 times its length at 200°. The same metal in the polycrystalline form would only extend 0·5 per cent. at 20°. An aluminium crystal may be rolled out into the thinnest of ribbon. The X-ray determinations confirm the visual observations.

The deformation of aluminium crystals, which have a face-centred cubic lattice, was followed in detail by geometrical and X-ray measurements.[2] Slip takes place on the octahedral (111) planes, and the direction of slip within that plane is the cube face diagonal [110]. It is a general rule that the plane of slip is the most densely packed plane in a crystal, and the direction of slip is the most closely packed line within that plane. This is true not only for extension, but also, as was shown for aluminium by experiments in compression [3] and in torsion,[4] for other forms of deformation. In zinc and other metals with close-packed hexagonal structures the basal plane (0001) is the plane of slip, and the prism edge of the first order [1010] the direction of slip. When, as in a cubic metal, there are several equivalent planes, slip occurs on that plane for which the resolved shear stress in the direction of slip is a maximum, and this has been confirmed for the most varied kinds of deformation.

There appears to be no exception to the rule that in a face-centred cubic metal slip occurs on (111) planes in a [110] direction, but the behaviour of body-centred cubic metals is less regular. There has been some doubt as to the behaviour of α-iron. Slip undoubtedly follows the direction of the most closely packed lines in the lattice, namely [111], but it appeared [5] that there was no preferred plane among those containing that direction, so that the movement was like that of a bundle of rods. In conformity with this explanation, the slip-bands are irregular and curved or jagged on all faces except those parallel with the direction of slip. Other observers [6] have

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[1] H. Mark, M. Polanyi, and E. Schmid, *Z. Physik*, 1922, **12**, 58.

[2] G. I. Taylor and C. F. Elam, *Proc. Roy. Soc.*, 1923, **102**, A, 643; 1925, **108**, A, 28.

[3] G. I. Taylor and W. S. Farren, *ibid.*, 1926, **111**, A, 529.

[4] H. J. Gough, S. J. Wright, and D. Hanson, *J. Inst. Metals*, 1926, **36**, 173.

[5] G. I. Taylor and C. F. Elam, *Proc. Roy. Soc.*, 1926, **112**, A, 337.

[6] L. B. Pfeil, *Iron Steel Inst. Carnegie Schol. Mem.*, 1926, **15**, 319; W. Fahrenhorst and E. Schmid, *Z. Physik*, 1932, **78**, 383; C. S. Barrett, G. Ansel and R. F. Mehl, *Trans. Amer. Soc. Metals*, 1937.

arrived at rather different conclusions, but it is certain that the slip is not of the usual simple type, and irregularities are also found in the deformation of β-brass, which has a similar lattice.[1] A re-examination of these two metals shows that both present the same anomalies.[2] Even the [111] direction, although the most frequent, is not strictly observed, and complex deformation is evidently possible.

It would seem necessary that a finite stress should be applied to a crystal before any slip can take place, but the value of the stress is low, less than 1 kg./mm.^{2} for most metals. The " elastic limit " of a crystal aggregate, as determined in technical testing, is a measure of the sensitiveness of the extensometer rather than a physical constant, and when, as by using a valve amplifier method, very small displacements can be detected, much lower values are found, even for metallic aggregates of small crystals.[3] Using single crystals of silver, gold and copper, permanent deformation was found with the lowest practicable loads,[4] and it has often been assumed that such crystals have no elastic limit. Such a limit must, however, exist, and in a few instances has been measured by using sufficiently delicate methods. The resistance to slip increases with falling temperature, but for zinc and cadmium crystals the change is relatively small.[5] Experiments have been conducted at the temperature of liquid helium (1·2° abs.),[6] and there is no indication that slip becomes impossible at the absolute zero, or that there is any considerable increase in the critical stress.

The resolved shear stress needed to produce slip is independent of the orientation of the crystal in relation to the axis of the specimen, whilst the apparent elastic limit in tension varies within wide limits.[7]

It has been found impossible to reconcile the values obtained for the resistance to slip with current views as to the much greater forces of cohesion in a crystal. For non-metallic substances, especially rock-salt, in which the forces between the ions can be calculated, the discrepancies have been very thoroughly discussed, but the subject is too large to be entered on here.[8] There is much more uncertainty as to the forces in a metallic lattice. It is usually assumed that actual solids contain ultra-microscopic flaws, and the original suggestion of Griffith[9] has been extended to account for many of the mechanical properties of solids. Considerations of this kind bring up the general

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[1] G. I. Taylor, *Proc. Roy. Soc.*, 1928, **118**, A, 1; Frhr. v. Göler and G. Sachs, *Naturwiss.*, 1928, **16**, 412.

[2] C. F. Elam, *Proc. Roy. Soc.*, 1936, **153**, A, 273.

[3] C. Handford, *Phil. Mag.*, 1924, [vi], **47**, 896.

[4] C. F. Elam, *Proc. Roy. Soc.*, 1926, **112**, A, 289.

[5] E. Schmid, *Proc. 2nd Intern. Congr. Appl. Mech.*, Zurich, 1926.

[6] W. Meissner, M. Polanyi, and E. Schmid, *Z. Physik*, 1930, **66**, 477.

[7] P. Rosbaud and E. Schmid, *ibid.*, 1925, **32**, 197.

[8] See, for a review of this subject by the leading investigators, vol. ii of *Proc. Intern. Conf. Physics*, London, 1934.

[9] A. A. Griffith, *Phil. Trans.*, 1920, **221**, A, 163.

problem of a mosaic or secondary structure in crystals (Chap. XI). Further reference to the subject will be made later.

The hardening of a metal by cold work implies that the resistance to slip increases with progressive deformation. This suggests that the planes of slip have been in some way distorted, so that the process is no longer one of simple translation. That hardening by cold work is brought about by distortion of the slip-planes equivalent to crumpling was suggested by Ludwik.[1] Two steel sheets will slip over one another freely if flat, but not if corrugated across the direction of movement, and since optical evidence of distortion of lattice planes was available from transparent substances, this seemed to be a plausible explanation. The same view put forward later[2] attracted more attention.

That distortion of the lattice planes takes place is shown by abundant evidence. A Laue photograph of a single crystal shows, after deformation, the circular spots extended into radial lines.[3] This " asterism " had been previously observed in such non-metallic substances as mica and gypsum, and had been interpreted to mean that the planes of the lattice had been bent into a cylindrical form, an observation according with the behaviour of such flexible crystals as ammonium nitrate when viewed optically.[4] There is, however, an alternative explanation of the patterns thus produced, namely, that the crystal is broken into fragments of varying orientation, and this will be discussed later.

A pure metal may be hardened in two ways: by cold working or by the addition of another element which can enter into solid solution with it, and the analogy of the two effects has suggested that both are due to a common cause, lattice distortion.[5] The introduction of the " stranger " atoms into the lattice, differing in size and probably also in attractive force from their neighbours, is considered to cause a crumpling of the lattice planes, with increased resistance to slip, the hardness due to cold working being attributed to the same origin.

A metal which has been hardened by cold working differs in many respects from the same metal in the annealed state, which may be regarded as one of equilibrium. It has greater tensile strength but lower ductility, a higher elastic limit, and somewhat lower electrical conductivity, and presumably contains an additional quantity of energy stored either as elastic energy or through the production of a new phase of higher energy content. The original properties may be restored by annealing. Attempts have been made to determine the energy absorbed in the process of cold working, but the experimental difficulties are great, as by far the greater part of the work done in

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[1] P. Ludwik, *Z. Metallk.*, 1919, **11**, 117; *Z. Ver. deut. Ing.*, 1919, **63**, 142.

[2] Z. Jeffries and R. S. Archer, *Chem. Met. Eng.*, 1921, **25**, 697.

[3] F. Rinne, *Z. Krist.*, 1924, **59**, 230.

[4] O. Lehmann, *Ann. Physik*, 1916, [iv], **50**, 555.

[5] W. Rosenhain, *Proc. Roy. Soc.*, 1921, **99**, A, 196.

deformation is converted into heat, and only a small residue remains to be measured. Tensile tests on steel, copper, and aluminium, with special precautions against loss by conduction, indicated that from 5 to 13 per cent. of the work done was stored in the metal.[1] The reductions of area were small, being only 14 to 36 per cent. By drawing wire through a die in a calorimeter similar figures were obtained,[2] but the friction in the die causes errors which are difficult to allow for. A different method, consisting in finding calorimetrically the energy released by a cold-worked bar on heating, gave 12–6 per cent. of the total work for brass.[3]

Cold working can be carried further by torsion or by compression than by tension, and a series of experiments in which the work done was compared with the heat developed, determined calorimetrically, showed that as much as 11 per cent. of the work done could be stored in copper.[4]

Indirect methods have also been tried. Drawn wires were found [5] to be anodic to the same metals in the annealed condition, and an attempt has even been made to relate the potential difference thus obtained to the value of the work done in tensile deformation, as found from the area under the curve obtained in a tensile test.[6] A determination of the heat of solution of a metal in the two states is, in principle, a satisfactory means of determining the stored energy, since this should reappear when the metal is dissolved. Difficulties arise from the high value of the heat of solution of metals in most available solvents, making the quantity sought for only a small fraction of the total development of heat, and thus lessening the accuracy. It is necessary to choose a solvent, such as a solution of iodine, which does not produce an evolution of gas. Experiments under the direction of the author [7] gave values for the stored energy of from 2 to 7 cals./grm., according to the amount of deformation, both rolling and wire drawing being employed. All methods give results of the same order, but no great accuracy can be claimed. The energy stored increases with increasing deformation, but reaches a maximum, which in Taylor and Quinney's experiments coincides with the attainment of maximum mechanical strength.

The difference between the energy contents of worked and unworked metals thus being small, of the order of only a few calories per gramme, the question remains as to the difference in structure of the metal, beyond the simple deformation recognizable from the external form or from that of the individual crystal grains. One view, which has provoked much discussion and has been the cause of

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[1] W. S. Farren and G. I. Taylor, *Proc. Roy. Soc.*, 1925, **107**, A, 422.

[2] W. Rosenhain and V. H. Stott, *ibid.*, 1933, **140**, A, 9.

[3] S. Sato, *Sci. Rep. Tôhoku Univ.*, 1931, **20**, 140.

[4] G. I. Taylor and H. Quinney, *Proc. Roy. Soc.*, 1934, **143**, A, 307.

[5] W. Spring, *Bull. Acad. roy. Belg.*, 1903, 1066.

[6] T. F. Russell, *J. Iron Steel Inst.*, 1923, i, 497.

[7] C. J. Smith, *Proc. Roy. Soc.*, 1929, **125**, A, 619; R. W. France, *Trans. Faraday Soc.*, 1934, **30**, 450.

great progress in knowledge through experiments intended to test its validity, was based on observations made in the course of polishing metals, and it is convenient to give an account here of the work on this subject.

THE NATURE OF POLISH.

It has been stated in Chapter VI that there is a fundamental difference between the process of abrasion by a material such as emery and that of polishing. The action of an abrasive material is one of cutting. Each particle cuts a fine groove in the surface over which it rubs, the groove being ploughed in a soft substance, or broken out in a series of chips in a brittle substance. The form of the groove, which is made up of minute paraboloids, is approximately a parabolic cylinder.[1] The use of a somewhat finer abrasive material effaces the coarser scratches by substituting for them a system of finer grooves. This process may be carried very far, but even the finest abrasive material only cuts grooves, although these may be of microscopic fineness. Robert Hooke, who examined the surface of a steel razor under his microscope, in 1665, was of opinion that it was impossible ever to prepare a smooth surface.[2]

Lord Rayleigh[3] suspected that the polishing process was really molecular in character. The union between the powder and the polished surface is very intimate. If a polishing cloth covered with rouge is allowed to become dry, the rouge may attach itself so firmly to the metal surface that it cannot be removed without destroying the smoothness of the latter, and similar phenomena, indicating some degree of interpenetration between the two substances, are well known.

Beilby showed[4] that the effect of polishing is to cause a surface flow of the substance being polished. When an alloy containing lead together with a harder metal is rubbed vigorously on the polishing block, the lead is caused to flow, and may cover the whole surface, completely masking the underlying structure. This effect is well known to beginners who attempt to polish soft alloys. Flow takes place, although only to a small depth, on the surface of even the hardest crystalline substances, and Beilby demonstrated the existence, on polished surfaces, of a thin layer of flowed, structureless material, strongly resembling in its behaviour a highly viscous fluid. The " forced polish " produced by burnishing is due to the formation of a deep layer of this flowed material. Its formation is well shown on the surface of such a brittle metal as antimony. A surface crossed by emery scratches is lightly polished on a wet cloth block with alumina, and by examining from time to time under the microscope,

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[1] F. Osmond and G. Cartaud, *Rev. gén. Sciences*, 1905, **16**, 51.

[2] " Micrographia," Observation II. This was also the opinion of Herschel.

[3] *Proc. Roy. Soc.*, 1901, **16**, 563.

[4] (Sir) G. T. Beilby, *ibid.*, 1903, **72**, 218, 226 ; *Phil. Mag.*, 1904, [vi], **8**, 258 ; *J. Soc. Chem. Ind.*, 1903, **22**, 1166 ; " Aggregation and Flow of Solids," London, 1921.

the gradual conversion of a part of the metal into the viscous form may be watched. If the direction of the polishing be kept constant and transverse to the scratches, the flowed material is seen to form an overhanging ledge or cornice at the edge of the grooves, then extending to form a complete bridge. By forced polishing it is easy to cover up even deep scratches in this way with a flowed layer, presenting the appearance of a perfectly smooth, polished surface. That the scratches are only covered, and not removed, is readily seen on etching with a reagent which dissolves the film and exposes the original grooved surface. In the same way, an etched pattern may be completely effaced by polishing, and a light re-etching removes the film and again exposes the underlying pattern. Plate XIVA is a photo-micrograph of a surface of bismuth crossed by numerous scratches produced by emery paper. Plate XIVB is a photo-micrograph of the same specimen polished with alumina on a cloth. Most of the scratches are completely covered by a film, some fine ones appear broken, having been bridged in places, whilst one broad scratch is in process of being filled. It is from this cause that etching a polished micro-section so often reveals scratches which had apparently been removed during its preparation and finishing.

Beilby regarded this flowed layer as having essentially the properties of an undercooled liquid, and he preferred the term "vitreous" to that of "amorphous" for its description. Objections were raised [1] on the ground that the production of a liquid phase at a temperature below the melting-point was thermodynamically impossible, but the effects of unsymmetrical pressure, producing flow, are not the same as those of hydrostatic pressure,[2] and the objection is not fatal. An increase of hydrostatic pressure usually raises the melting-point (ice is exceptional in this respect), but such non-uniform pressure has been held to lower the melting-point, and calculations have been made [3] of the pressure necessary to melt various metals at atmospheric temperature under such conditions. At 27° lead would melt under a pressure of 1760 atmospheres and copper under 24,000 atmospheres. These values are high, but they are only supposed to occur locally, in a very thin layer (see p. 285).

The existence of a flowed layer on a polished surface is an experimental fact which cannot be doubted, but whether such a layer is correctly described as vitreous is a question on which opinions differ. X-rays fail to give a definite answer, as the depth of penetration is so great that the flowed layer is passed through, and the structure of the underlying solid is revealed. It is otherwise when the beam consists of electrons, the depth of penetration of which is only of the order of 10^{-6} cm. Patterns obtained from polished surfaces of

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[1] G. Tammann, *Z. anorg. Chem.*, 1915, 92, 37; M. Hasselblatt, *ibid.*, 1915, 93, 75.

[2] J. H. Poynting, *Phil. Mag.*, 1881, [v], 12, 32.

[3] J. Johnston, *J. Amer. Chem. Soc.*, 1912, 34, 788. See also H. Jeffreys, *Phil. Mag.*, 1935, [vii], 19, 840.

A. Surface of bismuth, marked with emery scratches. × 200

B. Surface of bismuth, partly polished. × 200

PLATE XIV

silver, copper, gold, and chromium[1] resembled those from a liquid, being quite different from those given by the same metals in the crystalline state, even with very small grain size.

Further, on the view that the vitreous layer has the properties of an undercooled liquid, it may be expected to dissolve foreign atoms more rapidly than the same substances in the crystalline state. This has been confirmed by using the electron beam method. When a thin layer of zinc is condensed on a polished surface of copper, the diffraction pattern of crystalline zinc may be seen for a few seconds, but it rapidly fades, and this condensation and disappearance may be repeated a number of times, until the copper is saturated with zinc, after which a further layer of condensed zinc is permanent.[2] This effect is not seen when a crystalline surface of copper, prepared by etching, is used.[3]

The electron beam method has also been used to measure the thickness of the "Beilby layer." Using gold, as a metal little affected by oxidation, polishing was found to produce a layer giving a diffraction pattern similar to that of a liquid, approximately 30 Å. thick over much of the surface, whilst down to a depth of 100 Å. the crystals were very small, perhaps 5 or 6 atoms to each cube edge.[4]

The conclusions arrived at from the study of surface films were applied by Beilby to explain the hardening of metals by cold working. It is not enough, however, to consider only static deformation; the changes produced by repeated alternations of stress must also be taken into account, and this aspect must now be discussed before entering into the theory of hardening.

FATIGUE.

It is well known that materials subjected to frequent alternations of stress become "fatigued," so that a metal subjected to rapid alternations of stress may break, even when the stress has never exceeded the known elastic limit of the material. A steel shaft in a factory, supported by brackets and carrying pulleys with belts, is subjected, not only to a more or less constant torsional stress, but to bending stresses which are varying in direction within the shaft at every moment during its revolution. It becomes important to discover the nature of the fatigue observed in such structures, and to determine the permissible limit of stress in each material. The stresses applied may also consist of alternate tension and compression, as in the connecting-rod of a locomotive, and many other varieties of stress are possible.

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[1] R. C. French, *Nature*, 1932, **129**, 169; *Proc. Roy. Soc.*, 1933, **140**, A, 637.

[2] G. I. Finch, A. G. Quarrell, and J. S. Roebuck, *ibid.*, 1934, **145**, A, 676.

[3] The layers on the surfaces of most polished metals contain oxygen, and when polished under a liquid which excludes oxygen the diffraction patterns are more characteristic of the several metals. S. Dobinski, *Phil. Mag.*, 1937, [vii], **23**, 397.

[4] H. G. Hopkins, *Trans. Faraday Soc.*, 1935, **31**, 1095.

Several different forms of machine have been employed in the experimental study of fatigue. In one of the most convenient, due originally to Wöhler, a cylindrical rod of the material is made to project from the end of a revolving shaft, the overhanging end being loaded by means of a ring slipped over it, bearing a weight or forming the upper attachment of a spring balance. The stress is in this case a bending one, varying rapidly and continuously within the metal, as in the factory shaft referred to above. By polishing a portion of the surface of the test-piece, and examining from time to time under the microscope, the mechanism of fatigue has been studied.[1]

Other forms of fatigue-testing machines apply alternations of tensile and compressive stress or torsional stress, or of combinations of these, for which reference should be made to works on mechanical testing.

Even although the stress, calculated on the specimen as a whole, may be well below the elastic limit, it may not be uniformly distributed throughout the mass, so that certain crystal grains are more severely stressed than others. Slip-bands make their appearance in these grains after a certain number of reversals, and their number increases as the test is continued. The slipping which takes place leads to a re-distribution of stress among the crystal grains, and after a time many more grains are found to exhibit slip-bands. Some of the slip-bands develop into cracks, and a crack once started propagates itself rapidly, through causing a local intensification of the stress. From this point onwards, the behaviour of the specimen is similar to that of a bar containing an internal flaw; the remainder of the metal is little affected by further alternations of stress, but that in the immediate neighbourhood of the crack or flaw is very greatly affected. An important result obtained by Ewing and his co-workers is that fracture does not take place along the boundaries of the crystal grains, but preferably through the grains, along the path of the slip-bands.

It has been seen that the production of a slip-band is due to the gliding of crystal elements over one another along a plane of translation, and that this action does not bring about a change of crystal structure. As the stress is reversed, motion along the same plane, but in the opposite sense, may take place. If this were the only action, it would be possible for reversible deformations to occur at each alternation, the displaced layers gliding to and fro over one another without destroying the crystalline structure of the metal. The fact that fatigue occurs is itself a proof that the actual sequence of events is not so simple.

Ewing and Humfrey observed that the slip-bands on the polished surface of a sample of mild steel, after 40,000 reversals of stress, showed a marked change in appearance. By careful focussing it was found that a distinct ridge was produced along the elevated edge of the slip-band, having the effect of a burr produced by the friction.

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[1] J. A. Ewing and J. C. W. Humfrey, *Phil. Trans.*, 1902, **200**, A, 241, and many later workers.

It is also known that a strained plastic metal, such as iron, recovers its original properties to some extent after being kept for some time, or very rapidly if heated to a moderate temperature, such as 100°.[1] This indicates that the strained, hardened metal is in an unstable condition, and that its parts are under some degree of restraint, from which they are prevented from escaping by the high viscosity of the solid. Return to the stable condition is enormously facilitated by rise of temperature.

Fractures resulting from the opening-up of slip-planes, consisting as they do of systems of cleavage planes, commonly present a bright, crystalline appearance, which has led to the popular belief that metals subjected to alternating stress become "crystalline." This is not so; a microscopical examination of the metal immediately behind the fracture shows that the structure has not become coarser, that there is no increase in the size of the crystal grains, but that the brilliant facets on the fractured surface are merely cleavage planes. The same metal will exhibit entirely different fractures if broken under tension and under alternating stress, the whole of the crystals being gradually deformed in the former case, giving a fine fracture, whilst in the latter the yielding is confined to a few cleavage planes. Fracture by shock, causing separation to take place along the planes of greatest weakness, without giving time for a re-adjustment of stresses by the plastic yielding of other crystals, also produces a coarsely faceted or "crystalline" surface.[2]

On Beilby's view, the repeated rubbing of one crystal plane over another would lead to the breaking down of a part of the crystal structure to form the vitreous phase, and this being harder than the crystalline material would present greater resistance to further deformation, hence the production of the burred edge noticed by Ewing and Humfrey, and the dark lines seen by other observers. Later work has shown, however, that the dark lines on the surface of a fatigued test-piece cannot be due to the broadening of a single slip-band, but represent accumulations of slip-bands close to one another, which require high magnification (1400 diam.) to reveal their true character.[3] These bands appear at stresses below the fatigue limit, and there is no change in the microscopic structure which indicates when the stresses applied exceed that limit. Experiments with single crystals of aluminium[4] showed that the type of distortion found geometrically was the same for static and for alternating stresses, and this has been abundantly confirmed by later work.

In experiments on alternating stress, the greater the range of stress the smaller the number of cycles of stress which the specimen can withstand without fracture. Plotting the endurance (number of

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[1] J. Muir, *Phil. Trans.*, 1899, **193**, A, 1; 1902, **198**, A, 1.

[2] For a full review of the subject of fatigue in relation to structure, see H. J. Gough, *Proc. Amer. Soc. Test. Mat.*, 1933, **33**, ii, 3.

[3] H. J. Gough and D. Hanson, *Proc. Roy. Soc.*, 1923, **104**, A, 538.

[4] H. J. Gough, D. Hanson, S. and J. Wright, *Phil. Trans.*, 1927, **226**, A, 1.

cycles required to fracture) or its logarithm against the range of stress, an asymptotic value of the range is found, which the metal

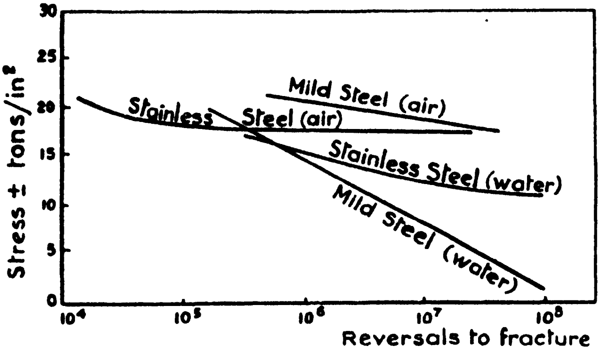

Fig. 124.—Corrosion-fatigue curves.

should be able to resist indefinitely. Half the range of stress, when the mean stress is zero, is known as the fatigue limit of the metal, and prolonged experiments confirm the view that such a limit does indeed exist, provided that chemical influences are excluded. A fact of great metallurgical importance has, however, been discovered in recent years. The endurance is greatly reduced when chemical attack is occurring during the alternations of stress, and "corrosion fatigue" is one of the commonest causes of the failure of engineering parts.[1] In this case there is no fatigue limit, but even at stresses much below the normal limit failure will occur in time, as indicated in Fig. 124, which represents endurance curves for mild steel and stainless steel, tested in a brackish river water.[2] The effect is entirely independent of any general weakening of the metal by corrosion, and is usually attributed to the rupture of the oxide film which normally protects most metals, but it may also be accounted for by the penetration of chemical agents into minute ultra-microscopic cracks in the surface during tension, the high pressure produced during the compressive phase of the cycle having the effect of activating the molecules, so that reaction with the metal

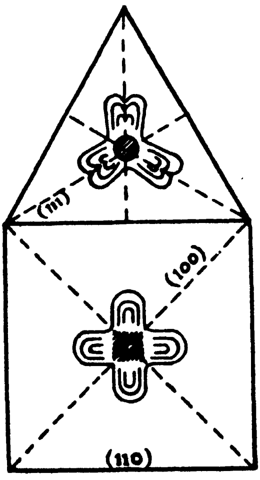

Fig. 125. — Percussion-figures on iron.

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[1] See, for a survey of the subject, H. J. Gough, *J. Inst. Metals*, 1932, 49, 17. Earlier work was mainly due to B. P. Haigh and to D. J. McAdam.

[2] N. P. Inglis and G. F. Lake, *Trans. Faraday Soc.*, 1931, 27, 803.

occurs at temperatures at which they would otherwise be inactive. Even air can react under such conditions, so that the true fatigue limit can only be determined, at least for some metals, by experiments *in vacuo*.[1]

The directions of slip and cleavage in single crystals have been studied in a qualitative manner by means of "percussion figures." When a crystal face is struck with a pointed instrument a pattern is produced, which gives an indication of the relation of the slip-planes to the face exposed.[2] Fig. 125 represents such figures on two principal faces of an iron crystal.

TWINNING.

Besides slip (translation) there is a second mode of deformation which is possible for crystals. This is twinning, which results in a part of the crystal assuming a symmetrical relation to another part, according to certain rules depending on the crystal system. The usual illustration, the formation of a twin in calcite by pressure on a rhombohedral edge with a knife,[3] is misleading, as no such change of outward form occurs in the mechanical twinning of metals, whilst another usual illustration, that of the rôtation of certain crystal elements into new positions, also calls for movements which are impossible in the mass of a metal. Twinning is very commonly found in native metals, and is also seen in metals and alloys which have been cold-worked and afterwards annealed (see Plate IIB). The face-centred cubic metals twin readily, the composition plane being (111), whilst the twinning axis is [111], but twins have not been observed in aluminium, although it belongs to this group, and the banded structures sometimes seen in it have not the geometrical properties of twins.[4]

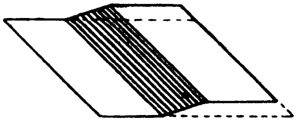

FIG. 126.—Twinning by "Einfache Schiebung."

The German term "Einfache Schiebung" gives a good idea of the twinned structure, as illustrated in Fig. 126, which may be contrasted with the simple shear in Fig. 122. The new position may be arrived at by a displacement of successive planes by amounts proportional to their distance from the twinning plane, producing an arrangement which is symmetrical about that plane. Deformation under stress can take place by twinning as well as by slip, and in some metals, such as zinc,[5] both processes may occur together. The cracking noise which is heard on bending a bar of tin, known

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[1] H. J. Gough and D. G. Sopwith, *J. Inst. Metals*, 1932, **49**, 93.

[2] F. Osmond and G. Cartaud, *Rev. Métall.*, 1905, **2**, 811.

[3] E. Reusch, *Ann. Phys.*, 1867, **132**, 441; *Proc. Roy. Soc. Edinburgh*, 1867, **6**, 134; O. Mügge, *N. Jahrb. Min.*, 1883, **1**, 81.

[4] C. F. Elam, *Nature*, 1927, **120**, 259.

[5] C. H. Mathewson and A. J. Phillips, *Trans. Amer. Inst. Min. Met. Eng.*, 1927, **75**, A, 143.

popularly as the "cry" of tin, is caused by the rearrangement producing twins, and a similar effect is noticed in zinc. Although antimony may be deformed under suitable conditions, and bismuth is plastic enough to be extruded into wire, both metals being usually regarded as brittle, the deformation of both appears to take place by twinning rather than by slip.[1]

In spite of the very extensive literature of the subject, which cannot be further referred to here,[2] the mechanism of twinning in a metallic crystal, especially when forming part of an aggregate, is by no means clear. Many of the diagrams which have been published fail to give a true picture, since they involve an impossibly close approach of certain of the atoms. It has been pointed out[3] that no scheme can be accepted which brings atoms closer together than their closest approach in the lattice, and the components of the twin must have at least one plane of atoms in common.

The body-centred cubic metals do not twin readily, but a special form of twinning is seen in α-iron. Narrow bands were observed in the kamacite of meteorites (α-iron-nickel solid solution), which did not differ chemically from the rest of the crystal. These "Neumann lines"[4] are not usually seen in artificially prepared α-iron. They are readily developed by a blow, and this is the usual way of producing them. If a specimen of ferrite be slowly deformed so as to produce a large number of slip-bands, and then immediately struck, no Neumann lines are produced,[5] and a rest of one or two days is needed before the original property is recovered. This curious fact is in accordance with what is known of the behaviour of ferrite immediately after being overstrained. That the Neumann lines are true twins has been sometimes doubted, but a very careful investigation[6] has shown that microscopical and X-ray measurements and observations of etching pits combine to prove their twin character.

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[1] H. J. Gough and H. L. Cox, *Proc. Roy. Soc.*, 1930, **127**, A, 431; *J. Inst. Metals*, 1932, **48**, 227.

[2] A useful survey is given by C. H. Mathewson, *Trans. Amer. Inst. Min. Met. Eng.*, 1928, **78**, 7.

[3] G. D. Preston, *Nature*, 1927, **119**, 600.

[4] First observed by F. E. Neumann in 1848.

[5] W. Rosenhain and J. McMinn, *Proc. Roy. Soc.*, 1925, **108**, A, 231.

[6] S. W. J. Smith, A. A. Dee, and J. Young, *ibid.*, 1928, **121**, A, 477, 486, 501.

CHAPTER XVII.

THE STRUCTURE OF COLD-WORKED METALS.

COLD-WORKING a polycrystalline metal produces a change in the shape of the crystal grains, which assume a spindle shape in drawn specimens or flattened lenticular forms in compressed specimens, rolling leading to a structure intermediate between the two. As followed by means of the microscope, the changes in shape are slight when the deformation is small, and become rapidly more conspicuous as it increases. For α-brass the change becomes very marked at 30 per cent. reduction of thickness.

At high reductions the crystals are severely crushed and correspondingly difficult to etch clearly. Statements have often been made that with sufficient cold-working the structure vanishes and the metal seems to be homogeneous, but such appearances may be safely put down to defective technique. Some alloys continue to etch clearly and to show distinct grain boundaries even when greatly reduced by rolling, cupro-nickel being a good example[1] (see Plate XIIIB). The confused appearance which is usually seen is mainly due to differences of electrolytic potential between the most severely deformed regions—grain boundaries and planes of slip—and the relatively less distorted parts.

Since the change of shape has been brought about by slip on a number of planes, their direction being determined by that of the stress, rotation must have occurred, bringing certain planes more nearly into coincidence with the axis of stress. This leads to a condition in which certain crystalline directions tend to predominate in the aggregate, and a " fibre structure " is produced, the term indicating an analogy with the structure of natural fibres, such as silk or cotton. The nature of fibre structure has been made clear by X-ray examination. Asbestos, a naturally occurring mineral fibre, was found to give a 10-rayed star when a beam of X-rays was passed transversely through it, the pattern being altered by tilting, but unchanged when the fibre was rotated on its axis.[2] Such a pattern would be accounted for if the prismatic crystals of which an asbestos fibre is made up were all parallel to its length, but with their other

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[1] F. Adcock, *J. Inst. Metals*, 1922, **27**, 73.

[2] S. Nishikawa and S. Ono, *Proc. Tokyo Math.-Phys. Soc.*, 1913-14, [ii], **7**, 131.

axes pointing at random. This is typical of a fibre structure. Under similar conditions, a hard-drawn copper wire gave a 4-pointed star.

The effect of deformation, in wire-drawing for example, is to cause those planes on which slip occurs most readily to arrange themselves more nearly parallel with the axis of the wire. In general, these are the most densely packed planes in the crystals, and the most densely packed line in such a plane also tends to set itself parallel with the axis of the wire. The conditions have now been worked out for many metals. In a wire of copper or other metal having a face-centred cubic lattice, the cube diagonal [111] takes this direction, but some preferential orientation of the cube axis [100] is also found. In α-iron and other body-centred cubic metals it is the face diagonal [011] which becomes parallel with the axis.[1]

A perfect orientation is never observed; there is always some scattering, occasionally as much as 30°, about the preferred direction, but the general nature of the fibre structure is quite apparent. Its character is affected by the features of the cold-working process, as for instance by the shape of the die in wire-drawing. With face-centred cubic metals drawn into wire a zonal structure was found, the outer zones having a conical arrangement, the preferred axes leaning towards the axis of the crystal, but not coinciding with it, and only the central core having the complete fibre pattern.[2]

The conditions in rolled sheet or foil are rather different, as the material is only compressed in one direction. One set of planes will set themselves parallel with the rolled surface, with one crystal axis in the direction of its length.[3]

The crystal grains in a rolled sheet form two symmetrical groups which, as far as the arrangement of their lattice planes is concerned, are mirror images of one another about the plane which lies half-way between the rolled surfaces.[4] In other modes of deformation the arrangement will be different, but its general character may always be inferred from the study of the slip in single crystals of the same metal. In tensile tests and in wire-drawing the individual grains must retain a more or less circular section during elongation. This suggests slip along three sets of planes, and leads to the [111] direction becoming the fibre axis in face-centred cubic metals, as is actually observed. The conditions in rolling are much more complex. The results of Owen and Preston are in accordance with the fact that, owing to friction between the surface of the metal and that of the rolls, plane transverse sections through the strip do not remain plane. It is not, therefore, usual to find a pure fibre structure in rolled metals, and several preferred directions may coexist. A bar of aluminium

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[1] M. Ettisch, M. Polanyi, and K. Weissenberg, *Z. Physik*, 1921, 7, 181.

[2] E. Schmid and G. Wassermann, *ibid.*, 1927, 42, 779; *Z. Metallk.*, 1927, 19, 325.

[3] First observed by A. Ono, *Mem. Coll. Eng. Kyushu Univ.*, 1922, 2, 241; N. Uspenski and S. Konobejewski, *Z. Physik*, 1923, 16, 215 (published in Russian, 1922).

[4] E. A. Owen and G. D. Preston, *Proc. Phys. Soc.*, 1926, 38, 122.

which is " square-rolled " has the same fibre structure as if it had been drawn into a wire,[1] but if rolled into a sheet the crystal direction which approximates to that of rolling is [335], whilst the plane face in the plane of rolling is (135), a curiously complex structure which does not appear to be accounted for completely by the overlapping of two simpler structures, unless a large amount of scattering is involved.[2]

WORK-HARDENING.

The reasons for the hardening of metals by deformation (cold working) have now to be considered. The hypothesis of Beilby assumed that in ordinary materials the process of slip was never one of simple translation, but that some friction between adjacent planes occurred, with the result that part of the lattice was broken down to form the vitreous modification, as in the process of polish. The quantity of vitreous matter formed at each slip would be small, but by offering an obstacle to further slip it would bring new surfaces into play. This could go on until the crystals were broken up into small masses, each enclosed in a rigid vitreous shell, when further deformation would cease and rupture would occur. Beilby considered that the microscopical examination of gold wires, drawn through dies until their ductility was exhausted, confirmed this view.[3] It is now usually regarded as too simple, but it still deserves consideration. X-rays naturally fail to reveal the presence of vitreous material, which would not give lattice reflections. The energy stored in cold-worked metals would on this view represent the latent heat of formation of the undercooled liquid phase.

The suggestion has been advanced[4] that the process of flow is one of actual melting.[5] The order of the pressures required to melt the metals, as calculated from their latent heat of fusion and their density, corresponds perfectly with the observed order of plasticity, and although the pressures seem enormous, they are only assumed to prevail in regions a few atoms thick, and for a short time.

A second explanation of hardening depends on distortion of the lattice. Laue pictures of single crystals after deformation no longer give sharp spots, but these are drawn out into bands. This would be explained either by a bending of the planes into curved surfaces, or by an actual breaking-up of the crystal, the fragments being grouped as if they lay along curves. With specimens composed of many crystals, photographs by the powder method show diffuse lines.

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[1] J. Thewlis, *Phil. Mag.* 1930, [vii], **10**, 953.

[2] Thewlis, *loc. cit.*, and V. Göler and G. Sachs, *Z. Physik*, 1927, **41**, 873.

[3] G. T. Beilby, *Proc. Roy. Soc.*, 1905, **76**, A, 462 ; 1907, **79**, A, 463.

[4] J. Johnston, *J. Amer. Chem. Soc.*, 1912, **34**, 788. See also A. W. Stepanow, *Phys. Z. Sowjetunion*, 1933, **4**, 609.

[5] See p. 276, also F. P. Bowden and K. E. W. Ridler, *Proc. Roy. Soc.*, 1936, **154**, A, 640 ; F. P. Bowden and T. P. Hughes, *Nature*, 1937, **139**, 152 ; for direct experimental evidence.

In a series of experiments on copper,[1] the broadening of the lines set in with even a small amount of deformation, increased steadily until the thickness of the strip had been reduced 30 per cent. by rolling, and then remained constant. Similar results were obtained for other metals. At the point at which distortion reached its maximum value the specimens began to show preferred orientation, that is, crystals or portions of crystals were taking up new positions relatively to the direction of stress.

This limiting value of line-broadening may, however, be exceeded if the crystals are broken down into fragments. X-ray lines become diffuse when the grains are less than 10^{-4} cm. across.[2] It is difficult to distinguish between the two causes of broadening, but where sufficiently precise measurements can be made, it appears that they affect the different orders of spectra unequally,[3] but it is rarely possible to apply this test, and certain anomalies make its interpretation difficult.[4]

The mechanical behaviour of solids cannot be accounted for on the assumption of a perfect crystalline arrangement. In a perfect crystal every plane in a given direction is equivalent to every other which is parallel with it, but when deformation occurs slip is confined to a few planes only, spaced some thousands of atoms apart. Many attempts have been made to find a unit of spacing, but all that can be said is that for a given specimen there is a statistical uniformity of spacing at a given temperature and stress, and that the variations about the mean spacing are not large. Goetz[5] obtained a value 1·4 μ for the spacing in bismuth, and 0·8 μ has been found in zinc,[6] but these are also probably an average. However, the facts of deformation call for some kind of imperfection within the crystal, either a mosaic of the kind discussed in Chapter XI, or flaws of the Griffith type distributed statistically. On this basis views have been put forward as to the mechanism of slip. There is evidence that slip does not proceed continuously, but rather by a series of jumps, an effect first observed in rock-salt,[7] but single crystal wires of zinc show it well.[8] The steps are of about equal height, about 1 μ, and their frequency increases rapidly with rise of temperature.

The conception of a special type of "dislocation" in the lattice of an actual crystal, distinguishing it from an ideally perfect crystal, has been ingeniously used[9] to explain the actual process of slip, resulting in work-hardening. The application of the theory leads to

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[1] W. A. Wood, *Phil. Mag.*, 1932, [vii], **14**, 656.
[2] M. v. Laue, *Z. Krist.*, 1926, **64**, 115.
[3] U. Dehlinger, *ibid.*, 1927, **65**, 631 ; *Z. Metallk.*, 1931, **23**, 147.
[4] W. A. Wood, *Nature*, 1932, **129**, 760.
[5] A. Goetz, *Proc. Nat. Acad. Sci.*, 1930, **16**, 99.
[6] M. Straumanis, *Z. Krist.*, 1932, **83**, 29.
[7] M. Classen-Nekludowa, *Z. Physik*, 1929, **55**, 555.
[8] R. Becker and E. Orowan, *ibid.*, 1932, **79**, 566.
[9] G. I. Taylor, *Trans. Faraday Soc.*, 1928, **24**, 121 ; *Proc. Roy. Soc.*, 1934, **145**, A, 362.

a parabolic form for the early part of the strain-hardening curve for a single crystal, which gives fairly good agreement with observation.[1]

All the evidence goes to show that the mechanism of breakdown of a metallic crystal or aggregate of crystals is the same, whether brought about by static deformation or by fatigue. A study of the process under a variety of conditions by means of X-ray examination [2] led to the conclusion that the original crystals break into fragments inclined to one another at small angles, not exceeding 2°, whilst fragments only about 10^{-4} cm. across are also produced, these small particles having a random orientation, as shown by the merging of the X-ray spots into continuous rings. In fatigue, no change in the original pattern is seen as long as the alternating stress is within the safe range, but when that range is exceeded, progressive breakdown into minute fragments occurs, until the whole of the metal close to the ultimate fracture is composed of them. Distortion of the lattice also becomes important in these last stages. This information must, however, be combined with that derived from microscopical examination, which shows, as already explained, that deformation is not uniform throughout a specimen, or even throughout a single grain, but proceeds by slipping of blocks over one another, regions of almost undeformed material being separated by highly distorted bands. In fatigue tests, those bands in which the structure has been most severely disturbed tend to persist, until fracture finally takes place within one of them. Whether the fragments are, as suggested, all of about the same size, 10^{-4} cm. across, possibly corresponding with the blocks of the original mosaic structure, or whether, as Beilby supposed, a vitreous material is also produced, has not been clearly established.

An anomalous result is obtained on cold-working eutectic alloys of the softer metals, such as lead and tin. Whilst the pure metals are hardened, if only temporarily, by cold work, the eutectics show a reduction of Brinell hardness immediately after being deformed, the original value being restored after some time at atmospheric temperatures, or more rapidly by heating to 100°.[3] The effect is connected with the behaviour in creep, the alloys which show this effect being those which give widely varying results for Brinell hardness according to the time of loading.

THE EFFECTS OF TEMPERATURE AND TIME.

The ease of deformation of metals varies greatly with the temperature. Most metals become more plastic as the temperature rises, and more rigid at low temperatures, but the variation is not

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[1] G. I. Taylor, *Proc. Roy. Soc.*, 1934, **145**, A, 388. For a review of this aspect of deformation, see W. G. Burgers and J. M. Burgers, *K. Akad. Wiss. Amsterdam* (Report on Viscosity and Plasticity), 1935, 172.

[2] H. J. Gough and W. A. Wood, *Proc. Roy. Soc.*, 1936, **154**, A, 510.

[3] F. Hargreaves, *J. Inst. Metals*, 1927, **38**, 315; 1928, **39**, 301.

always continuous. "Hot working" is possible, partly on account of the greater ease of movement within the lattice at high temperatures, and partly because work-hardening is annulled by the process of recrystallization which keeps pace with it. At very low temperatures most metals increase in strength but lose the greater part of their ductility, but slip is still possible at the absolute zero, and some surprising results have been found. At the temperature of liquid air [1] or of liquid hydrogen [2] the face-centred cubic metals, such as copper, lose much less of their ductility than does iron, whilst nickel and an alloy of iron containing 57·5 per cent. of nickel actually showed an increase of ductility as well as of tensile strength at the lowest temperature.

The critical shear stress appears to be of the same order at the absolute zero as at ordinary temperatures, but the capacity for hardening is far more dependent on temperature.

The effect of temperature on plastic deformation has been discussed theoretically in relation to the stress.[3]

Plastic deformation is not instantaneous, although the time required to produce slip may be very small. This has been indicated by the existence of steps in the deformation of a single crystal, mentioned above. A copper wire may be stressed beyond its yield point and even beyond its static breaking stress, and yet remain elastic, provided that the time of application of the stress does not exceed 0·001 second.[4] On the other hand, when a stress is allowed to act for a long time, deformation may proceed at a diminishing, constant, or even increasing rate. This phenomenon, the "creep" of metals, plays a most important part in engineering design, especially for structures at high temperatures. It may be observed at atmospheric temperatures in the softer metals. In tensile tests under prolonged stress, the load is usually kept constant, and if appreciable elongation should occur, the reduction of area brings about an increase in true stress. This may be avoided by using a device, such as a weight of hyperbolic section partly immersed in water,[5] or a pulley of similar section on which the loading cord is wound.[6]

For the soft metals, tin and lead, Andrade found a simple relation between elongation and time, represented by

$$l = l_0(1 + \beta t^{1/3})e^{kt},$$

where l is the elongation, t the time, and β and k constants. The

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[1] (Sir) J. Dewar and (Sir) R. A. Hadfield, *Proc. Roy. Soc.*, 1904, **74**, A, 326; R. A. Hadfield, *J. Iron Steel Inst.*, 1905, i, 147; H. C. H. Carpenter, R. A. Hadfield, and P. Longmuir, *Proc. Inst. Mech. Eng.*, 1905, 857; G. T. Beilby and H. N. Beilby, *Proc. Roy. Soc.*, 1905, **76**, A, 462.

[2] W. J. De Haas and (Sir) R. A. Hadfield, *Phil. Trans.*, 1933, **232**, A, 297.

[3] R. Becker, *Phys. Z.*, 1925, **26**, 919; E. Orowan, *Z. Physik*, 1934, **89**, 605.

[4] B. Hopkinson, *Proc. Roy. Soc.*, 1905, **74**, A, 498.

[5] E. N. da C. Andrade, *ibid.*, 1914, **90**, A, 329.

[6] C. E. Pearson, *J. Inst. Metals*, 1934, **54**, 111.

term in brackets, which Andrade called the β-flow, is plastic deformation occupying a short time, whilst the exponential term represents viscous flow. At lower temperatures the viscous flow becomes small and finally vanishes. X-ray examination connected the β-flow with the rotation of the crystal fragments.[1]

Creep is not confined to aggregates, but occurs also in single crystals, such as tungsten [2] and aluminium,[3] but as the precaution of keeping the stress constant was not adopted, quantitative relations could not be expected.

Creep at high temperatures over long periods was first studied in steels.[4] In prolonged experiments, the material itself undergoes changes during the test, so that at the end it may have quite different properties from those with which it started, and this makes a systematic description difficult. In particular, steels, which are the most important technically of the materials subjected to stress while hot, undergo recrystallization and also a rearrangement of the carbide particles. To determine the relation between stress, temperature, and time needed to produce failure, experiments lasting weeks or months are required, and short-period tests, although widely used in industry as a guide to the choice of structural materials, do not give the same results.[5]

In a metallographic study of the conditions of creep it is advisable to conduct the experiments in a high vacuum. Any change in the surface of the metal while under stress may affect the result, owing to penetration of oxygen along grain boundaries or some similar effect. A vacuum was used in an examination of the behaviour of iron at high temperatures.[6] When iron is broken, for instance in tension, at temperatures below 400° the fracture passes through the crystal grains, taking the path indicated by the closely packed planes within the crystal. At higher temperatures, when the load applied is such that a considerable time is required to break the specimen, the fracture is likely to pass between the crystals, following the grain boundaries. This was found in ingot iron (a highly oxidized product) at 400°, but only at higher temperatures in steel or wrought iron. This intercrystalline type of fracture may occur even in rapid loading tests if the temperature be high in relation to the melting-point of the

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[1] R. E. Gibbs and N. Ramlal, *Phil. Mag.*, 1934, [vii], 18, 949.

[2] H. Schönborn, *Z. Physik*, 1922, 8, 377.

[3] D. Hanson and M. A. Wheeler, *J. Inst. Metals*, 1931, 45, 229.

[4] J. H. S. Dickenson, *J. Iron Steel Inst.*, 1922, ii, 103.

[5] Shortened methods are given by A. Pomp and A. Dahmen, *Mitt. K.W. Inst. Eisenforsch.*, 1927, 9, 33; W. Rohn, *Proc. Intern. Assoc. Test. Mat.*, Zurich, 1932, i, 183; W. Barr and W. E. Bardgett, *Proc. Inst. Mech. Eng.*, 1932, 285; W. H. Hatfield, *ibid.*, 773. For a general account of creep, see R. G. Batson and H. J. Tapsell, *Proc. Intern. Assoc. Test. Mat.*, Zurich, 1931, i, 160; H. J. Tapsell, "The Creep of Metals," Oxford, 1931.

[6] C. H. M. Jenkins and G. A. Mellor, *J. Iron Steel Inst.*, 1935, ii, 179. See, for some early experiments, W. Rosenhain and J. C. W. Humfrey, *ibid.*, 1913, i, 219.

metal, as was recorded for copper,[1] tin,[2] aluminium.[3] It was facts of this kind which were explained by the assumption (p. 190) of an amorphous intercrystalline cement, a view not usually held at present.

ANNEALING, RECRYSTALLIZATION AND GRAIN GROWTH.

A cold-worked metal tends to revert to a more stable condition if opportunity occurs. For this some degree of mobility among its atoms must be possible, and different metals and alloys differ widely in the ease with which the change occurs. In general, metals of low melting-point lose their acquired hardness at a lower temperature than the more refractory metals, and for a given metal the temperature is lower, the less the quantity of impurity. Tin and lead are described as "self-annealing," as they soften at atmospheric temperatures after being cold-worked, but the effect varies greatly with the purity of the metal. Thus lead containing 0·0012 per cent. of total impurities, reduced in section only 5 per cent. by rolling, recrystallized completely in 1½ hours at 18°, whilst with 0·0082 per cent. of impurities there was no change, and even after 20 per cent. reduction recrystallization was incomplete after 24 hours.[4] Earlier work, with less pure metal, had required higher temperatures to produce the same effect.[5] Highly purified aluminium is largely self-annealing and slowly recrystallizes even at 0°,[6] but this is not true of the ordinary commercial metal.

The changes brought about by a rise of temperature in a metal which has been cold-worked take place in three stages. There is first a partial removal of the internal stress, which, as in severely cold-worked brass, may go so far as to eliminate the danger of season-cracking without greatly affecting the hardness. The same process carried rather further lessens the hardness without changing the micro-structure. The second stage is recrystallization—the appearance of new crystals among the old or among the debris of shattered crystals. The third stage is grain growth, some of the new crystals growing in size at the expense of the rest, leading in extreme instances to very coarse crystals, or even converting the whole specimen into a single crystal.

The physical as well as the mechanical properties change during the process. Measurements of hardness and of electrical conductivity and X-ray determinations are most frequently used as a means of following the change, combined with observations of the grain size. The principal conclusions may be summed up as follows:

In the first stage of heating, at low temperatures, internal stresses

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[1] G. D. Bengough, *J. Inst. Metals*, 1912, **7**, 123.
[2] W. Rosenhain and D. Ewen, *ibid.*, 1913, **10**, 119.
[3] Hanson and Wheeler, *ibid.*, 1931, **45**, 229.
[4] R. S. Russell, *Proc. Australian Inst. Min. Met.*, 1932, [ii], 135.
[5] J. C. W. Humfrey, *Phil. Trans.*, 1902, **200**, A, 225.
[6] J. Calvet, J. J. Trillat and M. Paić, *Compt. rend.*, 1935, **201**, 426.

are relieved and the tendency to crack, if originally present, is removed or lessened, whilst the strength and hardness are not reduced. Maintaining the metal at the same temperature for a longer time does not bring about the further softening. In some instances the hardness and tensile strength actually increase during this stage, and this is particularly noticeable in iron and carbon steel, for which the curve showing the influence of temperature on the hardness of cold-worked material takes the general form shown in Fig. 127,[1] which is complicated, however, by the abnormal variation of the properties of iron with temperature (p. 351).

The differences between a metal in the cold-worked and annealed states are conveniently followed by measurements of the thermoelectric force between them. Beilby used such a couple, composed of cold-drawn and annealed silver wires, and by gradually raising the temperature found a point at which annealing set in rapidly.[2] When the softening process is complete the two wires become identical, and the E.M.F. falls to zero. With most metals this change sets in rather suddenly, but the temperature at which it occurs is not to be regarded as a true transition temperature, as it is not reversible and depends on the degree of deformation. In experiments with copper rods of which one-half of the length had been annealed, reproducible values were obtained.[3] With cubic metals the effect is independent of the direction of rolling, but with hexagonal metals there is a marked directional effect.[4]

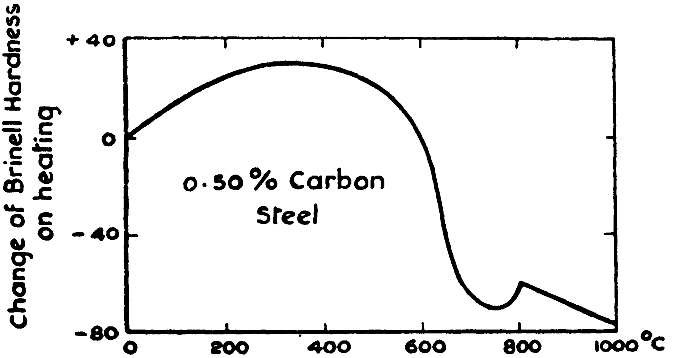

FIG. 127.—Temperature-hardness curve.

Beilby also made use of the elastic properties as a convenient means of following the change. The specimens being tested were used in the form of thin strips used as reed vibrators on a wind

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[1] A. Sauveur and D. C. Lee, *J. Iron Steel Inst.*, 1925, ii, 323.

[2] G. T. Beilby, *Proc. Roy. Soc.*, 1907, **79**, A, 463.

[3] W. F. Brandsma, *Z. Physik*, 1928, **48**, 703.

[4] G. Borelius, *Ann. Phys.*, 1919, [iv], **60**, 381. See also G. Tammann and G. Bandel, *ibid.*, 1933, [v], **16**, 120.

chest and blown by compressed air. Cold-working lowers the pitch of the note emitted and annealing restores it, a curve showing the relation between pitch and temperature to which the strip has been heated giving a clear indication of the softening temperature.[1]

Tammann studied similar changes by wrapping a cold-rolled strip into the form of a helix, holding in place by a wire, and observing the amount of uncoiling after heating to various temperatures and releasing. The disappearance of "springiness" could be compared with the changes of hardness, electrical resistance, thermo-electric E.M.F., and other properties, including even the spreading of drops of mercury on the surface. For copper, silver and gold all the properties showed changes within the same range of temperature, whilst for iron, nickel, platinum and palladium the elasticity and electrical resistance change at a much lower temperature than the hardness. The grouping shows that the differences are not determined solely by the space lattice, but also by the position of the metal in the periodic system.[2] Solid solutions show two inflections on the curve of recovery.[3]

In the second stage, new crystals appear, growing from nuclei in the deformed metal. It was formerly thought that these were crystals which had escaped deformation, and now grew at the expense of their less perfect neighbours, but modern investigations have made it certain that the nuclei arise in the most disturbed regions. They are first observed in grain boundaries,[4] in twin boundaries,[5] and in the strain-lines which are often seen on etching.[6] The new grains are at first small, but they increase in size when the temperature is further raised, and the third stage, that of grain growth, sets in. The growth takes place by migration of boundaries, and not, as was at one time suggested, by change of orientation on the part of one grain to bring its lattice into parallelism with another. The migration is particularly well observed in an alloy of tin containing 1·5 per cent. of antimony, used by Carpenter and Elam.

As the grains increase in size, the metal becomes softer. Three-dimensional "recrystallization diagrams" have often been constructed,[7] showing the relation between the degree of deformation, temperature of annealing, and grain size. The greater the deformation the lower the temperature at which recrystallization sets in, but the

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[1] G. T. Beilby, *loc. cit.*, and *J. Inst. Metals*, 1911, **6**, 5.

[2] G. Tammann, *Z. Metallk.*, 1934, **26**, 97, giving a bibliography of Tammann's former papers on the subject, mostly in *Z. anorg. Chem.*

[3] The German word "Erholung" is conveniently translated "recovery."

[4] C. H. Mathewson and A. Phillips, *Trans. Amer. Inst. Min. Met. Eng.*, 1916, **54**, 608; H. C. H. Carpenter and C. F. Elam, *J. Inst. Metals*, 1920, **24**, 83.

[5] H. C. H. Carpenter and C. F. Elam, *ibid.*, 1921, **25**, 259.

[6] F. Adcock, *ibid.*, 1922, **27**, 73.

[7] J. Czochralski, *Intern. Z. Metallogr.*, 1916, **8**, 1 (tin); P. Oberhoffer and H. Jungbluth, *Stahl. u. Eisen*, 1922, **42**, 1513 (mild steel); E. Rassow and L. Velde, *Z. Metallk.*, 1920, **12**, 369 (copper).

effect on the grain size varies for different metals. The production of exceptionally large grains after a critical deformation followed by annealing has been described in connection with the preparation of single crystals (p. 187).

As the hardness and tensile strength diminish, the ductility increases, the one curve being practically the inverse of the other. A typical diagram is shown in Fig. 128, which represents the changes in hardness and in grain size for sheet brass containing 31 per cent. of zinc, reduced 35 per cent. in thickness by rolling, and heated for 30 minutes at various temperatures.[1] For copper, α-brass and α-bronze the hardness is directly proportional to $3\sqrt{n}$, where n is the number of grains per sq. mm.[2] This number represents the amount of boundary surface per cub. mm., on the assumption that the grains are cubic in form.

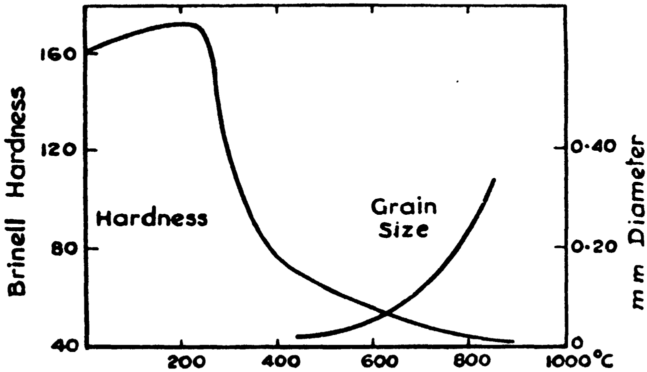

FIG. 128.—Changes of hardness and grain size in the annealing of brass.

Quantitative relations between the time required to produce a given amount of softening of a cold-worked metal and the temperature have been sought. For a number of metals a straight line relation between the temperature and the logarithm of the time is found over a considerable range of temperature, the lines representing the softening of specimens cold-worked to different degrees being parallel with one another.[3] This result has been applied to the case of creep, but here other factors intervene, and it is hardly to be expected that any single formula will cover the behaviour of different metals over a wide range of conditions. Formulæ for the growth in size of grains in a crystal aggregate have also been obtained, from observations on copper and aluminium.[4]

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[1] W. H. Bassett and C. H. Davis, *Trans. Amer. Inst. Min. Met. Eng.*, 1919, 60, 428.

[2] H. T. Angus and P. F. Summers, *J. Inst. Metals*, 1925, 33, 115.

[3] R. W. Bailey, *ibid.*, 1926, 35, 27.

[4] R. Karnop and G. Sachs, *Z. Physik*, 1930, 60, 464.

The chemical composition influences the processes of recrystallization and grain growth. Pure metals have a lower recrystallization temperature than their alloys, elements which enter into solid solution naturally having a greater effect than those which form a separate phase. The most marked effects are shown by elements which produce age-hardening, by passing into solid solution at a high temperature and separating on cooling. The commoner impurities in copper, when present to the extent of 0·1 per cent., raise the softening temperature by 50°-200°.[1] Dissolved gases may have a large effect, hydrogen raising the softening temperature of gold by 150°.[2]

Small quantities of insoluble impurities, while not affecting the softening temperature greatly, have a very great influence in inhibiting grain growth. A notable example is the use of thorium oxide as an addition to metallic tungsten in order to prevent the excessive grain growth, causing brittleness, which occurs during the prolonged heating of lamp filaments.[3]

In the practical treatment of cold-worked metals, it is often necessary to take precautions against excessive grain growth, as in the production of sheet metals suitable for deep-drawing processes. With large grains, the anisotropic character of the crystals becomes evident, whilst when the crystals are small it may be neglected. Consequently the large grains, if severely deformed, do so unequally, and their boundaries become conspicuous, so that after pressing or drawing the surface, instead of being smooth, shows markings in relief, of which the " orange peel " pattern is a typical example. For this reason, small deformations, which are apt to be critical, should be avoided before annealing, a drastic reduction of thickness by rolling giving rise to a suitably small grain size.[4] Mild steel presents a further difficulty on account of the marked flow at the yield-point, which leads to the sudden yielding of wedges of metal, leaving undeformed areas between them, and again producing a pattern in relief, the so-called " stretcher strains." A time effect is here involved. A slight stretching of the steel before pressing or drawing removes the liability to form such markings, but this immunity disappears after a day or so, or on heating to 100° even for a few minutes.[5]

That grain growth may occur it is usually necessary that the metal be previously deformed beyond the elastic range, and metals cast under normal conditions are not changed by annealing. An exception has been noted in cadmium,[6] which shows growth when

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[1] D. Hanson and C. B. Marryat, *J. Inst. Metals*, 1927, **37**, 121 ; D. Hanson, S. L. Archbutt and G. W. Ford, *ibid.*, 1930, **43**, 41 ; S. L. Archbutt and W. E. Prytherch, *ibid.*, 1931, **45**, 265.

[2] J. Phelps, *ibid.*, 1914, **12**, 125.

[3] Z. Jeffries, *ibid.*, 1918, **20**, 109 ; C. J. Smithells, *ibid.*, 1922, **27**, 107.

[4] See discussion in *Proc. Inst. Automob. Eng.*, 1935, 582 ff.

[5] H. S. Rawdon, *Bur. Stand. J. Res.*, 1928, **1**, 467 ; J. C. Arrowsmith, *Proc. Inst. Automob. Eng.*, 1931, 370.

[6] M. Cook, *Trans. Faraday Soc.*, 1923, **19**, 43.

the cast metal is annealed without intentional strain. Cadmium, however, is anisotropic in its properties, and its coefficients of expansion differ considerably along different axes.[1] It is therefore possible that the stresses set up by the different degree of contraction in neighbouring grains during cooling may be enough to cause grain growth. Many alloys, if cast in chill, are sufficiently strained to show grain growth.

Electrolytically deposited metals undergo recrystallization and grain growth when heated, although not subjected to deformation. This is well seen in copper[2] and in nickel.[3] Here again, the original crystals are in a condition of stress, caused in part by the presence of hydrogen, so that the softening effect on annealing may be of a complex kind.

The temperature at which a compressed clean metallic powder unites to form larger crystals, which grow on further heating, is approximately the same as the recrystallization temperature for the same metal when cold-worked.[4] The temperature is, however, dependent on the size of the original grains and on the pressure applied. The process may be well studied in the production of tungsten filaments by heating the compressed powder.[5]

The orientation of the new grains is not always independent of that of the original metal before deformation, but may be such as to produce a marked fibre structure. This is most readily studied in single crystals. A single crystal of aluminium, if severely deformed and then annealed, forms new crystals which prove, from their X-ray pattern, to have been produced by rotation around axes perpendicular to the planes of slip and to the lines of slip within those planes.[6] Even heating to 600° for a few seconds will produce this orientation. The correspondence is not exact, but there are deviations up to 10° from the main directions. Polycrystalline specimens of aluminium, deformed as uniformly as possible by compression, gave a fibre structure after annealing which corresponded closely with that caused by the deformation.[7] Similar relations have been found in rolled electrolytic iron sheet.[8] That thin sheets of electrolytic iron, if bent and annealed, developed very large crystals, the orientation of which could be determined by the strong reflections after etching, had been observed much earlier,[9] the fibre structure relation being obvious from the directions of reflection.

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[1] $52{\cdot}6 \times 10^{-6}$ along the principal axis; $21{\cdot}4 \times 10^{-6}$ perpendicular to it. (E. Grüneisen and E. Goens, *Z. Physik*, 1924, **29**, 141.)

[2] A. K. Huntington, *Trans. Faraday Soc.*, 1905, **1**, 324.

[3] G. E. Gardam and D. J. Macnaughtan, *ibid.*, 1933, **29**, 755.

[4] F. Sauerwald, *Z. anorg. Chem.*, 1922, **122**, 277.

[5] C. J. Smithells, W. R. Pitkin and J. W. Avery, *J. Inst. Metals*, 1927, **38**, 85.

[6] W. G. Burgers, *Z. Physik*, 1930, **59**, 651.

[7] W. G. Burgers and P. C. Louwerse, *ibid.*, 1931, **67**, 605.

[8] G. Kurdjumov and G. Sachs, *ibid.*, 1930, **62**, 592.

[9] J. E. Stead and H. C. H. Carpenter, *J. Iron Steel Inst.*, 1913, ii, 119.

The texture imparted to a metal by cold-working, with or without subsequent annealing, has an effect on the mechanical properties. This is particularly noticeable in sheet material. The mechanical tests in a direction transverse to that of rolling are inferior to those along the rolling direction, and this difference is more pronounced the greater the amount of deformation. As has been shown, some degree of fibre structure may be found after annealing, and differences between the longitudinal and transverse strength and ductility will then persist. Moreover, directional properties may be given by inclusions, which do not flow as readily as the mass of the material during deformation. An extreme example of this is seen in wrought iron. The included masses of slag or "cinder" are drawn out into threads in the process of hot-working, and resist deformation when cold. The metal therefore tends to tear along the length of the threads, giving the well-known fibrous fracture to the iron. A lower strength is obtained in a transverse test, as the threads are then perpendicular to the stress. In the light alloys of aluminium, such inclusions as those of $CuAl_2$ and Mg_2Si also behave as undeformable foreign matter.

Should the alloy solidify in such a way as to form dendrites the outer layers of which differ in composition from the cores, and this structure has not been destroyed by diffusion, forging processes tend to produce a banded structure, which will persist during later processes of treatment. An example is that of mild steel containing phosphorus. Alternating bands containing more and less phosphorus respectively affect the distribution of the carbide, giving rise to a well-known type of structure, seen in such materials as boiler plate.

INTERNAL STRESS.

The cracking of objects in a state of internal stress, often after a long interval, may be considered at this point. "Season-cracking" was first noticed in severely worked brass objects, such as cartridge cases.[1] The cracking, when it occurs, may seem to be spontaneous, but is usually caused either by a change of temperature or by chemical attack. The behaviour of such overstressed objects towards chemical agents is remarkable. In general, only specific reagents will cause cracking. Thus a heavily overstressed brass tube will dissolve evenly in nitric acid, but will crack, even explosively, on immersion in a solution of mercurous nitrate, and this reagent is used to detect internal stress in brass.[2] Ammonia will produce the same effect, but less rapidly. For other metals other agents are specific. Thus a hard-drawn alloy of gold, copper, and silver splits on touching with a solution of ferric chloride, which does not cause cracking in brass.[3]

[1] E. Heyn and O. Bauer, *Intern. Z. Metallogr.*, 1911, **1**, 16; E. Heyn, *J. Inst. Metals*, 1914, **12**, 3; H. Moore, S. Beckinsale and C. E. Mallinson, *ibid.*, 1921, **25**, 35.

[2] First introduced by F. Rogers at Woolwich in 1905. See *ibid.*, 1919, **22**, 114.

[3] W. C. Roberts-Austen; *Proc. Roy. Inst.*, 1886, **11**, 395.

It is characteristic of cracking of this kind that the cracks pass between the crystal grains, and not through them. A casting of β-brass, dipped into mercury, fell into separate polygonal grains in a few seconds,[1] although outwardly homogeneous. The much-debated occurrence of intercrystalline cracking in the steel plates of steam boilers, attributed to the effect of caustic alkali in the feed water, is also considered to be due to a combination of stress and chemical action.[2]

Liquid metals can also penetrate between the crystals of metals in a state of stress, and many such instances have been recorded, including the entry of molten solder and tin into β-brass,[3] of molten brass into mild steel,[4] and of low-melting metals into nickel-chromium steel.[5] The effect of composition of the steel has been studied,[6] but in all cases the presence of a tensile stress is necessary for penetration. No attack takes place on the side of a bent specimen which is in compression. The entrance of hydrogen into steel during pickling or electrolytic cleaning operations is well known to cause brittleness, and this evidently sets up stress in the grain boundaries, as molten brass readily penetrates between the crystals of steel so treated, but not if the hydrogen be first driven off by heat.[7]

The internal stress in such objects as brass tubes subject to season-cracking is removed by heating very gently to 175°-200° for 20-30 minutes, although this treatment has hardly any effect on the hardness, and the temperature is far below that at which recrystallization occurs.[8] Temperatures of 250°-400° had been used earlier.[9]

These facts show that it is important to have means of determining the presence and amount of internal stress in a specimen of metal. This is usually done by cutting, turning or boring the object in such a way as to relieve the stress or a part of it, and measuring the change of dimensions thus brought about. None of these methods can be said to be free from objection, and a non-destructive method is desirable.[10] It is clear that help cannot be sought from the microscope, as there is no visible difference between the stressed and the unstressed metal. X-ray examination seems more promising. The

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[1] C. H. Desch, *J. Inst. Metals*, 1914, **11**, 57.

[2] See, for a review and bibliography, E. P. Partridge and W. C. Schroeder, *Metals and Alloys*, 1935, 145.

[3] J. H. S. Dickenson, *J. Inst. Metals*, 1920, **24**, 315; H. J. Hartley, *ibid.*, 1927, **37**, 193; H. J. Miller, *ibid.*, 1927, **37**, 183.

[4] R. Genders, *ibid.*, 1927, **37**, 215; W. Riede, *Stahl u. Eisen*, 1929, **49**, 1161.

[5] L. J. G. van Ewijk, *J. Inst. Metals*, 1935, **56**, 241.

[6] W. E. Goodrich, *J. Iron Steel Inst.*, 1935, ii, 43.

[7] P. Bardenheuer and H. Ploum, *Mitt. K.W. Inst. Eisenforsch.*, 1934, **16**, 137.

[8] S. Beckinsale, *J. Inst. Metals*, 1923, **29**, 285.

[9] P. D. Merica and R. W. Woodward, *Proc. Amer. Soc. Test. Mat.*, 1918, **18**, ii, 165; W. B. Price, *ibid.*, 179; H. Moore and S. Beckinsale, *J. Inst. Metals*, 1920, **23**, 225.

[10] A review of the subject, including these methods and that of X-rays, is given by C. S. Barrett, *Metals and Alloys*, 1934, 131.

radial widening of lines in powder diffraction patterns is related to the internal stress, but agreement has not been reached as to its quantitative interpretation.

Internal stress does not only arise from cold-working; two other sources are of metallographic importance, namely, quenching stresses and those present in electro-deposited metal. The quenching of a mass of metal, as in the hardening of steel, necessarily sets up internal stresses through the unequal rate of cooling of the outer and inner portions, combined with the change of volume caused by the phase changes during cooling. Such quenching stresses may exceed the tensile strength of the steel, so that "hardening cracks" are produced, or they may approach it so closely that even a small change of temperature will add enough stress to cause cracking. An X-ray study of the surface then shows it to be in a state of compressive stress, the amount depending on the size of the specimen and the rate of quenching. Specimens of various alloys 1 mm. in diameter did not show the presence of stress when tested in this way, but the stress increased with increasing size and, less regularly, with increase of quenching temperature.[1]

Electrolytic deposits are frequently in a state of tensile stress, which in nickel may amount to 19 kg./mm.^{2}, determined mechanically. By suitably varying the conditions, alternating being superposed on direct current, deposits free from stress may be obtained.[2] Examination of such deposits by X-rays shows that lattice distortion is present. The extreme hardness of chromium deposits, however, is mainly due to the excessively small grain size.[3]

It is clear that no complete picture of the mechanism of hardening by cold work can yet be presented. Many contributions to the subject have been made from different angles, some of which have been discussed here, but their combination to form a synthetic theory of the process is still lacking. It is essential that metals belonging to different crystal systems should be examined, both as single crystals and as aggregates, as conclusions drawn from one type of lattice may fail to interpret the behaviour of a metal having a different lattice. Alloys have to be considered as well as pure metals. Analogies with ionic crystals such as rock salt, which have been so extensively used in recent physical research, must be applied with caution, as the ionic forces between metals and non-metals lead to a behaviour different from that of metallic atoms, united only by the less well-understood metallic linking. The writer feels that the Beilby hypothesis, which is not generally received with favour, contains an element of truth which should be capable of restatement in terms acceptable to modern physical theory.

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[1] G. Wassermann, *Mitt. K.W. Inst. Eisenforsch.*, 1935, 17, 167.

[2] R. H. D. Barklie and H. J. Davies, *Proc. Inst. Mech. Eng.*, 1930, 731. Earlier measurements of the stress in nickel deposits had been made by J. Stoney, *Proc. Roy. Soc.*, 1909, 82, 172.

[3] W. A. Wood, *Trans. Faraday Soc.*, 1935, 31, 1248.

CHAPTER XVIII.

THE CONSTRUCTION OF THE EQUILIBRIUM DIAGRAM.

THE thermal equilibrium diagram of a binary system of alloys, having temperature and composition as its co-ordinates, is divided into a number of fields bounded by lines, and the construction of the diagram depends on the experimental determination of the positions of these bounding lines and of their intersections. Neglecting the vapour phase, the lines which fall to be determined are :

1. The freezing-point curve, or liquidus.
2. The solidus, which may also be regarded as the melting-point curve.
3. Curves of liquid solubility, separating regions of immiscible liquid phases.
4. Horizontal lines, representing changes which occur at constant temperature over a range of composition, including eutectic lines (which form part of the solidus) and lines representing peritectic and eutectoid changes and polymorphic transformations.
5. Inclined lines, representing the limits of composition between which the solid phases present in the system are in equilibrium with one another. When a solid phase, such as an intermetallic compound, is invariable in composition, its bounding line is vertical, but most often there is some degree of inclination. Since the limiting composition of a solid solution usually changes less as the temperature falls, such bounding lines tend to become vertical at low temperatures, and even at higher temperatures refined methods may be needed to determine the slope.

An area within an equilibrium diagram, bounded by such lines as those just enumerated, is usually called a " field " of the diagram. Some rules stated by Portevin [1] are convenient for the interpretation of binary diagrams, and are repeated here :

1. Not more than two phases can be present in any one field.
2. On crossing an inclined line the number of phases changes by one.

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[1] A. Portevin, in " Traité de Chimie Minérale," ed. P. Pascal, vol. xii, Paris, 1934.

3. Every field, the boundary of which includes a horizontal portion, contains two phases. The fields adjoining a single horizontal line can only include three different phases, associated two by two.
4. Except for the field above the liquidus, representing a single homogeneous liquid, every single-phase field is occupied by a solid solution.
5. A phase which does not occupy a field by itself, but only appears in two-phase fields, is either a pure metal or a phase of invariable composition, which may be a definite compound.

In ternary alloys, the full representation is only possible in the three-dimensional model, in which volumes take the place of fields in the binary system, and surfaces that of lines, lines replacing points, and points being the intersections of lines. It is, however, common to make use of projections on to horizontal planes, and of vertical sections through the model, for purposes of convenience. When dealing with quaternary and more complex systems, such projections are inevitable, on account of the impossibility of constructing a model in more than three dimensions.

The diagram has certain inevitable limitations. It is an *equilibrium* diagram, that is, it represents the limits of temperature and composition within which each phase is, in the strict sense of the word, stable. But stability pre-supposes equilibrium conditions. An alloy may prove on examination to differ widely in properties from an ideal alloy having the same composition and the same temperature, but its condition is then not one of stability. The changes necessary to reach a state of stability may proceed so slowly, on account of the low velocity of diffusion, that the alloy presents a false appearance of being in equilibrium. Experiments continued over a long period may be required to determine the true equilibrium. Thus the alloys of lead and tin, frequently cited in the older text-books as a typical series composed of mutually insoluble solid metals, were found by later investigators to contain solid solutions of limited concentration; but annealing for six weeks at a temperature only 2° below the eutectic point was found necessary to enable the solid solutions, even in slowly cooled alloys, to attain their equilibrium concentration.[1] The complete diagram having once been constructed, however, an inspection of it affords at least qualitative information as to the metastable and labile conditions which may be obtained, for instance, by rapid cooling. The prolongation of branches of the liquidus curve below the eutectic point indicates the effect of undercooling, and points to the abnormalities which may be expected in the microstructure. The suppression of a transformation by rapid cooling through a certain range of temperature, causing the retention in the cooled alloys of a phase only stable at a higher temperature, is aimed at in all "quenching" processes, and a comparison of the microscopic structure with

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[1] W. Rosenhain and P. A. Tucker, *Phil. Trans.*, 1908, 209, A, 89.

the diagram will indicate the extent to which the transformation has been suppressed. Such systematic quenchings, if sufficiently rapid, are employed in the construction of the equilibrium diagram itself, as will be shown later.

Moreover, there are changes in solid phases, of great importance for metallography, which are not to be regarded as changes of phase. These are not therefore represented in the diagram by bounding lines, although for practical purposes it may often be convenient to insert them in such a form as dotted lines, in order to indicate what may be expected in the actual manipulation of the alloys. Such are the magnetic transformations in the alloys of ferromagnetic metals and the ordered-disordered changes in such solid solutions as β-brass at 470° and in the alloys of copper and gold round about the compositions Cu_3Au and $CuAu$ (see Chapter XX). In alloys subject to age-hardening, also, the properties vary so widely according to the degree of dispersion of the precipitated phase that the equilibrium diagram does not indicate them without a knowledge of the thermal history of the alloy, whilst the state of aggregation of carbides in steel influences the properties greatly, the relative quantities of the several phases remaining unchanged. These are inevitable limitations of the diagram, which in no way diminish its usefulness, but which must be borne in mind when using it as, for instance, a guide to technical practice.

After these general remarks, we may take the component curves and bounding lines of the diagram in order, enumerating in each instance the means which are at the disposal of the metallographer for fixing their positions.

1. *The freezing-point curve, or liquidus.*

The construction of this curve is always based on the determination of the cooling curves of the individual alloys. Either " direct " or " inverse-rate " curves may be used, as it is the initial freezing-point which is required. If undercooling takes place, the development of heat when freezing begins may be insufficient to raise the temperature of the mass to the true freezing-point ; it is therefore necessary to guard against undercooling by inoculation with the solid phase. For this purpose, a preliminary cooling curve is taken, and the approximate freezing-point determined. A small portion of the solid alloy is reserved and reduced to powder, the remainder of the mass is then re-melted and the cooling curve taken. As the freezing-point is approached, particles of the solid are introduced, the mass being thoroughly stirred.

The thermo-couple used should be calibrated by taking the freezing-points of a number of pure metals, using the same apparatus as in the investigation. Small errors due to a lag of temperature between the thermo-couple and the alloy are eliminated in this way ; large errors should not occur if the tube protecting the couple is of small diameter and the rate of cooling is sufficiently low. This calibration by means of pure metals, using the standard freezing-points given on page 87, affords a ready means of reducing all readings of temperature to the standard scale. The reduction should always be performed.

When the temperatures to be measured are too high for the convenient use of the thermo-couple, the optical pyrometer must be employed, a prism being fitted above the opening of the furnace to allow the pyrometer to be placed horizontally, as in the arrangement described on page 91.

It is of great interest to determine, with a high degree of accuracy, the initial portions of a freezing-point curve, as was done by Heycock and Neville for a large number of metals, the pyrometer used by them being of the very sensitive platinum resistance type. By taking a sufficient number of points at a short distance apart, the atomic depression may be determined, and the validity of Raoult's law tested. Information is thus gained as to the molecular condition of the dissolved metal. Moreover, it is only by determining such curves with accuracy that a comparison between different binary systems having the same solvent metal can be made, and from the relations thus obtained the behaviour on freezing of ternary alloys may be deduced, a procedure of great practical usefulness as well as theoretical importance.[1] Similar closely-grouped determinations in the neighbourhood of maxima in the liquidus also present a certain interest as a means of estimating the degree of dissociation of an inter-metallic compound into its components on melting.

Should the freezing-point curve be horizontal, or nearly so, for a part of its course, the existence of two liquid phases may be suspected, and one should proceed as under section 3 below.

The most difficult part of a freezing-point curve to determine is a branch ascending very rapidly from a eutectic point. Such branches are most likely to occur in systems in which the eutectic composition lies very close to one of the component metals. This is the case, for instance, in the alloys of copper and bismuth, the eutectic mixture of which is practically indistinguishable from pure bismuth. The curve representing the crystallization of pure copper rises very rapidly at first—to the extent of 400° for 20 atomic per cent. Cu.[2] The initial freezing-point of an alloy falling within this range is marked by only a very indistinct arrest on the cooling curve, since the quantity of copper deposited is very small. The use of large quantities of the alloy, a slow rate of cooling, a sensitive galvanometer, and the plotting of the results in the form of "inverse-rate" curves, are to be recommended in such cases.

The determination of the heating curve, whilst valuable in other directions, gives little help in the construction of the liquidus. The

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[1] W. Hume-Rothery, G. W. Mabbott and K. M. C. Evans, *Phil. Trans.*, 1934, **233**, A, 1.

[2] K. Jeriomin, *Z. anorg. Chem.*, 1907, **55**, 412.

initial freezing-point on cooling corresponds with the disappearance of the last solid particles on heating, a point which it is difficult to determine with the requisite accuracy.

The liquidus represents the limit of existence of solid phases. All points lying above it denote completely liquid alloys, assuming that the temperature is not raised above the boiling-point of one of the components. Each point on the liquidus gives the highest temperature at which a solid phase can exist in an alloy of that composition. All points below the liquidus denote alloys in which, under conditions of equilibrium, at least one solid phase is present.

It is sometimes impossible to complete the liquidus of a series of alloys, on account of the volatility of one of the components at temperatures approaching the melting-point of the other component. An investigation of the alloys of iron and zinc, for instance, is necessarily limited, under ordinary conditions, to the alloys ranging from pure zinc to a mixture containing a small percentage of iron; richer alloys lose zinc before melting. The alloys of arsenic with the less fusible metals, on the other hand, can only be investigated at the end of the series corresponding with the higher temperatures, the alloys containing small proportions of arsenic being stable, in spite of their high melting-point, whilst those rich in arsenic lose the excess of this element when melted under atmospheric pressure. It is possible, when the general aspect of the diagram is known, to construct the portion inaccessible to direct experiment by extrapolation from a ternary diagram. The alloys of zinc and nickel can be examined under ordinary pressure up to 54 per cent. of nickel, beyond which the melting-point is so high that zinc is lost by volatilization. The ternary system copper-zinc-nickel has been investigated, and the increase of fusibility due to the copper makes it possible to determine the freezing-points of almost the whole series of ternary alloys.[1] The general course of the liquidus and solidus has been determined as far as the volatility of the zinc allows, and extrapolation of the surfaces obtained gives the missing portion of the diagram of the binary system nickel-zinc without serious risk of error.

2. *The solidus.*

The construction of the solidus, dividing those regions in which only solid phases are present from those in which liquid is still present, involves much greater difficulties, both experimental and of interpretation, than that of the liquidus. The solidus may be made up of a number of separate parts—horizontal, vertical, and inclined. Taking the simplest case first, that of a eutectiferous series in which the only solid phases are the pure components (Fig. 4), the only line which falls to be determined is the eutectic horizontal. The points on this line are given by the lower arrests on the cooling curves. All of these arrests should occur at the same temperature, although

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[1] V. E. Tafel, *Metallurgie*, 1908, 5, 343, 375, 413.

small deviations are liable to occur as the ends of the horizontal are approached, that is, as the quantity of eutectic diminishes. A steady fall of the eutectic line in one direction points to experimental inaccuracy. The determinations nearest to the eutectic point, where the arrest is most strongly marked, are likely to be the most accurate, and should be chiefly trusted in fixing the position of the horizontal.

Undercooling at the eutectic point is a source of considerable difficulty. A pure eutectic mixture, like a pure metal, may be undercooled, and the addition of both solid phases simultaneously is necessary to prevent the undercooling. This is effected by the device of adding a portion of the previously cooled and powdered alloy; but when the eutectic forms only a small part of the alloy, this precaution is difficult to apply. When one phase is in excess it may continue to separate after the eutectic temperature has been passed, the remaining constituent continuing as an undercooled liquid. The final solidification of the latter is marked by a rise of temperature, by which the fact of the undercooling is rendered visible on the cooling curve, although its extent remains doubtful. The difficulty of resorting to inoculation is due to the fact that the liquid eutectic is distributed throughout a mass of the solid excess constituent, and is not readily brought into contact with the substance used for inoculation, although this may be partly remedied by thorough stirring. The existence of eutectic undercooling may sometimes be detected by the two branches of the freezing-point curve appearing to intersect at a point somewhat above the horizontal drawn in the preliminary diagram.

In cases of this kind a useful check is afforded by the examination of heating curves. When the eutectic temperature is reached in heating, a portion of the alloy melts; and this takes place without superheating, provided that segregation has not been so excessive as to prevent intimate contact of the solid phases. If segregation has taken place, the apparent eutectic point is too high. The correct temperature may be obtained by taking a heating curve after reducing the alloy to a fine state of division.

The temperature of the eutectic horizontal having been fixed, it remains to determine the limits of composition to which it extends in each direction. The component metals are generally capable of retaining a certain quantity of the other component in a state of solid solution, and in such a case the eutectic line must stop short of the limits of the diagram. Microscopical examination is a more sensitive method of fixing these limits than thermal analysis. Should an alloy of A and B, containing, for example, 0·1 per cent. of the metal B, show under the microscope distinct traces of inter-crystalline matter when quenched from just below the eutectic temperature, we may conclude that the solubility of B in solid A does not exceed 0·1 per cent.[1] With the necessary experimental skill, and by the use of

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[1] This only fixes an upper limit. Long annealing may show the solid solubility to be less.

suitable polishing methods, especially when dealing with soft metals such as lead, it is possible to detect very minute traces of included inter-crystalline matter. Heat-tinting or exposure to vapour is to be preferred for this purpose to etching with acids, since the latter treatment results in the production of grooves between the crystal grains, masking the feature sought for. The included metal B is more likely to appear as a film or band than to show a eutectic structure, on account of the tendency of eutectics, already noted, to undergo segregation in presence of a large excess of one of their component phases.

The second method of fixing the limits of the eutectic horizontal is that due to Tammann, consisting in plotting the duration of the eutectic arrest in each alloy of the series against the composition. This method is fallacious, and has been the cause of much inaccuracy in published diagrams.

In most laboratories inverse-rate curves are used in preference to direct curves. For students' purposes, however, the direct method has great advantages, and eutectic times may then be observed. It is then essential that the same volume of metal be used for each determination, owing to the crude thermal methods mainly used, making extrapolation of the times near to the eutectic point, which are the only times easily determinable, very uncertain.

The cooling curve usually presents a slight rounding of the horizontal portion, and it is therefore necessary to determine what are the limits of time between which the arrest is to be assumed to continue. This may be done with a satisfactory degree of accuracy by producing the horizontal line *bc* (Fig. 129) and the descending line *de* until they meet at *g*. The distance *bg*, measured on the time scale, may be taken as the duration of the arrest.

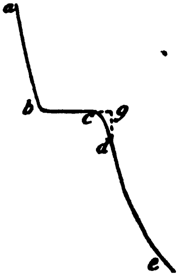

FIG. 129.—Correction of cooling curve.

In addition to eutectic lines, the solidus may comprise lines corresponding with peritectic reactions between solid and liquid, such as the line at 460° in the diagram of the antimony-gold alloys (Fig. 20, p. 38), which indicates the chemical reaction:

$$AuSb_2 \rightleftharpoons Sb + \text{liquid}.$$

Such a reaction, occurring during cooling, takes place in the direction of the lower arrow with development of heat, and is consequently marked by an arrest on the cooling curve, an arrest which is very liable to be affected by undercooling. The reaction is liable to be incomplete, owing to the fact that one of the reacting bodies is solid, the product being also solid. A reaction therefore takes place on the outer surface of the crystals, a layer of the new compound being formed, but the presence of this layer checks further chemical action, by isolating the interior of the crystals from the liquid with which they have to react. Unless sufficient time is allowed for the composition of the particles to become uniform through diffusion, the process is arrested at an incomplete stage. Evidently the error due to this cause will be lessened by thorough stirring, which favours the formation of very small crystals, presenting a larger surface in proportion to their mass, and therefore allowing the reaction to proceed further towards completion. We may also, after cooling the alloy, crush it to a fine powder to facilitate contact of the reacting substances, and reheat to the transformation temperature, taking a new cooling curve from that point.[1] The best plan is to chill the alloy immediately after solidification, so as to produce a fine-grained structure, and then to reheat to the temperature of the reaction. Both cooling and heating curves should be taken.

Turning to alloys in which solid solutions are formed, the determination of the exact position of the solidus now assumes greater difficulty. Consider first a pair of isomorphous metals, such as gold and silver. The solidus may be considered from two points of view. On the one hand, it represents the temperatures at which solidification is completed; on the other, it represents the composition of the solid phase in equilibrium with the liquid at each temperature. An experimental determination by the latter method is impracticable, for although means have been devised for isolating and analysing solid phases during crystallisation,[2] it is impossible to free the crystals from mother-liquor, and the accuracy obtainable is quite insufficient for the purpose. The uncertainty of the cooling curve method arises from the fact that the point *c* (Fig. 10, p. 28), at which the development of heat ceases and the curve joins that of the cooling solid, is marked by only a slight change of curvature, so that its position is not readily determined. The error is not avoided by plotting inverse-rate curves, as the return to the base line is ill-defined, as on the direct curve.

On the heating curve, however, it is precisely the beginning of melting that is more clearly marked, whether the direct or inverse-rate plotting be adopted, and it is in this way that the position of the solidus is most readily fixed. Special precautions have to be used when the temperature is high, as in the iron-chromium[3] and iron-manganese[4] systems. The dilatometric method supplements that of thermal analysis, and proves very convenient in this particular instance. The dilatometric method lends itself well to the study of alloys of low melting-point, such as the amalgams, which may be enclosed in a volume dilatometer. The changes of volume of the cadmium amalgams, for instance, are considerable.[5]

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[1] G. Tammann, *Z. anorg. Chem.*, 1905, 45, 24.

[2] C. van Eyk, *Proc. k. Akad. Wetensch. Amsterdam*, 1902, 10, 859. A device for estimating the proportion of mother-liquor retained is described by A. van Biljert, *Z. physikal. Chem.*, 1891, 8, 343; and W. D. Bancroft, *J. Physical Chem.*, 1902, 6, 178.

[3] F. Adcock, *J. Iron Steel Inst.*, 1931, ii, 99.

[4] M. L. V. Gayler, *ibid.*, 1933, ii, 293.

[5] H. C. Bijl, *Z. physikal. Chem.*, 1902, 41, 641.

An ingenious method of fixing the position of the solidus, different in principle from those described, was introduced by Heycock and Neville in their investigation of the copper-tin alloys.[1] It consists in quenching several alloys of the same composition from different, exactly determined temperatures, lying a short distance below the initial freezing-point. One of these alloys, let us suppose, is quenched before it is completely solid, and on microscopical examination it is easy to detect the suddenly chilled mother-liquor as an inter-crystalline material, filling the cavities between the crystals which separated during the slow cooling. Another alloy, quenched just after solidification was complete, is found to consist wholly of the solid solution. The point on the solidus corresponding with this alloy evidently lies between the quenching temperatures of these two alloys, and by a suitable choice of temperatures the solidus may be drawn with great accuracy, if adequate means of rapid quenching are available and enough alloys are examined.

This method, to which Hume-Rothery has applied the military term "bracketing," may be applied generally in the construction of the equilibrium diagram, and not merely in the determination of the solidus. Wherever, by quenching or otherwise, it is possible to fix a point which is clearly above a line of the diagram and another which is clearly below it, the accuracy may be increased by selecting two temperatures between those already used, and so narrowing the interval. The same plan is used in fixing inclined or vertical lines in the diagram, pairs of points being found between which the required line must lie.

The application of this principle may be illustrated by a concrete example. The alloys of aluminium and zinc had given results which were difficult to interpret, and in a re-investigation of the system[2] the precaution was taken of annealing for a long time to obtain homogeneity, and the bracketing method was used with close intervals. Chill-cast ingots were annealed for 12 days at 345° or at 416°, according to their composition, and then quenched to prevent segregation during cooling. Small pieces cut from these ingots were then heated rapidly to a temperature a little below the solidus, held for ten minutes, and then quenched. This was repeated, each time raising the temperature by 5°. On polishing and etching, any sign of melting was easily detected, and the position of the solidus was fixed accurately. The equilibrium diagram, slightly modified by later work,[3] is given in Fig. 107, p. 203.

3. *Curves of liquid solubility.*

The separation of an alloy into two immiscible liquid phases, or the failure of two metals when melted together to form a homogeneous

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[1] *Phil. Trans.*, 1903, **202**, A, 1.

[2] D. Hanson and M. L. V. Gayler, *J. Inst. Metals*, 1922, **27**, 267.

[3] W. L. Fink and K. R. Van Horn, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 132. This diagram requires still further modification.

liquid, introduces an important modification into the experimental determination. Should such a separation be suspected, the molten alloy must be thoroughly stirred and then allowed time for the separation into two layers to take place. After cooling, the ingot is sectioned vertically and examined. The difference between the upper and lower layers is usually obvious, but an emulsion is sometimes formed which separates with difficulty, one constituent being suspended in the form of solidified drops within the other. This condition is easily recognized microscopically. If any portion of a freezing-point curve is found to be horizontal, a separation into two liquid layers may be suspected, and all alloys falling within that range should be examined microscopically.

The upper parts of the curve of liquid solubility, lying above the liquidus, cannot be determined by the simple thermal method, as the development of heat is too small to be detected and other methods have to be used. These have been described on p. 55, in connection with the alloys of lead and zinc, and of lead and copper.

4. *Transformations of solid phases.*

The horizontal lines representing polymorphic changes in solid phases may or may not intersect the liquidus. In the former case, a change takes place at a certain temperature in the nature of the solid phase in equilibrium with the liquid, and this involves a discontinuity of direction in the liquidus curve. The effect on the liquidus is therefore the same as that of a peritectic reaction, and it becomes necessary to find a means of distinguishing between these two possibilities. The conditions are illustrated in Fig. 130. The ascending branch of the freezing-point curve presents two similar discontinuities, at *r* and *p* respectively, and alloys lying within the respective limits of concentration have arrests on their cooling or heating curves, represented by the lines *pq* and *rs*. The arrest *pq* is a maximum in the alloy corresponding with the formula AB_2, pointing to the formation of a definite compound. The second arrest is a maximum at the same composition, indicating that it is due to a polymorphic change of the compound AB_2, and not to the formation of a new phase of different composition. Quenching experiments, followed by microscopical examination, are applied as a check on the thermal method, and where a high-temperature X-ray camera is available direct evidence may be obtained by a study of the alloys above and below the lines representing a change of phase.

Transformations in solid solutions are marked by lines in the diagram which are not horizontal, but inclined. They are conveniently discussed along with other boundaries between solid phases, represented by vertical or inclined lines. The first essential condition is that the specimens shall be thoroughly annealed, otherwise wrong limits for the concentration of solid solutions and similar errors will occur. The need for long annealing is often under-estimated. Weeks may be required at temperatures of 300°-400°, whilst in the examination of dental amalgams, the solidus of which is at a low temperature, annealing at 70°, which is required for equilibrium, may have to be continued over many months.[1]

In Tammann's method of applying thermal analysis, plotting the duration of a eutectic, peritectic, or other similar arrest against the composition gave the point of disappearance of a phase or the appearance of a new one by producing the curve to zero duration. This method can rarely be depended on, as the arrests become fainter towards the end, and their exact cessation is uncertain. It is only of service in a preliminary study of a system.

Microscopical examination of fully annealed alloys is the most generally useful method. A series of alloys of progressively changing composition will bring out clearly the boundaries between successive regions by an examination of their structure. When suitable methods of polishing and etching are adopted the method is exceedingly delicate, as quite minute quantities of a separate phase can be detected. In spite of the popularity of physical methods, this must remain the most generally applicable of all means of fixing boundaries. In the study of equilibria at temperatures above that of the atmosphere, direct examination by the microscope is not often practicable, and quenched specimens have to be used. Their structure is interpreted as if they had been slowly cooled, but caution is necessary, as some transformations take place so quickly that it is impossible to suppress them by the most rapid quenching, and a careful study of the behaviour of the alloys at different rates of cooling is necessary.

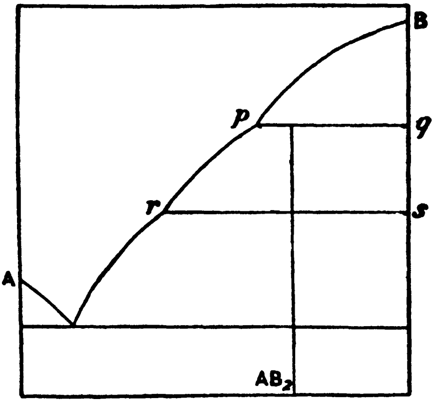

FIG. 130.—Compounds and polymorphic change.

The method of X-ray examination comes next in importance. Valuable as it is, it has certain limitations, as small quantities of a separate phase, clearly distinguishable under the microscope, may be quite undetectable by the X-ray method. It has, however, the advantage of giving information about the single-phase region as well as about regions containing two or more phases. The gradual change of parameter of a solid solution with composition can be measured with precision, and a sudden break in the parameter-composition curve is a clear indication that a new region has been

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[1] M. L. V. Gayler, *J. Inst. Metals*, 1937, 60.

entered. A concrete example of the study of a system by this means may be given.[1] Alloys of copper and silver were annealed in the form of ingots at 750°, and then reduced to fine filings and again annealed at various temperatures, after enclosing in evacuated pyrex tubes. Two phases might be present, each having a face-centred cubic lattice, the α-phase having a parameter near to that of silver but somewhat smaller, and the β-phase a parameter near to that of copper but larger. The determination of the β-phase boundary may be considered.

An alloy containing 69·5 per cent. of copper was first taken and annealed, one hour being sufficient at the higher temperatures, increasing to 72 hours at 290°. From 600° downwards the results were the same, whether the alloys were quenched or air-cooled. The measurements of the parameter of the β-phase are plotted on the curved line in Fig. 131 (*a*). Four alloys, containing 98·7, 97·6, 95·6, and 93·1 per cent. of copper were annealed and examined at selected temperatures. When the parameter is constant over a range of temperature, as shown by the horizontal lines in Fig. 131(*a*), the alloys consist of the homogeneous phase at that temperature, and the intersections of these lines with the curve give the temperatures at which those alloys enter the single-phase region. The relation between parameter and composition is then obtained from the figures, as shown in Fig. 131 (*b*), and the form of the β-phase boundary is then calculated as in Fig. 131 (*c*). A similar procedure is followed for the α-phase boundary.

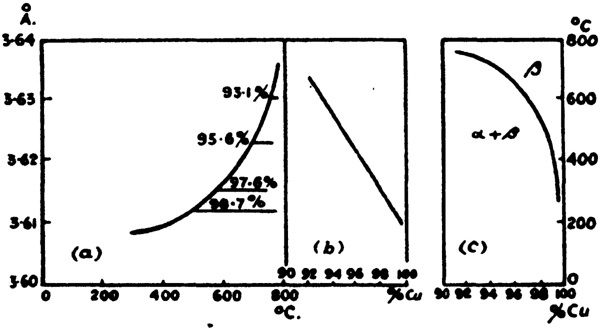

FIG. 131.—Parameters of silver-copper alloys (Owen and Rogers).

The X-ray method has also been widely used for fixing the phase boundaries in a complex system at atmospheric temperatures. In such a case the information must be regarded as supplementing the evidence of the microscope, and not as taking precedence over it, and special precautions must, of course, be taken to ensure that the specimens have been sufficiently annealed. A single example may be taken.

Aluminium and silver both crystallize with face-centred cubic

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[1] E. A. Owen and J. Rogers, *J. Inst. Metals*, 1935, 57, 257.

lattices, but at atmospheric temperatures there are two intermediate phases. The probable diagram is shown in Fig. 132.[1] The α-phase, a solid solution in silver, has a parameter which falls from 4·079 Å. for pure silver until the limit of saturation is reached at 20 atomic per cent. Al, when it has the value 4·053 Å. The parameter of aluminium is unchanged by silver, indicating a negligible solubility at room temperature. At the eutectic temperature, however, the solubility of silver in solid aluminium reaches 18 atomic per cent.[2]

The β′-phase is of invariable parameter, and is represented by a vertical line in the diagram. Its composition corresponds with the formula Ag_3Al, and its structure is cubic, the unit cell having an edge of 6·920 Å., and containing 20 atoms.[3] It is isomorphous with β-manganese, and in spite of its homogeneous character it does not appear to be a true compound, as the aluminium and silver atoms are distributed at random on the lattice. The γ-phase extends from 27 to 40 atomic per cent. Al, and is of the close-packed hexagonal type, the lattice constants changing continuously throughout the range of its existence. On account of the failure of the X-ray method to

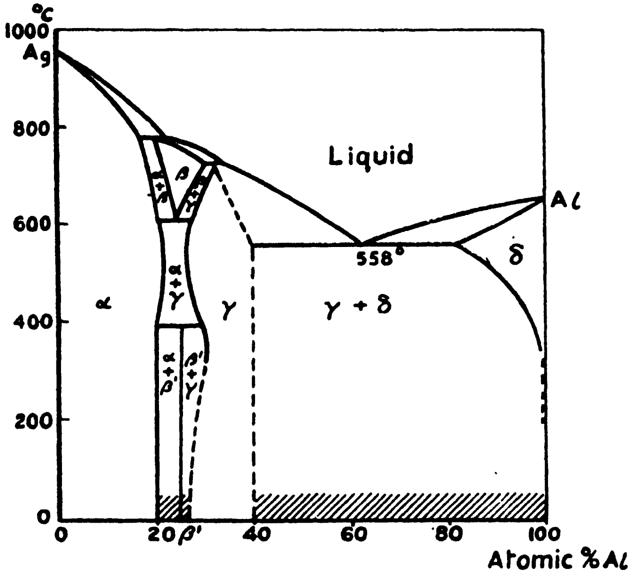

FIG. 132.—Aluminium-silver alloys.

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[1] G. J. Petrenko, *Z. anorg. Chem.*, 1905, **46**, 49; T. P. Hoar and R. K. Rowntree, *J. Inst. Metals*, 1931, **45**, 119; N. Ageew and D. Shoyket, *ibid.*, 1933, **52**, 119.

[2] M. Hansen, *Z. Metallk.*, 1928, **20**, 217.

[3] A. F. Westgren and A. J. Bradley, *Phil. Mag.*, 1928, [vii], **6**, 280. The change of parameter within the α-range was also determined accurately by C. S. Barrett, *Metals and Alloys*, 1933, **4**, 63.

detect small proportions of a new phase, the greatest weight is laid on the attainment of a constant value for the lattice constants at a given composition. Constancy beyond that range indicates that a two-phase field has been entered.

The central part of the diagram has been drawn in dotted lines, as the limits of the γ-phase at higher temperatures have not been fixed with accuracy.

The X-ray method is of special value in the examination of intermediate phases. Some systems, formerly regarded as simple, prove on detailed examination to include a number of such phases, some of which differ only very slightly in structure, so that they are easily overlooked when ordinary metallographic methods are used. This aspect of the problem has become more important since the introduction of the electronic rules, assigning certain probable constitutions to phases having a given lattice structure. Such phases are sometimes very complex, having a large number of atoms to the unit cell, so that they deviate appreciably from simple cubic or hexagonal structures. The alloys of aluminium with the transition metals are of this type. The X-ray method also serves to determine other changes, such as that from a disordered to an ordered solid solution (Chap. XX) which do not find a place in the equilibrium diagram, but are of importance in determining the physical and mechanical properties of the alloys.

The change of any physical property with variation of composition and of temperature may be used as an auxiliary means of fixing the phase boundaries, and when the property is such that continuous records may be taken, as in thermal analysis, its use may greatly facilitate the work of constructing a diagram. Dilatometric and electrical resistance methods are most often applied, but magnetic and electrolytic methods have been found useful by certain groups of workers. The dilatometer has become an indispensable instrument in the metallographic laboratory, and has been made available for ranges of temperature up to 1500° (p. 99). Arrests on the heating or cooling curve are plotted in the same way as thermal arrests, with the advantage that they are less dependent on the rate of cooling.

The method of magnetic analysis is also of value for the determination of constitution, and its use is not confined to alloys of the ferro-magnetic metals. The susceptibility of either paramagnetic or diamagnetic metals may be determined by the Weiss method, and its variation with composition at a fixed temperature, or with temperature at a fixed composition, may be measured.[1] Like the conductivity, the magnetic susceptibility usually varies linearly throughout a two-phase field, and changes rapidly with the composition within a series of solid solutions, sometimes with cusps corresponding with simple atomic ratios. Changes of phase on heating or cooling

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[1] A review of the work, most of which has been carried out in Japan, is given by K. Honda and H. Endô, *J. Inst. Metals*, 1927, **37**, 29.

a single alloy are well marked by breaks in the susceptibility curve, and in this way, for instance, the positions of the solidus and cementite line in the iron-carbon system have been determined.[1]

When undertaking the study of a ternary system it is important to realize that the number of alloys to be examined is necessarily large, and that their compositions should therefore be so chosen as to give the greatest amount of information from the smallest number of separate alloys. This means systematic planning. To prepare alloys at regular intervals, such as 5 per cent., over the whole system, may be highly wasteful, and a careful examination of the three binary systems involved should first be made. The liquidus surfaces in a ternary system are completely analogous with the liquidus curves in binary alloys, but at lower temperatures the arrangement is more complex. In place of the binary eutectic horizontal line which represents the freezing of a binary eutectic, there is now a sloping surface, in which lies the line of intersection of two liquidus surfaces, whilst the final solidification of a ternary eutectic is represented by a horizontal plane. The two-phase equilibrium which corresponds with the eutectic in the binary system should not be called a binary eutectic, as its temperature varies with the composition, but the term is often so applied, partly on account of the fact that the microscopic structure resembles that of a eutectic, and also because the eutectic point on the binary curve is the starting-point of a valley leading into the interior of the space model and terminating in a point which is undoubtedly a ternary eutectic point.

Where one of the constituent binary systems includes a well-marked intermediate phase, indicated for instance by a maximum freezing-point, it is often convenient to examine a series of ternary alloys along a line joining that point with the third component metal, as this section may prove to be pseudo-binary, admitting of the same treatment as a true binary system. "A crucial" method, first suggested by Guertler, may be used to save time in the preliminary study of a ternary system. In the system shown in Fig. 29 (p. 45), the metals A and C form a single compound or intermediate phase, Z, whilst B and C form two such phases, X and Y. It is sufficient to examine an alloy having the composition O, at the intersection of BZ and AY, to determine, microscopically or otherwise, whether it consists of the phases B and Z, or of A and Y, to decide which of the possible lines shown represents an actual pseudo-binary system, thus limiting the number of alloys required for a fuller investigation. Other series, equivalent to vertical sections through the space-model, may be selected in one of two ways, as described in Chapter III; on the one hand the percentage of one component being kept constant, or on the other the ratio between two of the components being constant, equivalent to the horizontal and inclined lines in Fig. 28 respectively. The thermal and other observations on each

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[1] K. Honda and H. Endô, *Sci. Rep. Tôhoku Univ.*, 1927, 16, 235.

series are plotted as if for a binary system, and from their combination the space-model is constructed.

Differences of opinion exist among metallographers as to the relative advantages of two methods of representing the results. They may be presented as described above, as a number of vertical sections, or in the form of horizontal sections parallel with the base of the model, that is, as pictures of isothermal equilibrium at successive temperatures. The former gives the clearer picture, but for the practical use the latter may be more convenient. This is so when only a small part of the ternary system is being studied, and in practice this occurs most frequently. For the study of the age-hardening of light aluminium alloys, for instance, it is the region close to the aluminium angle of the diagram that is of importance, whilst for the knowledge of the alloys of iron it is most often essential to examine the region close to the iron angle. To give anything like a full account of the thermal study of a ternary system would occupy far too much space, and it is best to examine in detail some records of typical investigations, of which a few examples are given in the footnotes.

As with binary alloys, the thermal observations have to be checked by the determination of physical properties, such as electrical conductivity, and by the X-ray method. The method of surveying a ternary system by X-ray examination has been greatly developed by Bradley. The greatest possible use should, however, be made of the microscope, both annealed and quenched specimens being examined. By a judicious choice of alloys and of quenching temperatures, much time may be saved in the study of a complex system. A word of warning is, however, necessary. With the increasing number of possible phases (three may be in equilibrium in a single solid alloy) the identification of the constituents becomes more difficult, especially when two of them are very similar in properties. It is therefore essential to make careful experiments to determine the etching characteristics of each phase, alone and in the presence of others, and this often means a preliminary research. It must be remembered that small quantities of impurities, such as oxygen, nitrogen, or silicon, may be present and cause the appearance of a distinct phase not allowed for in the equilibrium. The light alloys of aluminium present special difficulties of this kind, and much work has been done on the comparison of the etching behaviour, towards different reagents, of those phases which may possibly occur.[1]

Examination by means of X-rays provides a comparatively rapid means of surveying the whole field and of distinguishing single-phase regions from those containing two or more phases, leaving the exact

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[1] E. H. Dix and W. D. Keith, *Proc. Amer. Soc. Test. Mat.*, 1926, **26**, ii, 317. See also D. Hanson and S. L. Archbutt, *J. Inst. Metals*, 1919, **21**, 291; A. Meyer, *Z. Metallk.*, 1923, **15**, 257.

determination of the phase boundaries to microscopical and other methods.

The difficulties associated with ternary systems are naturally intensified in the study of quaternary and more complex systems of alloys. As a rule, information is only required concerning one corner of such a system, represented by one angle of the tetrahedral model, (p. 54) and thermal results are so complex that careful check by microscopical examination becomes necessary. An example of a complete study of a quaternary system is that of the alloys of lead, cadmium, bismuth, and tin, which is of a simple type, there being no intermediate phases. The investigation, however, did not cover the change of solid solubility with temperature, to which attention had not been directed at the time.[1]

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[1] N. Parravano and G. Sirovitch, *Gazz. Chim. Ital.*, 1911, **42**, i, 1.

CHAPTER XIX.

THE CONSTITUTION OF ALLOYS AND THE NATURE OF INTER-METALLIC COMPOUNDS.

ALLOYS being regarded as solutions, the consideration of their molecular condition forms a part of the general theoretical study of solutions. Whilst, however, the discussion of solutions in which the solvent is water or a similar liquid has been devoted mainly to dilute solutions, the solvent being in large excess, such a limitation is not possible in regard to alloys. The distinction between "solvent" and "solute" is only applicable to a very small range of alloys at the two ends of each series.

From the point of view of the molecular condition in solution, the alloys of mercury with other metals, the so-called amalgams, were naturally the first to receive attention, owing to the fact that mercury and its dilute alloys are liquid at atmospheric temperature, so that freezing-point determinations may be carried out in an ordinary Beckmann's apparatus, and measurements of vapour pressure and surface tension may also be made. The amalgams have also been much investigated from the point of view of their electrolytic potential, and of the velocity of diffusion within them.

THE FREEZING-POINT CURVE.

In examining the molecular condition of dissolved metals we make use of the *atomic fall*, which is obtained by dividing the depression of freezing-point by the atomic percentage of the added metal. Such a procedure is only legitimate so long as the solution is dilute, that is, so long as the percentage of the second metal in the alloy is small, hence the advantage of closely grouped freezing-point determinations in the neighbourhood of the pure metals (p. 302).

The theoretical depression of freezing-point is given by van't Hoff's equation—

$$\Delta = \frac{0{\cdot}02\ T^2}{Q}$$

in which Δ is the depression due to 1 mol. of the solute in 100 mols. of solvent, T the absolute temperature of freezing, and Q the latent heat of fusion. This formula allows the molecular weight of the solute to be calculated from the observations if the latent heat is known, or conversely, the latent heat may be calculated if an assumption be first made as to the molecular condition of the solute. The formula has been applied in both ways. In the first place, the molecular weight of most metals dissolved in mercury was found to be equal to their atomic weight,[1] the theoretical molecular fall being calculated as 2·12°, and the mean value obtained with several metals being 2·12°. Van't Hoff's equation is, however, only applicable if the solid phase separating on freezing is the pure solvent, in other cases the atomic fall does not coincide with the molecular. Thus cadmium, even in the smallest quantities, *raises* the freezing-point of mercury. Tammann obtained similar results with sodium as solvent, and these mixtures were independently studied at the same time by Heycock and Neville,[2] who also found that the dissolved metals behaved in most instances as if monatomic. For gold in sodium, the curve extending from pure sodium to the eutectic alloy, containing 3·5 atomic per cent. of gold, is strictly rectilinear, and gives the atomic fall 4·5. Similar results were obtained by the same investigators, using as solvents[3] bismuth, cadmium, lead,[4] thallium,[5] zinc,[6] silver, and copper.[7] The general conclusion arrived at was that the state of metals in dilute solution which do not form solid solutions is almost invariably that of single atoms.

The formula given only applies to very dilute solutions, and cannot be used to determine the form of the "ideal curve." A more complete formula, extending over the whole range of the freezing-point curve, was arrived at independently by I. Schröder[8] and H. Le Chatelier,[9] on the assumption that the latent heat of fusion is unaltered by the addition of the second metal. The modified equation assumes the form—

$$\ln x = \frac{Q}{2}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

in which x is the molecular concentration of the solvent metal, that is, the fraction of a molecular weight of the solvent contained in every molecular weight of the mixture. Assuming the metals to be both monatomic in the alloy, x = the atomic percentage of the solvent ÷ 100. The ideal freezing-point curve is then constructed by plotting the values of x from 1 to 0 against the values of T obtained from the equation. The curve thus constructed may have a point of inflection. The other branch is constructed by applying the same process to the freezing of the second metal. Heycock and Neville found that the ideal curve thus constructed for alloys of silver and copper

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[1] G. Tammann, *Z. physikal. Chem.*, 1889, 3, 441.

[2] *Trans. Chem. Soc.*, 1889, 55, 666.

[3] *Ibid.*, 1890, 57, 376.

[4] *Ibid.*, 1892, 61, 888.

[5] *Ibid.*, 1894, 65, 31.

[6] *Ibid.*, 1897, 71, 383.

[7] *Phil. Trans.*, 1897, 189, A, 25.

[8] *Z. physikal. Chem.*, 1893, 11, 449.

[9] *Compt. rend.*, 1894, 118, 638. See also J. J. van Laar, *Proc. k. Akad. Wetensch. Amsterdam*, 1903, 5, 424; 6, 21.

agreed fairly closely, as regards the position of the eutectic point at which the branches intersect, with that determined by experiment, although in this instance solid solutions are formed to a limited extent.

Since the ideal relation implied that plotting log x against $1/T$ should give a straight line, this method has been used[1] to detect deviations from the ideal condition. In simple eutectiferous systems the line is straight over a wide range, but when solid solutions are formed it takes other forms.

Values for the heat of fusion of metals are given in the usual tables of physical constants, but have only been determined accurately for a few metals. Values have also been determined for a certain number of alloys.[2]

Other methods have also been used to determine the condition of the solute in liquid alloys. Measurements of the vapour pressure of metals in mercury[3] indicated that Li, Ag, Au, Mg, Zn, Cd, Ga, Sn, Pb, and Bi were dissolved as single atoms. On the other hand, measurements of the velocity of diffusion of metals in mercury[4] indicated that whilst zinc, cadmium, tin, and lead diffused as single atoms, the alkali and alkaline earth metals, together with thallium, diffused as complexes, each atom carrying with it an unknown number of mercury atoms.

Many papers have been published, in which thermodynamical reasoning is used to determine the condition of metals in liquid alloys, and the existence of definite compounds in solution has been deduced, but the objections which have been raised to the assumption of dissolved hydrates in aqueous salt solutions apply here also, and the conclusions must be regarded with caution. The results are in any case entirely dependent on the accuracy of the experimental data used in obtaining them, and this is often less than had been supposed.

A more promising line of approach is by way of atomic conceptions.[5] A comparison between the liquidus curves of a number of alloys in which copper or silver was the solvent showed[6] that when the solute was an element in the same horizontal row of the periodic table as the solvent, the freezing-point curves of the several systems could be made to coincide by plotting, not the atomic composition, but the "equivalent atomic composition" (atomic composition × valency), against temperature. This relation holds good with considerable accuracy over a wide range of concentration. When the

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[1] D. H. Andrews and J. Johnston, *J. Inst. Metals*, 1924, **32**, 385.

[2] D. Mazzotto, *Mem. Inst. Lombardi*, 1891, **16**, 1; G. D. Roos, *Z. anorg. Chem.*, 1916, **94**, 329.

[3] W. Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 521.

[4] M. von Wogau, *Ann. Physik*, 1907, [iv], **23**, 345; G. McPhail Smith, *Z. anorg. Chem.*, 1908, **58**, 381.

[5] A convenient review of the subjects treated of in this section is given by W. Hume-Rothery in "The Structure of Metals and Alloys," *Inst. Metals Monograph*, 1936.

[6] W. Hume-Rothery, G. W. Mabbott, and K. M. Channel-Evans, *Phil. Trans.*, 1934, **233**, A, 1.

solvent and solute are not in the same period, the relation becomes more complex. Even then the same rule may be followed if the difference in size of the two kinds of atoms is not too large.

The initial depression of freezing-point is occasionally very small, so that the beginning of the liquidus is nearly horizontal. This happens for the alloys of gold and silver, which are completely miscible in both the liquid and the solid state. The depression at the gold end and the rise at the silver end of the liquidus are both less than 1 atomic per cent. per degree C. The atomic diameters are almost identical, and both metals have the same valency, so that the disturbing effect of alloying is very small. The atomic diameter of a given metal is not the same in all its alloys, and it appears that the electrical forces between the atoms may modify it to a considerable extent.

Regularities have also been found in regard to the solidus and to the limits of solid solubility. The atomic diameter (taken as the closest distance of approach in crystals of the solid element) is the most important factor, and when the atomic diameters of the solvent and solute differ by less than about 14 per cent. the "size-factor" is favourable, and extended solid solutions may be formed, unless certain other factors, to be mentioned later, intervene. With an unfavourable size-factor the formation of solid solutions is very restricted.

Using the same series of elements as in the study of liquidus curves, it was found that the slopes of the solidus curves, comparing elements in the same horizontal row of the periodic table, could be brought into approximate coincidence by multiplying the atomic composition by the *square* of the atomic valency. This relation is purely empirical, and is not exact, but holds well enough to give some assistance in the calculation of solidus surfaces in ternary systems.[1] The effect of the size-factor is very marked. Thus with copper as solvent germanium has a favourable size-factor, whilst tin is just on the border-line. The first additions of tin lower the freezing-point of copper about 1·5 times as much as germanium, atomic compositions being taken, but the lowering of the solidus is very much greater for tin. As the distance between the liquidus and solidus curves in an alloy system gives the freezing range of those alloys, it is pointed out that should the range in a binary system be inconveniently large for practical purposes, owing to the solute atoms being larger than those of the solvent, it may be reduced by adding a third metal, having the same valency but a small atomic diameter.

There are two other factors which affect the degree of solid solubility; designated by Hume-Rothery the electronegative valency effect and the relative valency effect. When the dissolved atoms are

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[1] It is probable that the ratio of the number of valency electrons to that of atoms is really the governing factor, and that in the instances studied this approximated to the square relation. (See p. 322.)

strongly electronegative with respect to the solvent atoms, there is a great tendency for stable intermediate phases—including intermetallic compounds—to be formed, with the result of lessening the solid solubility. Thus sulphur, selenium and tellurium form definite stable compounds with most metals, and therefore enter only to a very small extent into solid solutions. Phosphorus, arsenic, antimony and bismuth approach them, but can form solid solutions if the solvent metal be not too strongly electropositive. With such strongly electropositive solvents as the alkali metals and magnesium solid solutions are very limited, even when the size-factor is favourable.

The "relative valency effect" may be expressed by saying that, other things being equal, a metal of lower valency is more likely to take one of higher valency into solid solution than *vice versa*. This rule is very general for alloys of the univalent metals with elements of higher valency.

If two metals have the same crystal structure and a favourable size-factor, they usually form a continuous series of solid solutions, as in the pairs gold-silver, gold-copper, copper-nickel, bismuth-antimony, etc. Copper and silver form an exception, the size-factor being near to the limit. In the pairs magnesium-cadmium and thallium-indium, in which the two metals differ in structure, the range of solid solutions at each end extends nearly to the middle of the system, where a small gap of miscibility occurs. It is not enough to have similar space-lattices, if the atomic diameters differ widely. Thus beryllium (2·25 Å.) will not dissolve in solid (or even liquid[1]) magnesium (3·20 Å.) although both metals have close-packed hexagonal lattices. Continuous series are formed by many pairs of the transition elements, even when the two members do not belong to the same group in the periodic system, provided that the atomic diameters do not differ widely.[2] They must, of course, have space lattices of the same type.

The greatest solubility in the solid state is most often at the temperature of the solidus, the solubility decreasing with falling temperature, and even approaching zero, as in many of the systems which can undergo age-hardening (p. 331). Occasionally, however, the solubility increases as the temperature falls, as in the copper-zinc, copper-aluminium, silver-aluminium and silver-cadmium alloys. These anomalies are further discussed below.

The conception of an intermetallic compound arose before modern ideas as to the constitution of alloys had been developed. It was noticed that the action of acids on alloys of copper and zinc showed a discontinuity at the point at which the two metals were in equal proportions, and the formation of a compound was suggested.[3] Studies of the physical properties of alloy systems led to the discovery

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[1] R. J. M. Payne and J. L. Haughton, *J. Inst. Metals*, 1932, 49, 363.

[2] J. A. M. van Liempt, *Rec. Trav. Chim.*, 1926, 45, 203.

[3] Karsten, *Pogg. Ann.*, 1839, [ii], 16, 160.

of discontinuities, which were assumed to be due to compounds,[1] and later work on freezing-point curves showed that maxima often occurred at simple atomic ratios. Many workers sought to establish the formulæ of compounds by attacking alloys with various reagents, and assigning formulæ to the insoluble residues. The method is theoretically quite unsound, as the residue may be a limiting solid solution or even a mixture, but it has been responsible for introducing a large number of supposed compounds into metallurgical literature.

After this fact had been recognized and the formulæ of compounds had been based on thermal diagrams, two difficulties presented themselves. Many compounds were found to be able to take one or both of the component metals into solid solution, so that a homogeneous phase could persist over a certain range of composition including within it a compound of simple formula. Thus the β'-phase of the copper-zinc system extends from 46·5 to 50·0 atomic per cent. of zinc at 300°, whilst a cusp on the electrical conductivity-composition curve (see Chap. XIV) points to a compound CuZn.

Such behaviour is not characteristic of chemical compounds generally, although similar conditions are known among, for instance, the oxides and sulphides of iron. It involves a departure from the ordinary conception of a compound to suppose that it can vary the proportions of the two kinds of atoms of which it is composed, without losing its identity. In a sense, it involves a return to the position assumed by Berthollet in his controversy with Proust, and it was at one time proposed to call compounds of this kind "Bertholides."[2]

The second difficulty lay in the unusual formulæ which had to be assigned to the compounds, inconsistent as they were with the ordinary rules of valency. Such formulæ as $NaHg_2$, $AuSn_4$, and Au_2Al were found for well-defined compounds, and are irreconcilable with the known valencies of the metals composing them. The values for the valency of elements have, however, been built up from the study of ionic compounds, such as salts, in which one or more electrons have been transferred from one atom to another, and from homopolar compounds, such as organic molecules, in which electrons are shared by two atoms. When the linking is neither ionic nor homopolar, but metallic, it is to be expected that other relations would hold. It is not possible to reconcile the strange formulæ of intermetallic compounds with the ordinary conceptions of valency by, for instance, multiplying by some factor, as the whole study of the space-lattice of alloys goes to show that molecules, in the ordinary sense, are not present, so that there is no such thing as the molecular weight of a solid alloy.

Order was introduced into the conception by the enunciation by

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[1] F. Crace Calvert and R. Johnson, *Phil. Trans.*, 1858, 148, 349; A. Matthiessen, results summarized in *Brit. Assoc. Rep.*, 1863, 37.

[2] N. S. Kurnakow, *Z. anorg. Chem.*, 1914, 88, 109.

Hume-Rothery[1] of a principle which has since found wider applications. In the alloys of copper the so-called "β-phases" are very similar in crystalline structure and general character, and each appears, from its physical properties, to be grouped about a simple compound, which can take atoms of its components on either side into solid solution. In the copper-zinc series this compound is $CuZn$, in the copper-aluminium it is Cu_3Al, and in copper-tin it is Cu_5Sn. Whilst apparently dissimilar, these formulæ resemble one another in having three valency electrons for every two atoms, each copper atom contributing one, each zinc atom two, each aluminium atom three, and each tin atom four electrons. Further X-ray work by Westgren and others[2] proved that the lattices were actually similar, and relations of the same kind were found among other phases. Thus the γ-phases in the same systems correspond with Cu_5Zn_8, Cu_9Al_4, and $Cu_{31}Sn_8$, in all of which the ratio of the number of electrons to that of atoms is 21 : 13. This ratio again corresponds with a special type of structure, of which many other examples have been found, in all of which the same ratio is preserved.

The γ-structure is derived from the β by a relatively small amount of rearrangement.[3] The lattice of β-brass, for instance, is body-centred cubic, and the X-ray evidence shows that the atomic spacings are nearly the same in the γ-phase. Each unit cell, however, contains 52 atoms, and its side is therefore exactly three times that of the unit cube of β-brass, which would contain 54 atoms in a similar volume. The withdrawal of two atoms causes only a slight distortion of the structure, leaving cubic symmetry, but destroying the cleavage planes of easy slip, so that the γ-phase is quite devoid of ductility. The unit cell contains 20 copper and 32 zinc atoms, giving the formula Cu_5Zn_8. The corresponding phases in the copper-aluminium and copper-tin systems have the formulæ given above, and are similar in structure. Another typical phase is a close-packed hexagonal structure, including, for instance, $CuZn_3$, Cu_3Sn, and Ag_5Al_3, in which the ratio of electrons to atoms is 7 : 4. There are some exceptions to these rules, but they hold good for a large number of systems, and undoubtedly represent a general principle. A peculiar feature is the exceptional behaviour of the metals of the iron group. Compounds which contain metals of the iron and platinum groups can only be made to fit into the scheme if it be assumed that those elements do not contribute electrons to the structure. Thus, in the iron-zinc series, a γ-phase is found with the composition Fe_5Zn_{21}, with 26 atoms and 42 electrons, contributed only by the zinc.[4] Other γ-phases are Ni_5Cd_{21} and Pd_5Zn_{21}, whilst the β-phases include $FeAl$, $CoAl$, and $NiAl$.

The electron rules are not universally valid, but exceptions may probably be accounted for by differences in atomic diameters or other

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[1] W. Hume-Rothery, *J. Inst. Metals*, 1926, **35**, 195.

[2] A. Westgren and G. Phragmén, *Z. anorg. Chem.*, 1928, **175**, 80.

[3] A. J. Bradley and J. Thewlis, *Proc. Roy. Soc.*, 1926, **112**, A, 678.

[4] W. Ekman, *Z. physikal. Chem.*, 1931, **12**, B, 57.

factors. They hold good even in ternary systems, so that, for instance, in the copper-zinc-aluminium alloys the γ-structure is maintained, provided that the components are in such proportions as to keep the ratio between the valency electrons and the atoms constant at 21 : 13.[1] The magnetic Heusler alloys, $(Cu, Mn)_3Al$, have a β-structure.[2]

Although these rules were in the first instance arrived at empirically, a theoretical foundation has since been provided. Using the reasoning of wave mechanics, a study of the energies of the loosely bound electrons in alloys with the γ-structure shows that the ratio 21 : 13 comes very near to complete filling of a zone, and the magnetic properties are found to agree with such an arrangement.[3] Certain other lattices have been discussed on similar lines,[4] but the subject is a very complex one.

There is no sharp boundary between groupings of metallic atoms which simulate compounds on account of the stability of a particular electron-atom ratio, and true compounds approaching salts in their properties. It has long been known, for instance, that alloys containing antimony may contain compounds which obey the ordinary rules of valency, and this is the more likely to be true, the more electropositive the metal combined with the antimony. Such compounds with normal valency are mainly formed with elements of the periodic groups IV B, V B or VI B. Their stability, as Hume-Rothery has pointed out,[5] falls with increasing atomic number in any one group. Thus the compounds of magnesium, Mg_2Si, Mg_2Sn, and Mg_2Pb melt at 1102°, 780°, and 553° respectively. The melting-points also rise with increasing valency in any one period, Mg_3Sb_2 (1228°), and Mg_3Bi_2 (823°), comparing with Mg_2Sn and Mg_2Pb respectively. The selenides and tellurides form a series with the sulphides, which have been recognized on all grounds as true compounds. Bernal[6] has pointed out that three classes may be recognized: metallic ionic, metallic homopolar, and truly metallic groupings, the last being the most closely packed. Size of atom and electron ratio are more important than chemical character in determining the type of structure. Thus the lattice which is characteristic of the diamond is found in the series germanium, (Ge-Ge), GaAs, ZnSe, and CuBr, although the total of 8 electrons is contributed in different proportions; namely, 4-4, 3-5, 2-6, and 1-7.

A stable intermetallic compound may be regarded as an ordered

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[1] A. J. Bradley and C. H. Gregory, *Proc. Manchester Phil. Soc.*, 1927-28, **72**, 91.

[2] E. Persson, *Z. Physik*, 1929, **57**, 115.

[3] H. Jones, *Proc. Roy. Soc.*, 1934, **144**, A, 225.

[4] H. Jones, *ibid.*, 1934, **147**, A, 396; H. Perlitz, *J. Chem. Physics*, 1933, **1**, 335; C. D. Niven, *Phil. Mag.*, 1936, [vii], **21**, 291; U. Dehlinger, *Z. Physik*, 1935, **94**, 231. For a full discussion see N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys," Oxford, 1936.

[5] *Loc. cit.* See also G. Grube, *Z. angew. Chem.*, 1935, **48**, 714.

[6] J. D. Bernal, *Trans. Faraday Soc.*, 1929, **25**, 367.

structure (p. 339) of such stability that the temperature at which disorder sets in on heating is above the melting-point. There is clear evidence that some of them continue to exist as molecules in the molten alloy. Thus the curves representing the variation of electrical conductivity of liquid alloys with composition show strongly marked cusps at the compositions Hg_2Na and Hg_2K,[1] and the remarkably sharp peak of the liquidus in the Mg-Sb system at Mg_3Sb_2 points to a compound melting almost undecomposed. The flattening of the maximum on most liquidus curves, however, indicates extensive dissociation on melting. Attempts have been made[2] to determine the extent of the dissociation from the slope near the maximum.

Direct determinations of the heat of formation have been made in some instances. The first method was that of dissolving in a solution of a halogen or of an acid, and finding the difference between the heat of solution of an intermetallic compound and the sum of those of its component metals.[3] Other determinations have been made directly, by mixing the molten metals in a calorimeter.[4] It appears that when two metals which form a simple eutectiferous system are mixed in the molten state heat is absorbed, but that where intermediate phases are formed the heat of formation of the alloys passes through a maximum. It is remarkable that in all the examples studied there is only one such maximum, although the curve may show changes of direction corresponding with other phases.[5] The heats of formation vary greatly from one system to another, the largest approaching the values usual for salts. The electrochemical differences between the components make themselves strongly felt. Thus the heat of formation of Mg_3Bi_2 is considerably higher than that of Mg_2Pb.[6] In a complex series such as copper-aluminium, the maximum corresponds with the γ-phase, Cu_9Al_4, but there is a break in the curve at the composition CuAl. Ternary systems have been investigated in the same way.

A negative heat of formation was found for CdSb by determinations of electrolytic potential, using a mixture of fused alkali chlorides with cadmium chloride as the electrolyte.[7]

[1] K. Bornemann and P. Müller, *Metallurgie*, 1910, **7**, 396.

[2] R. Kremann, *Monatsh.*, 1904, **25**, 1215.

[3] W. Biltz and C. Haase, *Z. anorg. Chem.*, 1923, **129**, 141; and many later papers by Biltz and collaborators.

[4] M. Kawakami, *ibid.*, 1927, **167**, 345; *Sci. Rep. Tôhoku Univ.*, 1930, **19**, 521; H. O. von Samson-Himmelstjerna, *Z. Metallk.*, 1936, **28**, 197.

[5] F. Körber and W. Oelsen, *Mitt. K. W. Inst. Eisenforsch.*, 1936, **18**, 109; W. Oelsen and H. O. v. Samson-Himmelstjerna, *ibid.*, 131; W. Oelsen and W. Middel, *ibid.*, 1937, **19**, 1; F. Körber, W. Oelsen and H. Lichtenberg, *ibid.*, 131. A summary of the whole subject is given by F. Weibke, *Zeitsch. Elektrochem.*, 1938, **44**, 209.

[6] W. Seith and O. Kubaschewski, *ibid.*, 1937, **43**, 743. The order of magnitude of the heats of formation determined directly is similar to that found indirectly by Biltz.

[7] H. Seltz and J. C. de Haven, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **117**, 218.

Some indication of the energy involved in the formation of compounds is also afforded by determinations of the contraction of volume involved, which is as much as 14 to 34 per cent. for the alkali compounds NaPb, KHg_2, etc., but small for the closely packed phases of the copper-zinc and similar systems.[1]

No great importance can be attached to the actual figures found by these methods.

Many compounds of metals with certain of the non-metals have distinct metallic characters, including electrical conductivity and lustre. These include compounds with carbon, silicon, titanium, boron, nitrogen, and occasionally even hydrogen. The atoms of all these elements are small, and have a tendency to fit into the spaces between the metallic atoms instead of occupying points on the lattice. Such " interstitial " solid solutions play an important part in determining the properties of industrial alloys, the elements being taken up during the process of manufacture, and although the actual quantities are small, their influence on the physical and mechanical properties is relatively very great. Thus the solubility of carbon in γ-iron, and of nitrogen in chromium, play an important part in hardening.

Compounds are formed when the quantity of the non-metallic element is larger. The compounds of the transition elements with hydrogen, boron, carbon, and nitrogen have been particularly studied.[2] When the ratio of the atomic diameters is less than 0·59, compounds with simple structures, mainly face-centred cubic and close-packed hexagonal, are formed, but when the ratio is larger the resulting structures are usually complex. For carbon in iron or manganese the ratios are 0·61 and 0·60 respectively, and the carbides Fe_3C and Mn_3C have complex structures, but the ratio is so little in excess of the limiting value that an appreciable amount of solid solubility is possible. These complex compounds never have an extended range of solid solubility, so that iron carbide does not form solid solutions with an excess of either iron or carbon.

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[1] W. Biltz, *Z. Metallk.*, 1934, **26**, 230.

[2] G. Hägg, *Z. physikal. Chem.*, 1931, **12**, B, 33.

CHAPTER XX.

TRANSFORMATIONS IN THE SOLID STATE.

CHANGES of structure in solid alloys may result from changes in the solubility of a component in a solid solution, or from the polymorphic change of a solid phase. Besides these transformations, internal changes may occur which do not involve the production of a new phase as ordinarily defined, so that they find no place in the equilibrium diagram, although their effect on the properties of the alloy may be considerable. The present chapter deals with four classes of change of structure in solid phases: (*a*) the separation of a distinct phase from solid solution; (*b*) the simultaneous separation of two phases, as at a eutectoid point; (*c*) age-hardening, usually involving the precipitation of exceedingly small particles; and (*d*) changes of the degree of order within a solid solution, without the production of a new phase.

When, owing to a change of solid solubility with temperature, a new phase makes its appearance with falling (less often with rising) temperature, the new crystals are not as a rule distributed at random throughout the parent crystal, but make their appearance in one of two ways. Either they appear at the boundaries of the crystal grains, or along certain preferred crystallographic directions within the grains. Both conditions may present themselves at the same time, as in slowly cooled carbon steels. The effect on the physical properties depends largely on the properties of the precipitated phase, a brittle constituent separating at the grain boundaries, for instance, tending to make the whole mass behave as if it were brittle. The conditions which cause crystallization at grain boundaries have been little studied. In the iron-carbon alloys, the carbide, cementite, tends to separate in this way from slowly cooled low-carbon steels, in which the quantity is very small, and from steels containing so much carbon (over 0·9 per cent.) that cementite is in excess. The α-constituent separates in the same way from the β-phase in brasses during the first stage of crystallization, extending later into the interior of the grains. There is, no doubt, a difference in the concentration of a solid solution between the periphery and the interior, which may be connected with the effect of the dissolved element on the surface tension, and such a difference might well determine the first deposition of the new phase, but this is a subject calling for further investigation. Much more work has been done on crystallization of the second type, the new phase following certain crystallographic directions. The most familiar form which this takes is that of the so-called "Widmanstätten figures,"[1] first observed in meteorites. Kamacite is a solid solution of nickel in α-iron, and therefore has a body-centred cubic lattice. Taenite is a solid solution with a much higher proportion of nickel, and has the face-centred cubic structure of nickel and of γ-iron. The kamacite bands are very regularly arranged, and were early recognized as being parallel with the octahedral planes of the parent crystal from which they have crystallized. An X-ray study[2] showed that the (110) planes and [111] directions of the kamacite are parallel with the (111) planes and [110] directions of the original solid solution, the remains of which are represented by taenite. These are the most closely packed planes and lines in their respective lattices, and as the atomic spacings in the two planes differ only by 2 per cent., and the concentration of the atoms by 4 per cent., only a small displacement is needed to convert the one into the other. A crystal of kamacite, a few lattice planes in thickness, can extend itself in its own plane with very little disturbance of the structure, but less readily in the direction of its thickness. Actually, further adjustment is needed, as the concentration of nickel atoms in the two phases is different, and the slowness with which this diffusion occurs partly accounts for the difficulty of reproducing the meteoritic structure artificially. The iron-nickel system is under revision, and all that can be said with certainty at present is that the two phases, however they may have originated in the meteorite, do actually bear the above crystallographic relation to one another.

It would be reasonable to expect that the relation between the parent solid solution and a new phase would usually be of the kind just indicated, namely, that the process should involve the minimum of rearrangement, the most densely packed planes of the two phases coinciding, or, if the two kinds of atoms differed greatly in size, then the two planes most nearly alike in spacing. Whilst this rule is very generally found to be true, it is by no means universal. On the other hand, very few exceptions are known to the rule that the more closely packed *lines* in the two lattices coincide, so that it is probable that the transformation usually begins along such lines, and then proceeds in a manner determined by an approximate correspondence between planes which include them.[3]

The relation is fulfilled by ferrite (α-iron) crystallizing from austenite (solid solution of carbon in γ-iron) in slowly cooled steels,

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[1] The extension of the term from meteorites to include similar structures in alloys was first suggested by N. T. Belaiew, *Proc. Russ. Min. Soc.*, 1909; *J. Inst. Metals*, 1914, **12**, 46.

[2] J. Young, *Proc. Roy. Soc.*, 1926, **112**, A, 630.

[3] C. H. Mathewson and D. W. Smith, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 264.

the bands (which are really sections of plates) having been shown to be strictly parallel with the octahedral planes.[1] Extensive studies of this type of crystallization have been made by Mehl and his colleagues. In the aluminium-silver alloys (p. 311) the δ-solid solution has a face-centred cubic lattice, closely resembling that of aluminium, the atomic volumes of the two kinds of atoms being similar. The γ-phase is a close-packed hexagonal solid solution. When annealed at 550° and then slowly cooled to 387°, a well-defined Widmanstätten structure is seen, and the basal plane of the γ-phase is found to coincide with the (111) plane of the δ-phase.[2] The interatomic distances in the two planes differ by less than 2 per cent., and although the ratios of the two kinds of atoms differ, the adjustment is not difficult. The marked chemical difference between silver and aluminium no doubt makes diffusion more rapid than in the alloys of iron and nickel, in which the two kinds of atoms are similar in character as well as in size. Again, the conditions are such that the new crystals can grow in their own plane more readily than perpendicularly to it.

In the brasses, the β-solid solution can deposit crystals of either the α- or the γ-phase on cooling, according to its concentration. The α-crystals are usually rather irregular in outline, but with slow cooling they have the general appearance of following octahedral planes. They differ from kamacite or ferrite in being rods rather than plates, growth occurring in one direction only. The X-ray study[3] showed that no plane in the one lattice had a close similarity of pattern to a plane of the other, and although it was possible to find pairs of planes similar in atomic spacing, they were of high index, the best correspondence being obtained with the direction [55$\bar{6}$], which seems improbable. However, a later investigation,[4] using single crystals, showed that when the precipitation took place at a low temperature, the relation was simple, a (111) plane and [110] direction of α corresponding with a (110) plane and [111] direction in β. At higher temperatures the outlines were irregular, but the general orientation was similar, and as the [556] direction lies between the most densely packed planes of the two lattices, it may represent a compromise.

On the other hand, when the γ-phase crystallizes from β on cooling, small polyhedra or star-shaped growths are formed instead of long bands, and these maintain approximately the same orientation throughout a crystal grain. The γ-phase has the composition Cu_5Zn_8, and has a lattice with 52 atoms to the unit cell, derived from a body-centred lattice by a small alteration (p. 322), which, however, profoundly alters the properties of the phase, which, unlike the α- and

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[1] N. T. Belaiew, "Crystallisation of Metals," London, 1922.

[2] R. F. Mehl and C. S. Barrett, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, **93**, 78.

[3] R. F. Mehl and O. T. Marzke, *ibid.*, 1931, **93**, 123.

[4] M. Straumanis and J. Weerts, *Z. Physik*, 1932, **78**, 1.

β-phases, is very brittle, and is much more easily attacked by reagents than either of the others. The planes in the two lattices are so similar that there is no preferred plane of growth, and a polyhedral form can be assumed.[1]

Without the use of X-rays, information as to the planes on which precipitation has occurred may be derived from measurements of the angles of intersection with the plane of a specimen under the microscope, provided that a sufficient number of grains can be examined. Simple geometrical methods of projection on a sphere are used.[2]

An example which is of particular interest on account of the very simple structure is that of the alloys of copper and silver. No intermediate phase is formed, and the process is simply a precipitation of one metal from another, both lattices being face-centred cubic, but with differences of spacing between similar planes amounting to 10 per cent. By slow cooling to a suitable temperature and then quenching, well-defined patterns can be obtained at both ends of the series.[3] It is curious, however, that from the copper-rich alloys the silver separates parallel with (100) planes, whilst from the silver-rich alloys the precipitate of copper is parallel with (111), both lattices having the same orientation.

Other series which have been studied include aluminium-copper (α from β similarly to the brasses),[4] aluminium-copper and aluminium-magnesium ($CuAl_2$ and Al_3Mg_2 from aluminium),[5] copper-tin and silver-zinc (like the brasses), high carbon steel (Fe_3C forming plates, but only high indices found),[6] copper-zinc (the ϵ-phase separating from hexagonal zinc),[7] iron-nitrogen, and iron-phosphorus (Fe_4N and Fe_3P from α-iron).[8]

The theory of the process has been discussed on the basis of the experimental work referred to above.[9]

In the systems containing iron the crystallization of the new phase is associated with the allotropic change in the solvent metal, iron, and even when the quantity of dissolved matter is very small, as in electrolytic iron, a Widmanstätten pattern may be obtained under suitable conditions.[10] This fact suggests that the transformation of the pure metal follows a similar geometrical rearrangement.

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[1] Mehl and Marzke, *loc. cit.*

[2] N. T. Belaiew, *J. Inst. Metals*, 1923, **29**, 379.

[3] C. S. Barrett, H. F. Kaiser, and R. F. Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **117**, 39.

[4] Mehl and Marzke, *loc. cit.*

[5] R. F. Mehl, C. S. Barrett, and F. N. Rhines, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 203.

[6] R. F. Mehl, C. S. Barrett, and D. W. Smith, *ibid.*, 1933, **105**, 215.

[7] M. L. Fuller and J. L. Rodda, *ibid.*, 1933, **104**, 116.

[8] R. F. Mehl, C. S. Barrett, and H. S. Jerabek, *ibid.*, 1934, **113**, 211.

[9] H. Hanemann and O. Schroder, *Z. Metallk.*, 1931, **23**, 269, 297; C. H. Mathewson and D. W. Smith, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 264; as well as in some of the papers by Mehl and colleagues.

[10] A. Sauveur and C. H. Chou, *ibid.*, 1929, **84**, 350.

Experiments with electrolytic iron have usually given uncertain results, and most of the work has been performed on single crystals of iron containing nickel in solid solution. Several possible mechanisms have been described.[1] In this and other instances it is possible to represent the transformation as taking place by successive shears along certain planes, combined with expansions or contractions,[2] but in the absence of direct evidence the discussion of these mechanisms may be omitted, the fact of the transformation itself being thoroughly established. It is possible that intermediate structures have a temporary existence, as in the formation of martensite (p. 357) or in the breaking-up of other solid solutions when undercooled.

EUTECTOID STRUCTURES.

As a eutectic point in an equilibrium diagram represents the intersection of two branches of the liquidus curve at a minimum, so a eutectoid point represents the intersection of two curves of solid solubility, also at a minimum temperature. At the eutectoid temperature, two solid phases crystallize simultaneously, and it is therefore to be expected that there should be a strong resemblance between the structures of eutectics and eutectoids. Eutectoids have perhaps less variety of structure than eutectics, the lamellar form being the most frequent, but fewer observations are available. As crystallization has to take place from a solid matrix, the mobility is greatly reduced from that at the freezing-point, and the structures are sometimes very fine-grained. There is often a tendency for one of the components to segregate, forming a border to the duplex structure, and prolonged annealing frequently leads to extensive segregation, so that the typical structure is replaced by nodular aggregates of one constituent embedded in the other (p. 215).

The most familiar example is pearlite, the eutectoid of α-iron (ferrite) and iron carbide (cementite), formed at 690° by the decomposition of the solid solution of carbon in γ-iron (austenite). Its structure is typically lamellar, and much attention has been paid to its formation. The cementite forms thin lamellæ, parallel with one another throughout a single grain, embedded in ferrite of uniform orientation. The true spacing is seen if the plane of the lamellæ is normal to that of the section, but if the angle deviates from 90° the spacing appears too large, until when the two planes coincide only a single sheet of cementite is seen (see Fig. 144, p. 354). The general appearance does not alter greatly until the two planes differ by about 20°. At 20° the apparent spacing is five times too great,

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[1] G. Kurdjumow and G. Sachs, *Z. Physik*, 1930, 64, 325; H. Shôji, *Z. Krist.*, 1932, 84, 74; Z. Nishiyama, *Sci. Rep. Tôhoku Univ.*, 1934, 23, 637; G. Wassermann, *Mitt. K.W. Inst. Eisenforsch.*, 1935, 17, 149.

[2] For instance, in the transformation of the body-centred cubic modification of zirconium into the close-packed hexagonal form, W. G. Burgers, *Physica*, 1934, 1, 561.

at 16° ten times, and at 13° twenty times. Belaiew[1] has used the spacing Δ_0 as a measure of the heat treatment of different specimens of steels of similar composition. The value is easily determined if a number of grains of pearlite can be observed at once. A normal value for the spacing is 0·30 to 0·50 μ, and an average pearlite grain contains about 100 lamellæ.

Micrographic examination suggested[2] that the lamellæ were distributed on (210) planes, but the application of X-rays to a large dendrite[3] indicated that the (112) planes in the ferrite are parallel with the (110) in austenite, and the [110] direction in ferrite parallel with [112] in austenite. This is different from the Widmanstätten pattern formed by primary ferrite.

The eutectoid in the copper-aluminium system,[4] formed by the resolution of the β-phase at 537° on cooling into α and δ, strikingly resembles pearlite in its structure. The texture is often very fine, but when sufficiently magnified it is seen to be lamellar if in contact with the δ-phase, but usually granular if in contact with α.[5] As some degree of undercooling is always associated with the production of a pure eutectoid structure, it is probable that the details depend on the extent of that undercooling.

AGE-HARDENING.

A solid solution which normally deposits one of its constituents on cooling may often be retained in a supersaturated condition by quenching. The excess of dissolved substance may then separate in a fine state of dispersion when the alloy is maintained at atmospheric or somewhat raised temperature. This separation brings with it important changes in physical and mechanical properties, and "age-hardening" is now known to be characteristic of a very large number of alloys. In the course of experiments on alloys of commercial aluminium with 1 per cent. or more of magnesium, it was found that if quenched from a temperature not far below the melting-point and allowed to remain at atmospheric temperature, the hardness of the metal spontaneously increased, the rise being rapid in the first few hours and then becoming slower.[6] The effect was greater when copper was added, and this led to the introduction of the commercial alloy duralumin, containing about 4 per cent. of copper and 0·5 per cent. of magnesium. The first explanation was given in 1919,[7] when the hardness was attributed to the precipitation

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[1] N. T. Belaiew, *J. Iron Steel Inst.*, 1922, i, 201.

[2] N. T. Belaiew, *Rev. Métall.*, 1935, **32**, 145.

[3] R. F. Mehl and D. W. Smith, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **116**, 330.

[4] The equilibrium diagram was determined by H. C. H. Carpenter and C. A. Edwards, *Proc. Inst. Mech. Eng.*, 1907, 57, and has only been slightly modified by later workers.

[5] A. Portevin, *Intern. Z. Metallogr.*, 1913, **4**, 257.

[6] A. Wilm, *Metallurgie*, 1911, **8**, 225.

[7] P. D. Merica, R. G. Waltenberg, and H. Scott, *U.S. Bur. Stand. Sci. Paper*, 1919, **15**, 271.

of a constituent, in this instance $CuAl_2$, from a supersaturated solid solution. The corresponding solubility curve, determined with pure aluminium as a solvent, is given in Fig. 133.[1] When the alloy is heated, for example to 200,° the hardness at first rises to a maximum, and on prolonged heating again falls. This suggested that the maximum hardness was produced by a certain "critical dispersion," the whole of the excess solute being then precipitated as fine particles, which agglomerate on longer heating. Hardening would be produced by the distortion of lattice planes in the neighbourhood of the foreign particles, whilst their coalescence to form larger masses would lessen the distortion and consequently reduce the hardness. Although not a complete picture of the process, the idea is at the base of all later explanations of age-hardening. It was shown shortly afterwards[2] that a large part of the hardening of duralumin is due to the presence of magnesium, which combines with the silicon, always present in ordinary commercial aluminium, to form a compound Mg_2Si, which, like $CuAl_2$, enters readily into solid solution at the eutectic temperature, but becomes much less soluble with falling temperature.

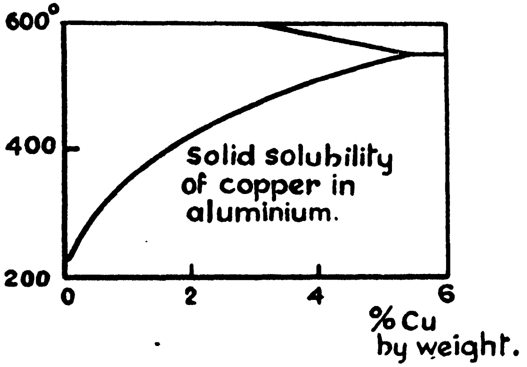

FIG. 133.

The microscope gives little help in this study, as no particles of either of the precipitated compounds can be seen until the maximum hardness has been passed, and coalescence has gone so far as to bring them within the range of vision. In some age-hardening alloys, discussed later, changes in chemical properties may be seen even at an early stage. There is every reason to suppose that the particles at the stage of critical dispersion are of ultra-microscopic size.

However, the precipitation of minute particles does not offer a complete explanation of age-hardening, which proves to be more complex than was at first supposed. Hardness and tensile strength were the only properties at first considered, but the process involves

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[1] E. H. Dix and H. H. Richardson, *Trans. Amer. Inst. Min. Met. Eng.*, 1926, **73**, 560.

[2] D. Hanson and M. L. V. Gayler, *J. Inst. Metals*, 1921, **26**, 321.

changes also in the electrical conductivity, density, X-ray pattern, and magnetic and other properties, and these changes do not always run parallel with one another (Fig. 134). It was soon noticed that the electrical conductivity of duralumin decreases during the initial stage of age-hardening, although the separation of a constituent would be expected to increase the conductivity of a solid solution.[1] This behaviour is found in several other alloys. Fig. 134 is a generalized diagram.

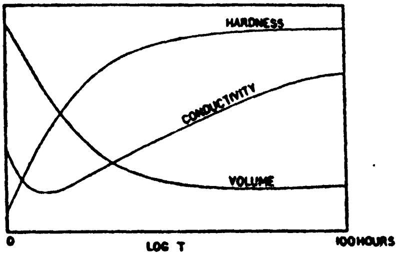

FIG. 134.—Changes in an age-hardening system.

A simple example, which has been repeatedly studied, is that of the alloys of copper and silver. The thermal diagram has been given in Fig. 15 (p. 35), and the curves of solid solubility, which have been arrived at by both thermal and X-ray methods,[2] are repeated on a more open scale in Figs. 135 and 136. The two metals have similar face-centred cubic lattices, and at the eutectic temperature their mutual solid solubility is considerable, but this diminishes rapidly at both ends of the system on cooling. The conditions for age-hardening of both metals are present, but there is no question of the formation of an intermediate phase, and no extreme hardness can be attained. Within the limits of solid solubility, the maximum attainable hardness increases with the quantity of substance separating, that is, with increasing proportions of the second metal.

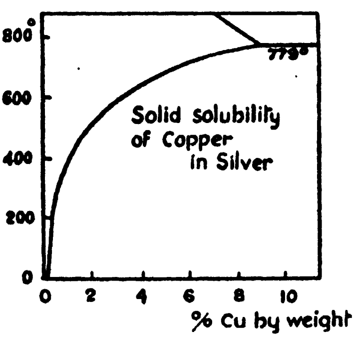

FIG. 135.

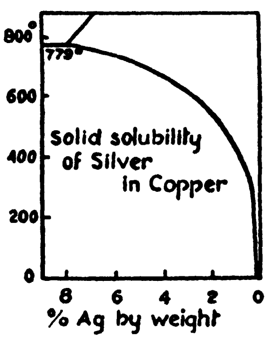

FIG. 136.

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[1] W. Fraenkel, *Zeitsch. Metallk.*, 1920, **12**, 427; W. Fraenkel and E. Scheuer, *Z. Metallk.*, 1922, **14**, 49, 111.

[2] N. Ageew and G. Sachs, *Z. Physik*, 1930, **63**, 293; N. Ageew, M. Hansen and G. Sachs, *ibid.*, 1930, **66**, 350 (X-ray); D. Stockdale, *J. Inst. Metals*, 1931, **45**, 127 (thermal); E. A. Owen and J. Rogers, *ibid.*, 1935, **57**, 257 (X-ray).

Standard silver, containing 92·5 per cent. silver and 7·5 per cent. copper by weight, is a convenient material for the study of age-hardening in its simplest form. Its composition falls within the range of complete solubility just below the eutectic temperature, and it is therefore homogeneous when quenched from 770°. Reheating or "tempering" causes an increase of hardness, which reaches a maximum when the tempering temperature is about 300°, and falls off rapidly when it is higher.[1] The greatest hardness reached is more than twice that of the quenched alloy. At the same time, a change of structure is seen under the microscope, beginning at the grain boundaries and extending inwards. The structures produced at various stages of the process recall those of hardened and tempered steel, the decomposition of the solid solution becoming most evident after the point of maximum hardness has been passed. The electrical conductivity increases, but not quite regularly, with the hardness, as would be expected if the effect were due to the precipitation of particles from solid solution.[2] The lattice parameter increases as the precipitation goes on, since the presence of copper atoms diminishes the parameter, but the change is not continuous, and the initial and final parameter may co-exist, suggesting local transformation. The same method is used in the examination of the copper end of the series. The limitations of the X-ray method are shown by the fact that it is impossible to detect the presence of particles of silver by its means, even after separation is complete, although when only 2 per cent. of silver dust is mixed with powdered copper, the lines of the two metals are clearly distinguished.[3]

An alloy which has proved of great value in the study of age-hardening consists of copper with 2·5 to 3 per cent. of beryllium, known as "beryllium bronze."[4] This forms an α-solution at high temperatures which is retained on quenching from, say, 800°, and only breaks up when heated at 200° or over. The maximum hardness reached is four times that of the quenched alloy. As hardening progresses, changes in the etching properties of the alloy become very marked. The α-crystals darken in a lattice-like pattern, pointing to separation of a constituent along a definite set of crystal planes, presumably those of the octahedron.[5]

These simple examples may provide a clue to the more complex behaviour of duralumin. At the higher temperatures, the age-hardening proceeds as in the alloys already mentioned, except that it has not been found possible to detect any change in the microstructure until the maximum hardness has been passed and the

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[1] A. L. Norbury, *J. Inst. Metals*, 1928, **39**, 145.

[2] W. Fraenkel, *Z. anorg. Chem.*, 1926, **154**, 386.

[3] H. Bumm, *Metallwirtsch.*, 1935, **14**, 429.

[4] G. Masing and others, *Wiss. Veröffent. Siemens-Konzern*, 1929, **8**, 101; G. Masing, *Z. Elektrochem.*, 1931, **37**, 414.

[5] Photographs are given in the author's "Chemistry of Solids," Ithaca, 1934.

precipitated matter has coalesced to form visible particles.[1] Duralumin, however, will harden at atmospheric temperatures, the process becoming more rapid as the temperature is raised. For each tempering temperature there is a limit to the hardness which can be attained, the maximum value being at 150°, above which softening readily occurs. The lattice parameter diminishes slightly during the short period at atmospheric temperature before hardening sets in and then remains unchanged.[2] The electrical conductivity at first falls, and this was attributed [3] to distortion of the aluminium lattice caused by the first aggregation of molecules to form nuclei of the constituent to be precipitated. The minimum conductivity is reached at 150° in 1-3 hours, but the maximum hardness only in 2-3 days, whilst the X-ray examination indicates a gradual diminution of lattice distortion at the higher temperatures as the process goes on.[4] It was concluded later [5] that hardening at atmospheric temperature took place without rejection of copper atoms from the lattice, but that at 200° precipitation occurred, which, however, was not regarded as the *cause* of the hardening. Mott has pointed out that groupings of five or six foreign atoms would produce a marked fall in electrical conductivity which would be reversed on further aggregation.

In ageing at room temperature there is no change in the X-ray pattern as ordinarily measured, but refined measurements indicate that a slight broadening and increase in intensity of the lines occur whilst the intensity of the diffused radiation becomes less.[6] Moreover, work on single crystals [7] indicates that the precipitation of $CuAl_2$ at 200° produces a complex tetragonal crystalline modification instead of the normal form, a process similar to the formation of martensite in steel. These complex effects are best accounted for by supposing that there are two processes involved; the formation of minute nuclei and the growth of these nuclei to form particles, first of ultramicroscopic and then of microscopic size. This is consistent with the migration of some of the copper atoms in the lattice, forming nuclei, but not separating in such a way as to constitute a new phase. This process is the reverse of diffusion, since it sets up a local difference of concentration. Precise measurements [8] suggested that the copper atoms, from a purely random arrangement on the aluminium lattice, move to take up more orderly positions. The arrangement might be one in lines, or in small "knots," or aggregations of

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[1] Distinct changes in the etching properties of the alloys after ageing have, however, been noticed. G. Sachs, *Z. Metallk.*, 1926, **18**, 209.

[2] E. Schmid and G. Wassermann, *Metallwirtsch.*, 1930, **9**, 421.

[3] W. Rosenhain, *J. Iron Steel Inst.*, 1924, **110**, 178.

[4] M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1929, **41**, 191.

[5] *Ibid.*, 1932, **48**, 197.

[6] J. Hengstenberg and G. Wassermann, *Z. Metallk.*, 1931, **23**, 114.

[7] G. Wassermann and J. Weerts, *Metallwirtsch.*, 1935, **14**, 605.

[8] J. Hengstenberg and H. Mark, *Z. Elektrochem.*, 1931, **37**, 524.

a few copper atoms, producing local distortion in their neighbourhood.[1] It seems reasonable to believe, however, that the atoms separate along certain closely packed planes of the aluminium lattice, as in the formation of a Widmanstätten structure. In doing so they must alter the position of the aluminium atoms nearest to them, with the result that a two-dimensional sheet is formed, in which the copper and aluminium atoms are so arranged that they either form molecules of $CuAl_2$, or can do so with very little change of relative place. These two-dimensional nuclei will cause local distortion, but will not give an X-ray pattern on account of their thinness, nor, since the movements involved are so small, will they produce a detectable change in the lattice parameter. They serve as crystalline nuclei, which can continue to grow in sheets, but are likely to thicken at higher temperatures, when growth can occur more readily, and so form discrete particles. The production of nuclei being a probability effect, there is usually a period of incubation before the hardening sets in.

This view is confirmed by an examination of pure copper-aluminium alloys which have been age-hardened at 200°.[2] The precipitation of $CuAl_2$ takes the form of minute plates, which have definite orientations in any one crystal grain, and therefore constitute a Widmanstätten structure on a small scale. It is reasonable to suppose that these plates have grown from nuclei which had a similar orientation, and even that the same process occurs at temperatures below that at which a visible precipitate can be formed. Single crystals of an alloy of aluminium with 5 per cent. of copper may be grown, and will undergo age-hardening at 100° without tending to break up into smaller crystals, and such aged crystals are remarkably stable after deformation and re-heating.[3] This again points to the probability that precipitation is on definite lattice planes.

When the hardening is due to the precipitation of a compound formed by the union of two kinds of dissolved atoms, such as magnesium and silicon, the process may be similar, but more complex. In the age-hardening of commercial duralumin, the processes overlap, the precipitation of Mg_2Si taking place at a lower temperature than that of $CuAl_2$.[4] This overlapping of two processes of precipitation is very noticeable in steels. When several elements are present together, the age-hardening due to one of them may be favoured or inhibited by another. This is probably owing to changes in mutual solubility, and not merely to an effect on the velocity of change. Thus iron retards the ageing of alloys of aluminium containing copper, whilst silicon partly corrects the influence of iron.[5]

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[1] P. D. Merica, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 13. This paper contains a valuable survey of the subject of age-hardening, with bibliography to 1931.

[2] Dix and Richardson, *ibid.*, 1926, **73**, 560.

[3] R. Karnop and G. Sachs, *Z. Physik*, 1928, **49**, 480.

[4] M. L. V. Gayler, *J. Inst. Metals*, 1922, **28**, 213.

[5] *Ibid.*, 1937, **60**, 75.

The process of precipitation involves diffusion in a solid solution. It might be expected, therefore, that the relations between temperature and velocity of change would follow similar laws to those of diffusion in solids, and this conclusion is largely borne out by the facts. On account of the slowness of change at low temperatures, it is convenient to represent the change in any property, such as hardness, as a function of the logarithm of the time.[1] The curves so obtained show a rise to a maximum (sometimes preceded by a period of induction), followed by a fall. The maxima are displaced towards shorter times with increase of ageing temperature, as in Fig. 137. The times at which these maxima occur are related to the absolute temperature by an equation of the form

$$t = Ce^{m/T}$$

where C and m are constants. On plotting the logarithm of the time

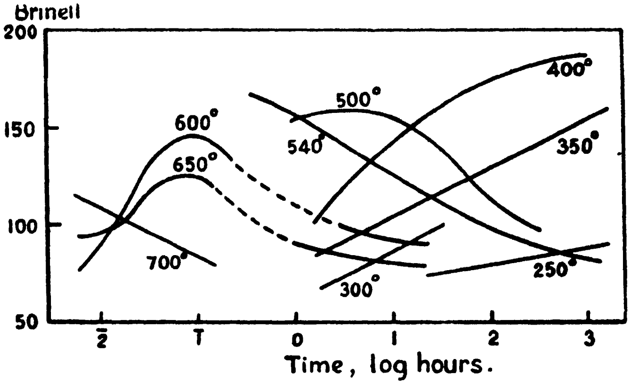

FIG. 137.—Curves of age-hardening (Bucknall and Jenkins).

taken to reach the maximum against the reciprocal of the corresponding absolute temperature, a straight line is obtained, and Bucknall and Jenkins have verified this relation over moderate ranges of temperature for a number of age-hardening systems. Deviations are to be expected from the facts that two separate changes may be going on in the same alloy, and that the time to reach the maximum at low temperatures is often so long that the experiments have been discontinued before the greatest hardness has been attained. The question is susceptible of mathematical treatment on the lines discussed later in connection with the transition from disordered to ordered solid solutions (p. 339). Other physical properties appear to vary in a similar way, but the maximum values of different properties do not always occur at the same times, and properties which might be expected to be related sometimes vary independently.

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[1] E. H. Bucknall and C. H. M. Jenkins, *J. Inst. Metals*, 1935, **57**, 156; E. S. Davenport and E. C. Bain, *Trans. Amer. Soc. Metals*, 1935, **23**, 1047.

Thus, although tensile strength usually follows hardness, copper containing 1 per cent. of iron hardens without increase of tensile strength,[1] and an alloy consisting of equal weights of aluminium and silver actually loses in tensile strength while gaining in hardness.[1] In this connection it must be remembered that the tensile strength does not represent the true cohesive strength, but is determined also by the resistance to slip in the crystals, and the two properties may not be affected in the same way.

Further evidence that the process is largely controlled by diffusion is given by the effect of cold working on age-hardening, which may be remarkably large. It may be illustrated by the example of iron containing nitrogen. The range of solid solubility is shown in Fig. 138.[3] The solid solution may be retained by quenching, and on ageing at 100° or higher temperatures the nitride, Fe_4N, is precipitated, producing a marked effect on the etching as well as on the mechanical properties of the iron. Cold working after quenching greatly accelerates precipitation, and the method of detecting regions of local deformation in iron and soft steel[4] depends on the precipitation of nitride in these regions being much more rapid than elsewhere. The same effect has been repeatedly found in other alloys. It is in accordance with the fact, already mentioned, that diffusion takes place more readily in a distorted lattice than in one which is perfect.

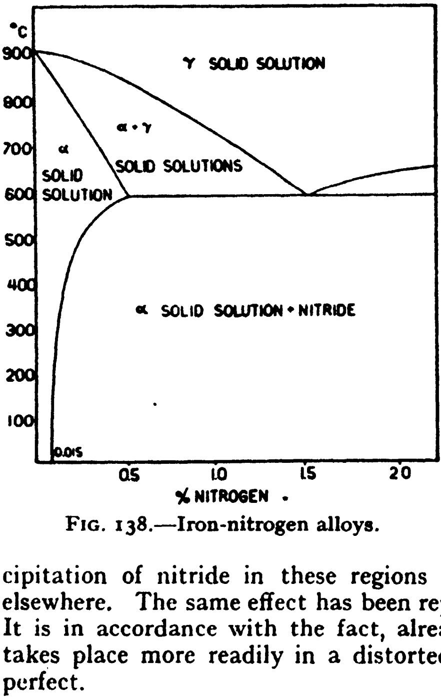

FIG. 138.—Iron-nitrogen alloys.

The precipitation theory of age-hardening, modified as described above, is now generally accepted. The method is in very general use for improving the mechanical properties of the softer metals, as a very small quantity of an added element is often able to bring about an extensive improvement without markedly affecting other pro-

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[1] D. Hanson and G. W. Ford, *J. Inst. Metals*, 1924, **32**, 335.

[2] R. S. Archer and D. W. Kempf, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, **93**, 114.

[3] W. Köster, *Arch. Eisenhüttenw.*, 1930, **3**, 353, 637; 1931, **4**, 145. A different solubility curve has, however, been found by A. Portevin and D. Séférian, *Compt. rend.*, 1934, **199**, 1613.

[4] A. Fry, *Krupp. Monatsh.*, 1921, **2**, 117; *Stahl u. Eisen*, 1921, **41**, 1093; T. H. Turner and J. D. Jevons, *J. Iron Steel Inst.*, 1925, i, 169.

perties. Precipitation-hardening may also have undesirable effects, the "ageing" of iron and mild steel with time, leading to an increase of brittleness and loss of magnetic quality, being caused by an exactly similar process.

The account given in this chapter can only represent the process in the most general way. The changes in any selected system may prove to be much more complex than this simple outline would indicate, and it is not safe to draw conclusions from the variations of a single property with time and temperature, whether that property be hardness, electrical conductivity, or X-ray parameter. A striking instance is provided by an alloy containing 90 per cent. of aluminium and 10 per cent. of magnesium, very free from impurities. This can harden by the precipitation of Al_2Mg_3. If rendered homogeneous by long annealing and then quenched, and afterwards aged at different temperatures, it was found [1] that 4 hours at 100° brought about precipitation which was visible under the microscope, but that after 30 days at 100° no change in the X-ray parameter could be detected. Again, after 1 hour at 300° the precipitation was visible, and after 4 hours had become a well-marked grouping of crystals, but 5 hours were required to produce a change in the parameter.

There is no doubt that two processes are involved, one being the formation, and the other the growth, of nuclei within a solid solution. Since this is also true of the disorder-order change discussed in the next section, which has already lent itself to theoretical treatment, it is certain that the same methods may be applied with advantage, and that a quantitative study of age-hardening systems, taking into account the change of energy involved in the change of place among atoms on a lattice, will prove fruitful.

THE ORDERING OF SOLID SOLUTIONS.

It was pointed out by Tammann [2] that a kind of isomerism was possible in alloys consisting of a solid solution, that is, there might be two alloys of the same composition, each consisting of a single phase and having the same crystalline form, but differing in properties. The differences would arise from the different distribution of the several kinds of atoms on the points of the space lattice. Taking a binary alloy of the metals A and B, the two kinds of atoms might be distributed at random among these points, so that only a statistical uniformity of composition could be predicated, or on the other hand they might be so arranged that corresponding points on the lattice were always occupied by A atoms, so that it would be possible to regard them as forming an A lattice, interpenetrating that of B. Suggestions were made as to the formation of the two kinds of alloys

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[1] W. L. Fink and D. W. Smith, *Mining and Metallurgy*, 1935, **16**, 228.

[2] G. Tammann, *Nachr. Ges. Wiss. Göttingen*, 1918, 190; *Z. anorg. Chem.*, 1919, **107**, 1.

under different conditions of temperature, thus accounting for differences of properties of solid solutions obtained by fusion and by electrodeposition respectively, but little use was made of the conception until precise X-ray methods were applied.

Certain anomalies in the behaviour of the β-phase in the copper-zinc system had attracted attention before this. This phase undergoes a change at 470°, giving out heat on cooling.[1] This was at first interpreted as a eutectoid transformation, corresponding with that in the copper-tin and copper-aluminium systems. The evidence was, however, inconclusive, and the view that the change was a polymorphic transformation was more generally held. The fact that homogeneous β- could be produced by diffusion in the solid state below 470° [2] was decisive and a polymorphic change had to be assumed, although no difference in micro-structure could be detected. Later [3] it was found that the X-ray pattern was unchanged by quenching the β-alloys. A parallel was drawn between this change and the Curie point in iron, which is also marked by a small thermal and volume change without change of lattice, other than a small contraction.[4] Two simultaneous and independent investigations, one using thermal and microscopical,[5] and the other electrical conductivity methods,[6] agreed in showing that the temperature of the β-β′ transformation was higher on the zinc side than on the copper side of the solid solution, confirming the view that it was not a eutectoid change. Finally, it was found that the lattice, as determined by X-rays, was the same above and below 470°, except for a small expansion at the higher temperature,[7] and was therefore not, in the ordinary sense, a polymorphic change.

The alloys of magnesium and cadmium, homogeneous in the neighbourhood of the composition MgCd at high temperatures, gave curious curves of hardness and electrical conductivity in the slowly cooled state, suggesting that at about 250° a compound of that composition separated, having however a limited power of taking both component metals into solid solution.[8] A more striking example presented itself in the alloys of copper and gold. The liquidus has a minimum, and on account of the unusual structure of the slowly cooled alloys this was at first taken to be a eutectic point,[9] but later proved to correspond with a continuous series of solid solutions. On cooling, these appeared to yield two compounds, Cu_3Au and CuAu, each having the

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[1] H. C. H. Carpenter and C. A. Edwards, *J. Inst. Metals*, 1911, **5**, 127. The point had been detected in the preliminary survey of the system by W. C. Roberts-Austen, *Proc. Inst. Mech. Eng.*, 1897, **31** ; but was overlooked in the complete study by E. S. Shepherd, *J. Physical Chem.*, 1904, **8**, 421.

[2] O. F. Hudson, *J. Inst. Metals*, 1914, **12**, 89.

[3] E. A. Owen and G. D. Preston, *Proc. Physical Soc.*, 1923, **36**, 49.

[4] W. Rosenhain, *J. Inst. Metals*, 1925, **34**, 254.

[5] M. L. V. Gayler, *ibid.*, 1925, **34**, 235.

[6] J. L. Haughton and W. T. Griffiths, *ibid.*, 245.

[7] A. Phillips and L. W. Thelin, *J. Franklin Inst.*, 1927, **204**, 359.

[8] G. G. Urazow, *Z. anorg. Chem.*, 1911, **73**, 31.

[9] W. Roberts-Austen and T. K. Rose, *Proc. Roy. Soc.*, 1900, **67**, 105.

above property of taking atoms of the component metals into solid solution.[1] This conclusion rested mainly on determinations of physical properties, especially electrical conductivity and hardness. The variation of these properties with composition is shown in the lower part of Fig. 139, for both quenched and annealed alloys. The curves indicate complete solid miscibility at high temperatures, with separation of the type mentioned above on cooling. The temperatures of transformation were determined more accurately by electrical resistance methods,[2] and are represented in the upper part of Fig. 139. A third maximum was found at the composition Cu_3Au_2, which has not, however, been detected on the property-composition curves.

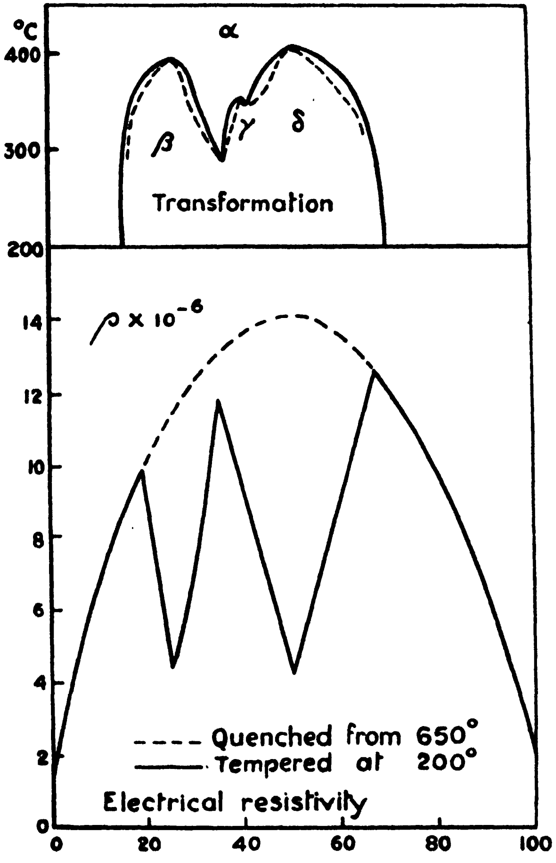

FIG. 139.—Copper-gold alloys. Transformations and resistivity.

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[1] N. S. Kurnakow, S. F. Schemtschuschny, and M. Zasedatelev, *J. Inst. Metals*, 1916, **15**, 305.

[2] J. L. Haughton and R. J. M. Payne, *ibid.*, 1931, **46**, 457.

An explanation of the facts came from X-ray determinations. The lattices of gold and copper being similar, all the alloys on freezing form face-centred cubic crystals, the two kinds of atoms being distributed at random among the points of the lattice. The structure becomes ordered on cooling. The two types are shown diagramatically in Fig. 140. The alloy Cu_3Au retains its cubic lattice, but the gold atoms segregate to the corners of the cubes, the copper atoms taking up positions on the face-centres (which are three times as numerous as the corners).[1] The change in the alloy CuAu is not quite so simple. The Cu and Au atoms arrange themselves in layers parallel with a cube face, and this slightly alters the symmetry, the lattice becoming tetragonal, with a *c*-axis perpendicular to the layers. This produces a marked change in the microstructure, strongly etching bands, very like twins, appearing with definite orientation.[2]

The conditions being simpler for the composition Cu_3Au, most of the theoretical work has been based on that alloy. The more regular arrangement of the ordered lattice gives rise to additional lines in the X-ray pattern,[3] and a "superlattice" is said to be present. The electrical, magnetic[4] and mechanical properties change with the rearrangement of the lattice. Whether the ordered alloy is to be called an intermetallic compound is a matter of definition (see Chapter XIX) remembering that the change extends over a range of composition, merely reaching a maximum at the stoichiometrical formula. A perfect superlattice is only possible with a simple atomic ratio, which accounts for the singular points on the property-composition curves. The transformation is not a phase change, as the ordered and disordered parts of a single crystal are not separated by a definite boundary. In the ordered condition, as shown by experiments on single crystals, the properties of the alloy of the composition Cu_3Au resemble those of a pure metal,[5] being relatively soft and with a high conductivity. Each

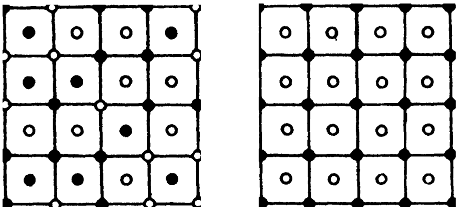

FIG. 140.—Disordered and ordered lattices.

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[1] C. H. Johansson and J. O. Linde, *Ann. Physik*, 1925, [iv], 78, 439; 1927, [iv], 82, 449; G. Borelius, C. H. Johannson, and J. O. Linde, *ibid.*, 1928, [iv], 86, 291.

[2] See, for good photographs of this structure, Haughton and Payne, *loc. cit.*

[3] First observed by E. C. Bain, *Trans. Amer. Inst. Min. Met. Eng.*, 1923, 68, 625.

[4] H. Seemann and E. Vogt, *Ann. Physik*, 1929, [v], 2, 976.

[5] G. Sachs and J. Weerts, *Z. Physik*, 1931, 67, 507.

alloy has a critical temperature above which no superlattice exists, and this bears a close relation, as already indicated, to the Curie point in ferro-magnetic materials. Below that point, the change takes place continuously down to low temperatures, but the velocity of change falls rapidly with falling temperature. The " time of relaxation " (τ) is defined as the time taken for the degree of disorder to be reduced to $1/e$[1] of its former value,[2] and the " characteristic temperature " as that at which the time of relaxation is one second. Representing this by T_1, and the temperature of experiment by T, the variation of the time of relaxation with temperature is shown by the following table:

T/T_1	τ *in seconds*	
1·2	0·01	
1·1	0·08	
1·0	1	
0·9	20	
0·8	10^3	(17 minutes)
0·7	$1·3 \times 10^5$	(36 hours)
0·6	10^8	(3 years)
0·5	10^{12}	(30,000 years)

The process has been studied very fully thermodynamically by Bragg and Williams,[3] and the effects of quenching at different rates may be deduced from the times of relaxation.

The first stage in the transition from disorder to order consists in the formation of minute nuclei, in which a higher degree of order prevails, corresponding with the equilibrium degree of order appropriate to the temperature of the specimen. At constant temperature, the nuclei, of which there are many in each crystal grain, grow and invade the surrounding lattice.[4] If the alloy be cooled, two processes occur, the nuclei growing in size, whilst the degree of order within them increases, the second process continuing down to a lower temperature than the first, as it involves changes of structure over only small distances. Once the alloy has become thoroughly ordered, nuclei cannot be produced unless it be thoroughly disordered, any change of structure proceeding through the whole lattice.

At the critical temperature there is a marked change in the specific heat and also in the electrical conductivity, the latter property providing the most convenient means of studying the approach to equilibrium and of measuring the departure from equilibrium under given conditions of cooling. The X-ray pattern also indicates the

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[1] e = base of Napierian logarithms.

[2] W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.*, 1934, **145**, A, 699; 1935, **151**, A, 540; W. L. Bragg, *J. Inst. Metals*, 1935, **56**, 275.

[3] *Loc. cit.* and *Proc. Roy. Soc.*, 1935, **151**, A, 540. See also H. A. Bethe, *ibid.*, 1935, **150**, A, 552; R. Peierls, *ibid.*, 1936, **154**, A, 207; E. J. Williams, *ibid.*, 1935, **152**, A, 231; U. Dehlinger and L. Graf, *Z. Physik*, 1930, **64**, 359; U. Dehlinger, *ibid.*, 1933, **83**, 832; W. S. Gorsky, *ibid.*, 1928, **50**, 64; G. Borelius, *Ann. Physik*, 1934, [v], **20**, 57.

[4] C. Sykes and H. Evans, *J. Inst. Metals*, 1936, **58**, 255.

nature of the process. Experiments with a single crystal of Cu_3Au showed that the reflections corresponding with the superlattice structure were diffuse unless a long annealing were given, and it was concluded[1] that the degree of order was only uniform throughout small volumes, and that these nuclei were not all in phase, there being four possible choices among the lattice points on which the gold atoms segregate to form the ordered structure. The determination of the true specific heat at each temperature (p. 95) provides, with X-ray examination, a means of following the kinetics of the process.[2]

Similar observations have been made in great detail on the alloys of iron and aluminium, especially at the compositions Fe_3Al and FeAl,[3] whilst the alloys of copper with platinum and with palladium[4] have also been found to show similar effects. There is no doubt that these rearrangements will prove to be of importance in many other systems of alloys. They are not, however, necessarily observed in every system which contains solid solutions. It has been shown by Bragg and Williams that the conditions under which they may be observed depend on the relations between the temperature T_c, at which the degree of order falls rapidly to zero; the temperature T_1 defined above, at which the time of relaxation is short, say one second, and the melting-point T_m. Should T_1 be considerably lower than T_c, the alloy relaxes so fast that it becomes completely ordered even with rapid cooling. This is the case for the β-CuZn phase, which changes into the ordered β' even when quenched. On the other hand, T_c may be even above T_m, so that the alloy solidifies from the molten state in a completely ordered condition, as is found by the X-ray method for Cu_3Sb. This and similar alloys have a strong claim to be called true intermetallic compounds, and this point is discussed in Chapter XIX. When T_c is much lower than T_1 no practicable time of annealing suffices to produce the ordered state. Thus such solid solutions as those of silver and gold show no tendency to become ordered, and the same condition accounts for the fact that only very simple superlattices, with the ratios 1 : 1 and 1 : 3, are observed.

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[1] Dehlinger and Graf, *loc. cit.*

[2] C. Sykes and F. W. Jones, *J. Inst. Metals*, 1936, **59**, 257.

[3] A. J. Bradley and A. H. Jay, *Proc. Roy. Soc.*, 1932, **136**, A, 210.

[4] C. H. Johansson and J. O. Linde, *Ann. Physik*, 1925, [iv], **78**, 439; 1927, [iv], **82**, 449; R. Taylor, *J. Inst. Metals*, 1934, **54**, 255.

CHAPTER XXI.

THE METALLOGRAPHY OF IRON AND STEEL.

THE technical importance of the metallography of iron and steel, and the extraordinary complexity of the relations exhibited by these metals, justify the separate treatment of this group, the literature of which probably equals in volume that of all the other departments of metallography taken together. The equilibrium of iron and carbon will therefore be considered in some detail, a briefer account being subsequently given of the modifications brought about by the introduction of other elements into the system.

Molten iron dissolves carbon very readily up to a certain limit, which increases rapidly with increasing temperature. The excess is deposited on cooling in the form of graphite, which separates very readily on account of its lightness, so that it is difficult to obtain solid alloys containing more than 6 per cent. C, and even this value can only be obtained under certain conditions. The very light, crystalline graphite which collects on the surface of iron rich in carbon is well known in iron works under the name of "kish" (Germ. Garschaum).

That the melting-point of iron is depressed by the addition of carbon is one of the most familiar facts of the iron industry. An alloy containing 4 per cent. C melts about 350° below the melting-point of pure iron. The first freezing-point diagram was constructed by Roberts-Austen in 1899,[1] and the data which it contained were utilized in the following year by Roozeboom[2] in the construction of a complete diagram of the phase equilibrium. The diagram represented in Fig. 141 embodies the facts which have been most definitely established,[3] but must be considered as being still under revision. (See below.)

The chemical study of iron and steel, which preceded the metallographic study, had established the fact that carbon may exist in steel or in cast-iron in three different forms, namely graphite, "carbide carbon," and "hardening carbon." Of these, the first is identical with natural graphite, the second corresponds with a carbide which is known to have the composition Fe_3C, whilst the third form of carbon

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[1] 5th Report, Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1899, 35.

[2] *Z. physikal. Chem.*, 1900, **34**, 437; *J. Iron Steel Inst.*, 1900, ii, 311.

[3] H. C. H. Carpenter and B. F. E. Keeling, *ibid.*, 1904, i, 224; with modifications from many later partial investigations.

has been assumed to be present in solid solution. The diagram has to account for these different conditions.

Beginning at the left-hand side of Fig. 141, the freezing-point of iron is taken as 1527°.[1] Iron, however, undergoes a series of further changes after becoming solid, which are indicated by arrests on either the thermal or the dilatometric cooling curves of the pure metal. These occur at 1400°,[2] 912°,[3] and 768° respectively, the last being of less magnitude than the others. The modification formed when the metal solidifies is called δ-iron, that which is stable between 1400° and 912° γ-iron, and the modification stable at low temperatures α-iron. The condition of iron between 912° and 768° was long a matter of controversy. It was denoted by β, and was regarded as a

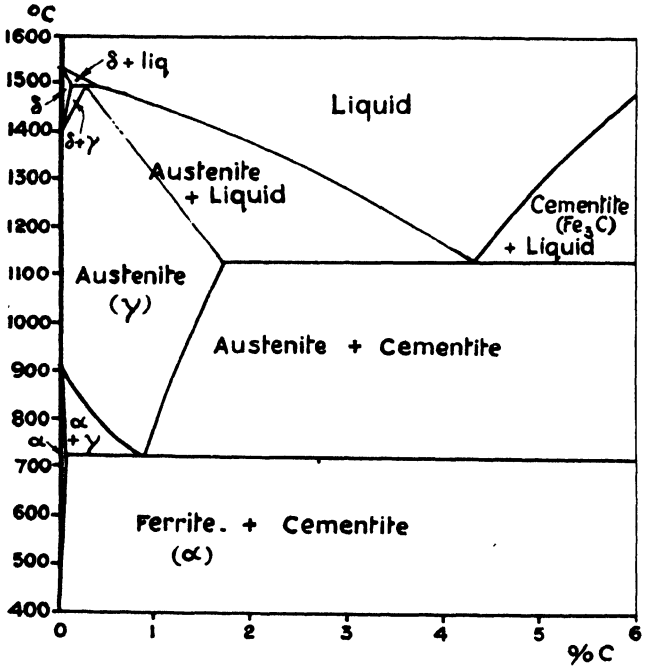

FIG. 141.—Iron-carbon diagram.

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[1] C. H. M. Jenkins and M. L. V. Gayler, *Proc. Roy. Soc.*, 1930, **129**, A, 91.

[2] This point was discovered later, E. J. Ball, *J. Iron Steel Inst.*, 1890, i, 85, and examined by R. Ruer and R. Klesper, *Ferrum*, 1914, **11**, 257. The other points were observed by Osmond (see Chapter I). The value 1400° is probably too high.

[3] There is still some uncertainty as to the equilibrium value of this transformation temperature. Determinations using highly purified iron gave 924° (F. Adcock and C. A. Bristow, *Proc. Roy. Soc.*, 1935, **153**, A, 172); 909·5° (C. Wells, R. A. Ackley, and R. F. Mehl, *Trans. Amer. Soc. Metals*, 1936, **24**, 46); 928° (J. B. Austin and R. H. H. Pierce, *ibid.*, 1934, **22**, 447); F. R. Hensel and E. I. Larsen, *Metals and Alloys*, 1933, 4, 37.

distinct allotropic form, usually supposed to be harder than either α or γ. Its existence was even invoked to explain the hardness of quenched steels. Actually, 768° is the magnetic change point or Curie point,[1] above which iron ceases to be ferro-magnetic, and the small changes of heat content and volume which occur at that temperature are simply to be attributed to the magnetic rearrangement. It is not necessary to enter here into the long controversies on this subject, but reference may be made to some of the outstanding papers.[2]

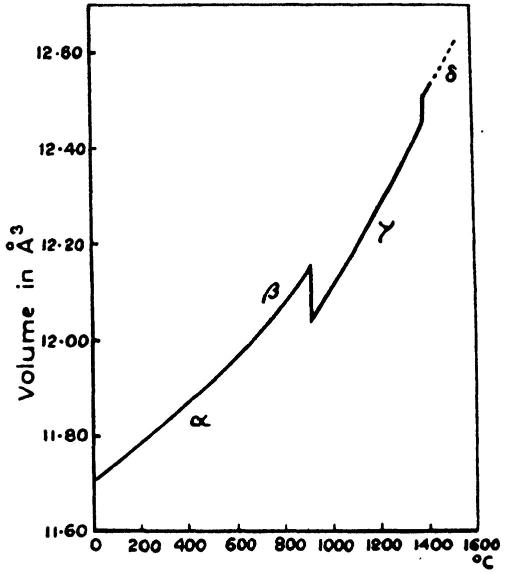

FIG. 142.—Changes in lattice dimensions in iron (Schmidt).

The most conclusive evidence as to the true nature of the allotropy of iron has been given by X-ray examination, although purely metallographic evidence points to the same conclusions. α-iron has a body-centred cubic structure, whilst γ-iron is face-centred cubic, like gold or copper.[3] The lattice of β-iron is identical with that of α-iron, allowing for the small change of dimensions. The remarkable fact is that the modification stable at high temperatures, δ, has the same body-centred cubic lattice, and is in fact identical with α-iron, the increase in lattice dimensions being merely that due to the higher temperature, Fig. 142.[4] Moreover, when iron is alloyed with certain elements, the γ-region is confined to narrower limits of temperature with increase of the alloying element, and finally vanishes. The δ- and α-modifications then merge into one another, and are seen to be identical.

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[1] P. Curie, *Thèse*, Paris, 1895.

[2] W. Rosenhain and J. C. W. Humfrey, *Proc. Roy. Soc.*, 1910, **83**, A, 200; C. Benedicks, *J. Iron Steel Inst.*, 1912, ii, 242; H. C. H. Carpenter, *ibid.*, 1913, i, 315; A. Sauveur, *ibid.*, 1913, ii, 171; K. Honda, *ibid.*, 1915, i, 199; G. K. Burgess and H. Scott, *ibid.*, 1916, ii, 258. A full review is given by E. Maurer, *Mitt. K.W. Inst., Eisenforsch.*, 1920, **1**, 39.

[3] A. W. Hull, *Phys. Rev.*, 1917, **10**, 661; A. Westgren, *J. Iron Steel Inst.*, 1921, i, 303.

[4] A. Westgren, *loc. cit.*; A. Westgren and G. Phragmén, *Z. physikal. Chem.*, 1922, **102**, 1; W. Schmidt, *Ergebnisse tech. Röntgenkunde*, 1933, **3**, 194; H. Esser and G. Müller, *Arch. Eisenhüttenw.*, 1933, **7**, 265.

The 768° point is therefore not a phase change, and does not introduce a new field into the equilibrium diagram. It occurs at the same temperature on heating and on cooling, but in the allotropic changes a thermal lag is usually found, and the transformation or "critical" points occur at rather lower temperatures on cooling, and at higher temperatures on heating. Osmond's designations for these points have been adopted. The points on cooling are denoted by Ar_4 at 1400°, Ar_3 at 910°, and Ar_2 at 768° (A standing for "arrêt," r for "refroidissement"). The corresponding changes on heating are denoted by Ac_4, Ac_3, and Ac_2, c standing for "chauffage." The equilibrium temperatures, lying between Ar and Ac, may be represented by Ae.

Returning to the upper part of the diagram, the freezing-point of iron is lowered by the addition of carbon. A peritectic point occurs near 1490°, corresponding with the change of iron from the δ- to the γ-condition, the solvent power of the two modifications for carbon being different. This part of the diagram has been recently revised. The point is usually placed at 0·35 per cent. of carbon,[1] but the actual number of points determined on the curve was small, and it is possible to draw the diagram differently. A series of experiments with commercial low-carbon steels [2] suggested that the peritectic line might reach as far as 0·7 per cent. of carbon. Using iron of the highest obtainable purity, and with refined pyrometric methods, the peritectic point was found to lie at 0·50 per cent. C.[3] The point is important, as it affects the process of freezing of ordinary steels, the primary structure of which will be due to crystallization of the δ or of the γ-modification, according as the carbon content is below or above the limit. The remaining part of the liquidus curve has been determined satisfactorily, as far as the eutectic point at 4·3 per cent. of carbon and 1130°. The solid phase which crystallizes along this branch is not pure iron, but a solid solution of carbon in γ-iron, known as austenite. The limit of solid solubility at the eutectic temperature may be taken as 1·7 per cent. of carbon.

The form of the solidus cannot be well determined from cooling curves, but the points which lie on it are much more clearly marked on heating curves, whilst the method of quenching from known temperatures gives decisive results, specimens quenched from above the solidus showing the presence of particles which were liquid at the time of quenching and solidified later, whilst specimens quenched below the line are free from them.[4]

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[1] R. Ruer and R. Klesper, *Ferrum*, 1914, 11, 257.

[2] W. Fehse, *Z. tech. Physik.*, 1927, 8, 119; J. H. Andrew and D. Binnie, *J. Iron Steel Inst.*, 1929, i, 309.

[3] F. Adcock, *ibid.*, 1937, i, 281.

[4] N. Gutowsky, *Metallurgie*, 1909, 6, 731. An electrical resistance method was used by S. Kaya, *Sci. Rep. Tôhoku Univ.*, 1925, 14, 529, to determine the solidus. Adcock's work shows that the solidus is nearly straight as far as 1 per cent. C, and not bowed as shown. This confirms the work of Carpenter and Keeling.

Alloys containing more than 1·7 per cent. of carbon deposit austenite on cooling until that limit is reached in the solid, after which the remaining liquid solidifies as saturated austenite together with a eutectic, sometimes known as ledeburite (Plate XVIIA). The two constituents of this eutectic are saturated austenite and cementite (iron carbide, Fe_3C). With a further increase of carbon cementite crystallizes first.[1] Although it has been suggested that the liquidus beyond the eutectic point has several breaks, indicating the formation of other carbides,[2] the evidence is not conclusive. The curve rises steeply, and it has not been possible to investigate alloys containing much more than 6 per cent. of carbon. This range covers the steels and the cast irons. No sharp line can be drawn between the two materials. Usually, steels contain less than 1·7 per cent. of carbon, so that they can form homogeneous austenite, whilst cast irons (only white irons are considered for the moment) contain the eutectic, ledeburite. The so-called "wortle plate" steel, however, which is used for making dies for the drawing of wire, may contain as much as 2·5 per cent. of carbon, but is made and handled as a steel.

Austenite is not a stable phase in this system over the whole range of temperature. As the temperature falls, the solubility of carbon in solid iron diminishes, and cementite separates as a second phase, the change being represented by the line SE.[3] At 700° the limit of saturation of austenite is only 0·81 per cent. The temperature of transformation of γ- into α-iron is depressed by the presence of carbon in solid solution, as shown by the line GS[4] (Fig. 141). It intersects the cementite line at 0·81 per cent. C and 700°. This is the eutectoid point, and the intimate mixture of α-iron and cementite is known as pearlite. Below this temperature austenite is no longer stable, and the rearrangement to α-iron and cementite persists on further cooling.

The temperatures indicated on the diagram are temperatures of equilibrium, and correspond with infinitely slow cooling. In practice, there is commonly a thermal lag, and the critical points on cooling and on heating have to be distinguished. The Ar_4 ($\delta \rightarrow \gamma$), Ar_3 ($\gamma \rightarrow \alpha$), and Ar_1 (eutectoid) arrests are therefore usually lower than the values given, and the Ac_1 (eutectoid), Ac_3 ($\alpha \rightarrow \gamma$) and Ac_4 ($\gamma \rightarrow \delta$) points higher, the difference being less as the rate of heating and cooling becomes slower. The Ar_2 and Ac_2 points, representing the magnetic change, coincide. The thermal arrest, usually difficult to recognize, which accompanies the separation of cementite along the

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[1] An alloy composed of almost pure cementite has been obtained by quenching (R. Ruer, *Z. anorg. Chem.*, 1921, **117**, 249).

[2] N. M. von Wittorf, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1613; O. Ruff and O. Goeke, *Metallurgie*, 1911, **8**, 417; O. Ruff, *ibid.*, 456.

[3] N. J. Wark, *ibid.*, 1911, **8**, 704; N. Tschischewsky and N. Schulgin, *J. Iron Steel Inst.*, 1917, i, 189.

[4] There is no break in this curve at the A_2 point, as formerly supposed. The curve is somewhat concave upwards (T. Sato, *Tech. Rep. Tôhoku Univ.*, 1928, **8**, 27).

line SE, is denoted by A_{cm}. Cementite itself undergoes a magnetic change, which like that of iron does not involve a change of lattice, at 218°,[1] below which temperature it is magnetic.

The diagram cannot, however, represent the whole truth. The facts that slowly cooled cast-iron contains practically the whole of its carbon in the form of graphite, and that cementite, or iron rich in cementite, deposits carbon when heated, are well known, but do not receive recognition in the equilibrium just described. An important series of experiments led to the conclusion [2] that the final equilibrium of the system, only reached after a very prolonged annealing, was one between the two solid phases ferrite and graphite. The suggestion was then made that two systems, a stable and a metastable, should be represented in the diagram,[3] and this representation has been adopted by most metallurgists, although open to considerable objection.

In the metastable system, the phases separating from the liquid alloy are austenite and cementite, as described above. In the stable system, on this view, they are austenite and graphite. The eutectic point lies somewhat above that of the metastable system, but not far from the same percentage of carbon. The curve representing the crystallization of austenite is the same in both systems. The graphite curve is placed somewhat above the cementite curve, CB, reaching 1800° at 6 per cent. C,[4] and the carbide system is thus represented as being produced by the undercooling of the graphitic system.

In Roozeboom's original scheme, cementite was supposed to separate from the molten metal as indicated here, but to break up at 1100° to form graphite, which thus became a phase in the diagram of the system. This view has been abandoned, but it has been shown [5] that in the freezing of cast iron, cementite separates first and then decomposes, so that the graphite found is a secondary product. A solubility curve for graphite in austenite, somewhat to the left of the curve SE, has been constructed by determining the quantity of carbon taken up at different temperatures, a procedure which is open to the objection that cementite may have been formed as an intermediate product. An iron-graphite eutectoid point, not far from the pearlite point, has been described, mainly on micrographic evidence.[6] It is a suspicious circumstance that the curves for the graphite and cementite systems so nearly coincide, and the hypothesis of a stable and a metastable system is not very satisfactory, but the problem cannot be regarded as solved.

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[1] S. Wologdine, *Compt. rend.*, 1909, **148**, 776; S. W. J. Smith, *Proc. Phys. Soc.*, 1912, **25**, 77.

[2] G. Charpy and L. Grenet, *Bull. Soc. d'Encouragement*, 1902, 399.

[3] E. Heyn, *Z. Elektrochem.*, 1904, **10**, 491; G. Charpy, *Compt. rend.*, 1905, **141**, 948.

[4] H. Hanemann, *Stahl u. Eisen*, 1911, **31**, 333.

[5] P. Goerens, *Metallurgie*, 1907, **4**, 137.

[6] R. Ruer, *Z. anorg. Chem.*, 1921, **117**, 249.

Changes in iron below 700°.

Iron of commercial purity and mild steel show certain anomalies even below 700°. The best known of these is "blue-brittleness." The tensile strength of iron, like that of other metals, is greatest at low temperatures and becomes very small as the melting-point is approached. The fall is not, however, continuous, but the curve takes the form shown in Fig. 143. There is a maximum in the neighbourhood of 200°-400°, the actual position depending greatly on the amount of impurities present. A similar maximum, varying in position, is found in the tensile properties of carbon steels, but it is much flattened, and may disappear, when alloying elements are added.[1] Within this region the iron or steel is hardened by deformation to an unusual extent, so that it is rendered brittle by hammering or bending, and such operations must be avoided within that range. The ductility, fatigue strength, and resistance to shock have minimum values at about the same temperatures,[2] but the actual form of the property-temperature curve depends greatly on the rate of straining.

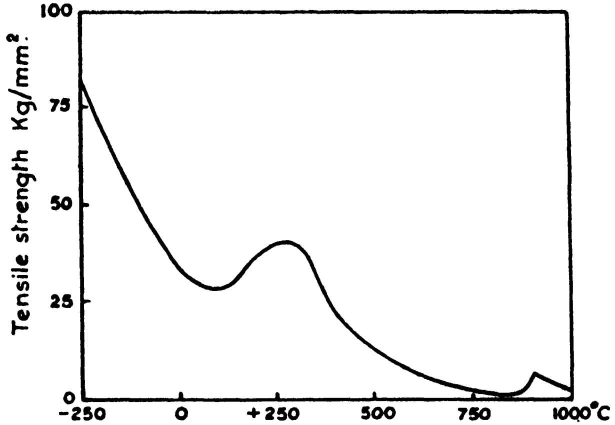

FIG. 143.—Strength-temperature curve for iron.

Low carbon steels undergo ageing after deformation, the metal losing ductility in the course of time. The effect is due to small quantities of impurities,[3] and it has been connected [4] with the phenomenon of blue-brittleness. It has not been proved that either effect is found in pure iron.

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[1] F. Robin, *Rev. Métall.*, 1908, **5**, 893; 1909, **6**, 162; *Iron Steel Inst. Carnegie Schol. Mem.*, 1911, **3**, 125.

[2] H. J. Tapsell and W. J. Clenshaw, *Dept. Sci. Ind. Res. Eng. Rep.*, No. 1, 1927.

[3] C. E. Stromeyer, *J. Iron Steel Inst.*, 1909, i, 404, and later workers.

[4] F. Fettweiss, *Stahl u. Eisen*, 1919, **39**, 1, 34; F. Körber and A. Dreyer, *Mitt. K.W. Inst. Eisenforsch.*, 1921, **2**, 59.

Moreover, many observers have recorded arrests in thermal, electric, or magnetic curves at temperatures between that of the atmosphere and 700°, often taking the form of several peaks at short intervals, or even of a fairly regular periodicity. Anomalies in the specific-heat which have been recorded have been shown not to exist.[2] It is not known whether the other anomalies would be found if the impurities could be completely removed. The precipitation of carbon, nitrogen, and perhaps oxygen, from ferrite within this range has a large effect.

Micrographic Constituents.—The micrographic constituents which make up the structure of steel and cast iron in the cast or annealed condition may now be described in turn.[3]

Ferrite.—This name is given to α-iron, crystallizing in the body-centred cubic form. It has a cubic cleavage, and on etching deeply shows well-developed cubic etch-figures.[4] Specimens of purified iron consist only of grains of ferrite, the boundaries being developed by etching with dilute alcoholic nitric acid. It is ordinarily free from twinning, but when deformed by shock, narrow twin bands, the Neumann lines, are conspicuously produced (Chap. XVI).

α-Iron containing silicon or other elements in a state of solid solution is indistinguishable from pure iron, and is therefore also considered as ferrite. Some solid solutions of this kind develop the cubical structure with remarkable perfection when etched deeply, and the best photo-micrographs of this sort have been obtained from iron containing silicon. It has been proposed that the micrographic constituent of alloys containing phosphorus, silicon, etc., should be called phospho-ferrite, silico-ferrite, etc.

In steels containing small proportions of carbon the ferrite forms a continuous network, shown to consist of distinct grains by etching (Plate XV), but from 0·4 per cent. C onwards the ferrite grains are isolated and surrounded by pearlite.

Cementite.—Cementite, Fe_3C, is the only carbide of iron which has been recognized by microscopical means. It is present in meteorites as cohenite.[5] It was first isolated chemically by Abel,[6] and its identity with the hard constituent of annealed steels was proved by Arnold and Read.[7] Cementite crystallizes in large plates belonging to the orthorhombic system.[8] When seen in a micro-section the plates, being cut transversely, have the appearance of needles. In a white

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[1] F. C. Thompson and E. Whitehead, *Proc. Roy. Soc.*, 1923, **102**, A, 587.

[2] C. Sykes and H. Evans, *J. Iron. Steel Inst.*, 1938, ii, 125.

[3] Fine photographs of the types of micro-structure met with in cast or annealed steels are given by H. Hanemann and A. Schrader, "Atlas Metallographicus," Berlin, 1927-37.

[4] See, especially, J. E. Stead, *J. Iron Steel Inst.*, 1898, i, 145.

[5] E. Weinschenk, *Ann. Museum Wien*, 1889, **4**, 94.

[6] F. A. Abel, *Proc. Inst. Mech. Eng.*, 1885, 30.

[7] J. O. Arnold and A. A. Read, *Trans. Chem. Soc.*, 1894, **65**, 788.

[8] S. Shimura, *J. Fac. Eng. Tokyo Univ.*, 1931, **20**, 1; S. B. Hendricks, *Z. Krist.*, 1930, **74**, 534; A. Westgren, *Jernkont. Ann.*, 1932, 457.

iron containing more than the eutectic proportion of carbide the crystals are very well formed and regular, in annealed steels containing more than the eutectoid proportion they form more or less irregular bands arranged as cell walls enclosing areas of pearlite, although well-formed crystals may be seen in some high carbon steels.

Cementite is not attacked by acid etching reagents, and remains brilliantly white when ferrite and pearlite have been darkened by etching. On the other hand, cementite is blackened by a hot solution of sodium picrate or other oxidizing reagent in an excess of sodium hydroxide, and this is characteristic for distinguishing cementite from a solid solution. The hardness of cementite (840 Brinell[1]) causes it to stand out in relief when the specimen is polished on a soft bed, and drawing a needle over the surface may also be employed as a means of recognition, and of distinction from ferrite when occurring as a network surrounding areas of pearlite.

Cementite may occur in several forms in a slowly-cooled alloy: primary (from molten iron containing more than 4·3 per cent. C); secondary or pro-eutectoid (from austenite along the line SE); and eutectoid (in pearlite). These have been shown to be chemically identical.[2]

The question whether any carbide of iron other than cementite is to be found in alloys of iron has been much discussed.[3] It has been suspected that they might be formed in the tempering of hardened steels, and the analysis of carbide residues isolated from steels tempered at different temperatures[4] indicated that a carbide FeC was formed up to 250°, Fe_2C up to 600°, and Fe_3C at higher temperatures. X-ray analysis, however, failed to show any lines but those of cementite, and the magnetic change point of all the preparations coincided with that of cementite, so that the evidence is not convincing.

Manganese carbide, Mn_3C, is isomorphous with cementite, so that in an alloy containing manganese only a single carbide is seen. Spiegeleisen is a white pig iron containing 12 to 20 per cent. of manganese, and the carbide forms very large plates, along which the alloy breaks with a mirror-like fracture. These plates have been used for the determination of the crystal structure, differing only in lattice parameter from ordinary cementite.

Pearlite.—The conglomerate of ferrite and cementite which constitutes the eutectoid is known as pearlite, on account of the mother-of-pearl lustre shown by an etched surface. This is due to the fine and regular alternations of the two constituents. The lamellar structure is characteristic, and is responsible for the mechanical properties of unhardened steels, since the combination of the soft ferrite and very hard cementite produces a tough structure. Acid

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[1] H. Cornelius and H. Esser, *Arch. Eisenhüttenw.*, 1934, **8**, 125.

[2] A. Ledebur, *Stahl u. Eisen*, 1887, **8**, 742; 1891, **11**, 294.

[3] E. D. Campbell and M. B. Kennedy, *J. Iron Steel Inst.*, 1902, ii, 288; S. Hilpert and T. Dieckmann, *Ber. deut. chem. Ges.*, 1915, **48**, 1281.

[4] F. Wever and G. Naeser, *Mitt. K.W. Inst. Eisenforsch.*, 1934, **16**, 201.

reagents etch pearlite much more readily than ferrite, on account of the local electrolytic couples set up by the proximity of two constituents differing in potential. Under a low magnification, therefore, an etched surface of a steel containing less than 0·81 per cent. of carbon appears as a mosaic of dark and light areas (Plate XV). Higher magnification (Plate XVIA) reveals the lamellar structure.

As a rule, the lamellæ appear to be more or less wavy in form. This is partly due to distortion by stresses during their formation, but in part is only apparent, the thin flakes being exposed at the surface and irregularly torn during grinding and polishing. The question of the inner structure of the pearlite grain has been examined in detail by Belaiew.[1] In a given field under the microscope, grains will be seen having the lamellæ variously spaced, but in a carefully polished specimen the spacing will be constant in any one grain. Belaiew regards the true spacing as constant throughout the specimen and as characteristic of the heat-treatment of the steel. The apparent variations are due to the grains being cut by the plane of the section at different angles (Fig. 144). Occasionally a grain may be cut almost parallel with the lamellæ, and then only a single lamella will be seen, whilst a section at right angles to this will give the closest possible spacing. The true spacing Δ_0 is related to the apparent spacing Δ_w by the equation $\cos w = \frac{\Delta_0}{\Delta_w}$ where w is the angle of intersection of the plane of the section with the normal to the lamellæ. When w is near to zero the lamellæ usually appear straight. For a given steel, the hardness is approximately inversely proportional to Δ_0.[2]

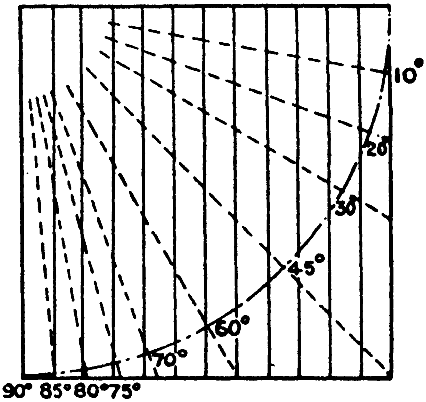

FIG. 144.—Variation of breadth of pearlite lamellæ with angle of section (Belaiew).

The crystallographic relations of the lamellæ are not quite clear (see p. 331).

As the carbon content of a steel increases, the proportion of pearlite also increases, until with 0·81 per cent. C the specimen consists solely of pearlite. With still more carbon free cementite appears, so that the relative areas of the constituents (regarding pearlite as

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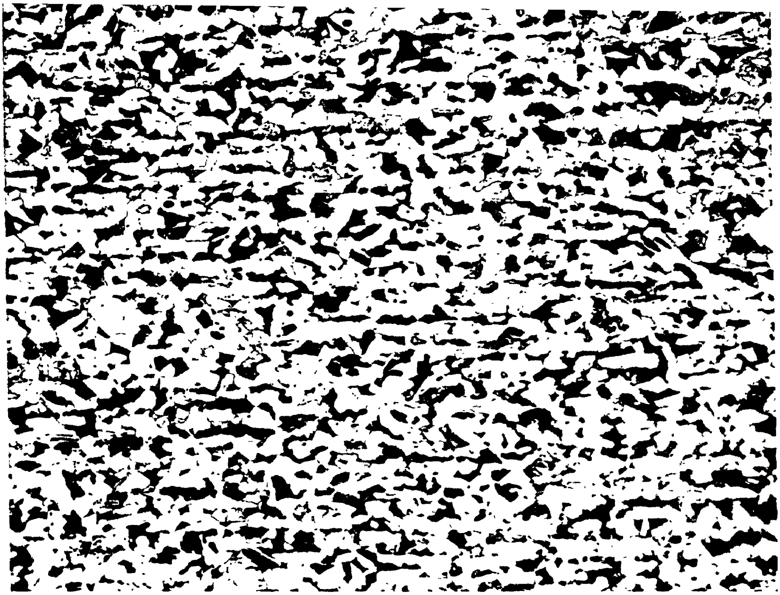
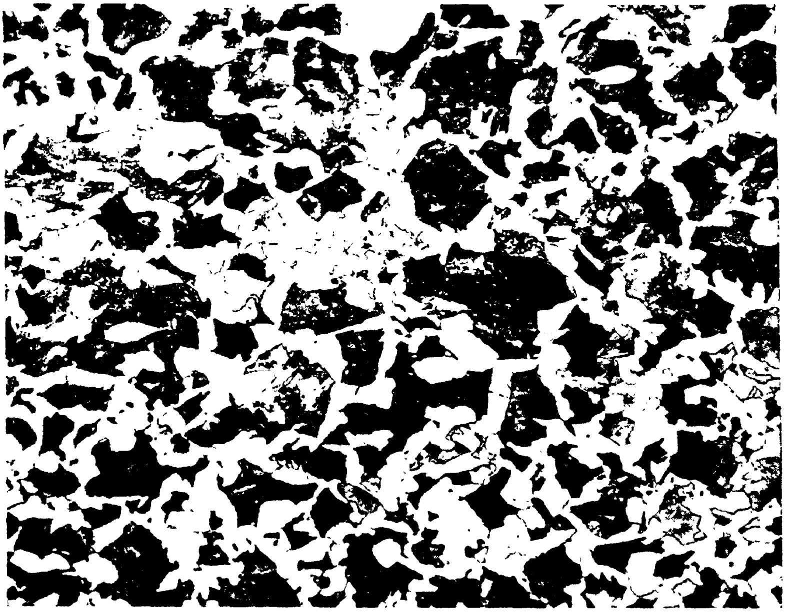
[1] N. T. Belaiew, *Proc. Roy. Soc.*, 1925, **108**, A, 295 ; *J. Iron Steel Inst.*, 1922, i, 201 ; *Rev. Métall.*, 1930, **27**, 680 ; 1935, **32**, 145 ; " La cristallisation des métaux," Paris, 1934.

[2] O. V. Greene, *Trans. Amer. Soc. Steel Treat.*, 1929, **16**, 57.

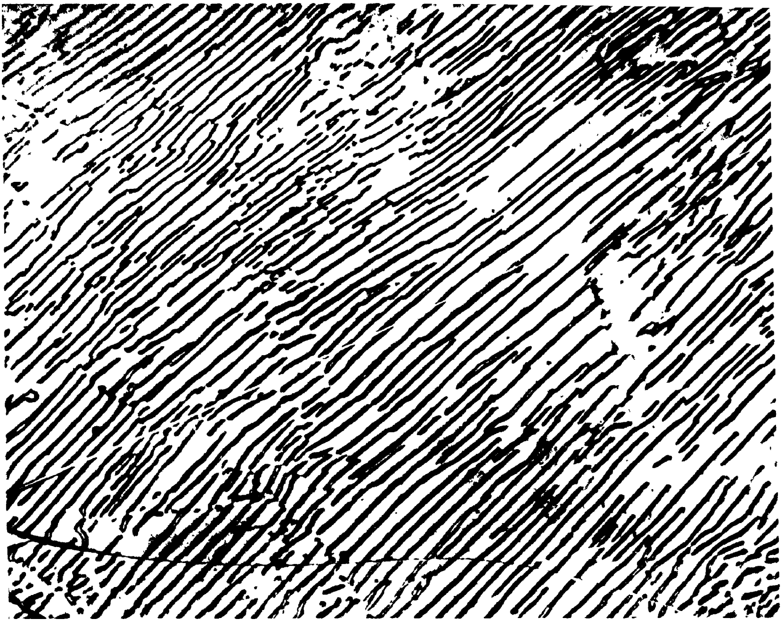


A. Rolled mild steel, with banded structure. × 150



B. Forged 0.39 % C steel. × 150

PLATE XV



A. Pearlite in steel

B. "Stainless" steel, 18 % Cr. 8 % Ni. × 150

PLATE XVI

a single micrographic constituent) are proportional to the carbon content. Provided that the steel is in a condition of equilibrium its carbon content may be judged from the micro-structure, and a quantitative determination may even be made by means of a planimeter.

In large steel forgings, cooled slowly in the austenite range, the ferrite forms a Widmanstätten pattern,[1] the (110) planes of the ferrite coinciding with the (111) planes of the austenite.[2] Annealing above the A_3 point brings about recrystallization, the ferrite then being deposited mainly at the grain boundaries. The original structure is brittle, on account of the large cleavage planes, and for this reason annealing is necessary in practice.

Graphite.—Graphite occurs in grey cast iron in the form of large, thin plates, crystallizing in the hexagonal system. These plates are very commonly curved, the soft, plastic character of the graphite allowing it to yield to the pressures produced in the growth of the neighbouring ferrite crystals (Plate XVIIB). The presence of both primary and eutectic graphite is rarely observed, owing, on the one hand, to the reluctance of the iron-carbon alloys to enter the state of stable equilibrium, and on the other to the low specific gravity of graphite, which causes it to float up to the surface of the solidifying mass. A good photo-micrograph, showing both the primary and eutectic graphite, was obtained by Goerens [3] from a grey iron containing 7 per cent. of graphite, prepared in the electric furnace.

Graphite is at once visible in the polished section, without etching. In specimens as ordinarily polished the graphite is largely removed during the grinding process, and its place is represented by fine cavities. Special precautions should therefore be taken in preparing sections of grey cast iron.

Temper carbon is a finely divided form of graphite, produced in the decomposition of cementite, or of a solid solution of carbon in iron ; it is therefore produced in the annealing of white cast iron, as in the making of malleable castings. It is commonly visible in the etched sections as minute aggregates, or " nests " surrounded by white areas of ferrite, owing to the withdrawal of carbon from the surrounding alloy by segregation. Temper-carbon has been proved to be chemically identical with graphite.[4]

Graphite is not a normal constituent of steel, but it may be found in high-carbon steels which have been repeatedly heated, and then arises from decomposition of cementite. It has been found in steel containing only 0·15 per cent. of carbon, which had been kept for three years at 600°, the whole of the cementite having been decomposed.[5]

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[1] J. O. Arnold and A. McWilliam, *J. Iron Steel Inst.*, 1905, ii, 27.

[2] R. F. Mehl and C. S. Barrett, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, **93**, 78 ; R. F. Mehl and O. T. Marzke, *ibid.*, 123.

[3] *Metallurgie*, 1907, **4**, 137.

[4] G. Charpy, *Compt. rend.*, 1907, **145**, 1173.

[5] A. B. Kinzel and R. W. Moore, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **116**, 318.

The constituents so far mentioned may all occur under conditions of equilibrium, in the sense of the phase rule, in pure iron-carbon alloys. It does not follow, however, that full physical stability has been reached. When, by raising the temperature, the freedom of movement of the atoms is increased, rearrangements may and do occur which involve no change in the relative quantities of the phases, but lead to a condition which is physically more stable. The effects resemble those which would be caused by surface tension. Apart from grain growth, which is dealt with elsewhere, the most important change is a breaking-up of the lamellæ of cementite in pearlite to form more or less spherical masses. This process is rather clumsily called " spheroidization " of the cementite.[1] The first stage is the separation of the lamellæ into a series of beads by the formation of constrictions at intervals.[2] With longer heating distinct globules are formed, which in time may aggregate to form larger globules.[3] The process clearly involves diffusion, so that it is natural that the time required for the process should vary with temperature in the same way as solid diffusion.[4] Globular cementite has far less strengthening effect than the lamellar form, so that spheroidization lessens the tensile strength and hardness. It is deliberately brought about in high-carbon steels which have to be drawn into wire or hardened in the form of thin strip, such as safety-razor blades,[5] preferably by long heating just below Ar_1.[6]

When nuclei of carbide are already present in a steel above the Ar_1 point, globular cementite is likely to be obtained on cooling below that point, in place of the usual lamellar form.[7]

In very low carbon steels, such as are used for tinplate, the pearlite structure is commonly absent, and the cementite occurs in the form of globules at the grain boundaries.[8] When the cementite forms intergranular films it produces brittleness, and this condition is to be avoided.[9]

Austenite.—This is γ-iron, holding carbon, and frequently other elements, in solid solution. Austenite has a face-centred cubic lattice, the parameter of which increases with increasing carbon

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[1] *Not* of pearlite. Pearlite is the lamellar eutectoid, and it is the cementite which becomes globular.

[2] C. Benedicks, *Metallurgie*, 1909, **6**, 567 ; H. M. Howe and A. G. Levy, *J. Iron and Steel Inst.*, 1916, ii, 210.

[3] This process was called by Howe the " divorcing " of the pearlite.

[4] R. W. Bailey and A. M. Roberts, *Proc. Inst. Mech. Eng.*, 1932, 209. See, for the relation of this effect to surface tension, F. C. Thompson, *Trans. Faraday Soc.*, 1921, **17**, 391.

[5] C. H. Desch and A. T. Roberts, *J. Iron Steel Inst.*, 1923, i, 249.

[6] F. Körber and W. Köster, *Mitt. K.W. Inst. Eisenforsch.*, 1924, **5**, 145.

[7] J. H. Whiteley, *J. Iron Steel Inst.*, 1922, i, 339.

[8] H. Kornfeld and G. Brieger, *Arch. Eisenhüttenw.*, 1931, **5**, 315.

[9] See, for further facts concerning globular and intergranular carbides, K. Honda and S. Saito, *J. Iron Steel Inst.*, 1920, ii, 261 ; A. Portevin and V. Bernard, *ibid.*, 1921, ii, 145 ; R. S. MacPherran and J. F. Harper, *Trans. Amer. Soc. Steel Treat.*, 1924, **6**, 341 ; A. Pomp and R. Wijkander, *Mitt. K.W. Inst. Eisenforsch.*, 1926, **8**, 55.

content up to the limit of saturation.[1] It is not a stable phase in the iron-carbon system at ordinary temperatures, and like γ-iron itself cannot be wholly retained by quenching, although it may be identified among the constituents of hardened steel, as described below. Its stability is greatly increased by alloying with other elements which enter into solid solution, and it therefore becomes prominent in many alloy steels. Homogeneous austenite has been obtained by quenching a steel containing 0·93 per cent. C and 1·67 per cent. Mn from 1050° in ice-water.[2] Austenite forms polygonal grains, frequently twinned, and generally resembling α-brass and other non-ferrous alloys having the same space lattice (Plate XVIB). It is little harder than ferrite, and is non-magnetic. Its structure at high temperatures may be seen by etching with gaseous hydrogen chloride at 1120°,[3] or by means of the electron microscope.[4] The quenched solid solution, being metastable, is readily converted into other constituents by heating to moderate temperatures.

Austenite is an interstitial solid solution, the points on the space lattice being occupied only by iron atoms, whilst the smaller carbon atoms are packed into the spaces in the interior of the cubic cells.

Martensite.—This is the principal constituent of iron-carbon alloys hardened by rapid quenching. It is the essential constituent of hard steels, and is the cause of their hardness. It represents the first stage in the resolution of undercooled austenite into α-iron and cementite. A quenched, but untempered, tool-steel shows the structure well. When etched with nitric or picric acid, it is resolved into parallel lines, forming three systems intersecting at angles of 60°. This structure is often called "acicular," but the lines, described as needles, really represent cleavages of octahedra. Long supposed to be homogeneous, and to represent the original solid solution stable above the transformation point, martensite is found to be a product of partial resolution. It contains α-iron, and is therefore magnetic, but the constrained molecular condition gives it a high coercive force. It is the essential constituent of permanent magnets.

A steel containing 1·6 per cent. C, quenched from 800° in ice-water, consists of cementite in a ground-mass of pure martensite, whilst the ground-mass of the same steel, quenched from 1100°, consists of a mixture of austenite and martensite. In such mixtures, the martensite forms characteristic, angular crystals, designated "fers de lance" by Osmond. The behaviour of these crystals on etching is variable. Sometimes they appear black on the white background of austenite, at other times the austenite is etched more rapidly than the martensite. Kurbatoff's complex reagents produce better contrasts than the simple acids commonly used for etching. A needle

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[1] A. Westgren and G. Phragmén, *J. Iron Steel Inst.*, 1924, i, 159.

[2] E. Maurer, *Metallurgie*, 1909, **6**, 33.

[3] A. Baikoff, *Rev. Métall.*, 1909, **6**, 829.

[4] E. Brüche and W. Knecht, *Z. techn. Physik*, 1935, **16**, 95; W. G. Burgers and J. J. A. Ploos van Amstel, *Nature*, 1935, **136**, 721.

may also be used to distinguish austenite from martensite, the greater hardness of the latter being very marked.

It is difficult to reveal the structure of martensite of exactly eutectoid composition, and this was regarded by Sorby as homogeneous. Howe called it *hardenite*, but this term, although popular for a time, has fallen into disuse.

The nature of martensite has been the subject of much controversy. That it contains α-iron is shown by its magnetic quality and by the X-ray structure.[1] It is most often described as a supersaturated solution of carbon in α-iron, owing its hardness to internal strain, but it is unlikely that a new phase should be formed in quenching, holding an excess of carbon in solution beyond that corresponding with equilibrium. The characteristic etching properties suggest that decomposition has already occurred along the octahedral planes of the austenite, but that the cementite liberated has not had time to agglomerate into masses large enough to give an X-ray pattern or to be isolated by chemical means. On the whole, it would seem most probable that in the changes involved in the transformation of γ- into α-iron each carbon atom has taken up such a position as to stand in close relation to three iron atoms, so that a molecule of the carbide Fe_3C may be regarded as in incipient formation. These molecules arrange themselves parallel with the (111) planes of the original austenite, and form sheets, probably one molecule thick, which suffice to cause the characteristic etching effects, and to cause hardening by distortion of the ferrite in their neighbourhood. In such a case the phase rule becomes inapplicable. The X-ray study of the decomposition of martensite at 150° confirms this view.[2]

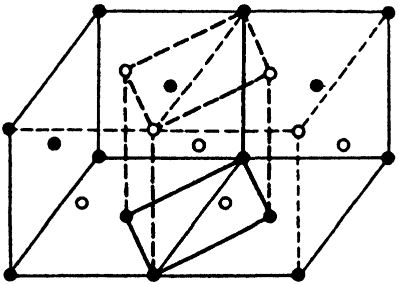

FIG. 145.—Cubic and tetragonal structure in austenite.

X-ray evidence has thrown some light on the process of transformation. Between the face-centred structure of austenite and the body-centred structure of ferrite an intermediate tetragonal structure has been found, in which the axial ratio $c : a$ increases with increasing carbon up to a maximum of 1·06.[3] The lattice of γ-iron is equivalent to a body-centred tetragonal lattice with the axial ratio $1 : \sqrt{2} = 1 : 1{\cdot}414$ (Fig. 145), and the tetragonal lattice of martensite may be formed from this by compressing its height and increasing

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[1] A. Westgren, *J. Iron Steel Inst.*, 1921, i, 303.

[2] G. Hägg, *ibid.*, 1934, ii, 439.

[3] W. L. Fink and E. D. Campbell, *Trans. Amer. Soc. Steel Treat.*, 1916, 9, 717; N. Seljakow, G. Kurdjumow and N. Goodtzoe, *Z. Physik*, 1927, 45, 384.

its cross-section. The mechanism of the change has been discussed by several workers.[1] A slight further arrangement gives rise to the lattices of α-iron and of cementite.

Martensite is not a transitional phase in the transformation of austenite into the stable condition of pearlite.[2] It is not formed until quite a low temperature has been reached. Osmond found that quenched austenite can be changed into martensite by plunging into liquid air, the change being accompanied by an increase of volume, so that the martensite "needles" appear in relief on a polished surface. Dilatometric experiments[3] have shown that martensite is only formed in the quenching of steel when the cooling has been so rapid as to depress the Ar_1 point below 300°, and advantage has been taken of this fact to study the process at leisure. Rods of steel containing 0·8 per cent. C quenched in a molten salt bath at 232° remain austenitic, and therefore soft, for some five minutes, becoming hard only when further cooled.[4] Using a steel of 1·6 per cent. C, quenching from 1150° in a bath of molten metal at 160° retained the austenite in such a stable form that it could be ground and polished at 100°, when etching showed it to be homogeneous. On lowering the temperature, martensite needles appeared on the surface, each standing out in relief.[5] The striking fact is that each needle makes its appearance instantly and of full size, no growth occurring later. Further transformation takes place only by the production of more needles. The experiments have been recorded on a kinematographic film.[6]

The formation of martensite from a single crystal of austenite has been followed by means of X-rays.[7] Iron containing as little as 0·0025 per cent. of carbon will give an orientated structure on drastic quenching,[8] but ordinarily the change from γ- to α-iron begins at nuclei distributed at random, and no connection between the orientations of the initial and final crystals can be detected. By quenching steel with 0·75 per cent. C in baths at temperatures between 480° and 380° a range of structures has been obtained, forming a transition from the Widmanstätten to the martensitic structure,[9] thus supporting the view that the geometry of the two transformations is essentially the same, but that in martensite the cementite is precipitated only as two-dimensional sheets.

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[1] E. C. Bain, *Trans. Amer. Inst. Min. Met. Eng.*, 1924, **70**, 25; E. Öhman, *J. Iron Steel Inst.*, 1931, i, 445; K. Heindlhofer and E. C. Bain, *Trans. Amer. Soc. Steel Treat.*, 1930, **18**, 673.

[2] The opposite view has been maintained by K. Honda. See, for instance, *Sci. Rep. Tôhoku Univ.*, 1927, **16**, 279, but the evidence is clear.

[3] A. M. Portevin and M. Garvin, *J. Iron Steel Inst.*, 1919, i, 469; A. M. Portevin and P. Chevenard, *ibid.*, 1921, ii, 117.

[4] D. Lewis, *ibid.*, 1929, i, 427.

[5] H. Hanemann and H. J. Wiester, *Arch. Eisenhüttenw.*, 1931, **5**, 377.

[6] H. J. Wiester, *Z. Metallk.*, 1932, **24**, 276.

[7] G. Kurdjumow and G. Sachs, *Z. Physik*, 1930, **64**, 325.

[8] A. Sauveur and C. H. Chou, *Trans. Amer. Inst. Min. Met. Eng.*, 1929, **84**, 350.

[9] J. M. Robertson, *J. Iron Steel Inst.*, 1929, i, 391.

Both austenite and martensite, being unstable, break up into mixtures of ferrite and cementite on moderate heating, but they differ greatly in their ease of resolution. Martensite is "tempered," yielding fine granules of carbide, at as low a temperature as 100°, whilst any residue of unchanged austenite does not break up until 235°, also giving dispersed carbide.[1]

The structure of the "fers de lance," the masses of martensite which appear on a background of austenite, is interesting. They have a median line which suggests a twin structure, and on each side of this, when examined under very high magnification, fine parallel striations, about $0{\cdot}15\ \mu$ apart, are seen.[2] Deformation shows, however, that the two halves have the same orientation, so that they cannot represent twins.[3]

Troostite.—This constituent, frequently present in hardened steels, is characterized by the deep brown or black surface tint produced by etching, especially with reagents containing nitro-compounds. It commonly presents itself as nodules, or as a border invading crystals of austenite or martensite. The physical and chemical properties of troostite all indicate that it is a mixture of cementite and ferrite, only differing from pearlite in its extremely fine state of division. Benedicks describes it as a colloidal solution of carbide in iron.[4] It was described by Arnold as "emulsified carbide,"[5] a term which also expresses the fine state of subdivision. It may be obtained in an almost pure condition by quenching steel containing 0·9 per cent. of carbon from 725°. The fine state of division is sufficient to account for the readiness with which carbon is liberated from it by the action of etching reagents.

The definition of troostite has given rise to much controversy. The product as obtained above has been regarded as identical with that produced when martensite is tempered by moderate heating, on the ground that both constituents are made up of ferrite and cementite, as is shown by their density and by the X-ray method, and that both are unresolved at moderate magnifications. However, the use of high powers shows that the nodular troostite formed during quenching is lamellar in structure, although very fine, being sometimes only just resolved at a magnification of 3500 diameters.[6] It is best to retain the name troostite for this constituent. Its growth is spherulitic, the fine lamellae radiating from a centre, so that in plane section it appears fan-shaped. This form of growth has also been

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[1] H. Esser and H. Cornelius, *Arch. Eisenhüttenw.*, 1934, **7**, 693. The relation between the rate of transformation of austenite and the degree of undercooling has been studied in detail by E. S. Davenport and E. C. Bain, *Trans. Amer. Inst. Min. Met. Eng.*, 1930, **90**, 117. See Appendix.

[2] F. F. Lucas, *Trans. Amer. Soc. Steel Treat.*, 1924, **6**, 669; 1929, **15**, 339.

[3] E. Scheil, *Arch. Eisenhüttenw.*, 1935, **9**, 61.

[4] C. Benedicks, *J. Iron Steel Inst.*, 1905, ii, 352; 1908, ii, 217; *Kolloid Z.*, 1910, **7**, 290.

[5] J. O. Arnold, *Proc. Inst. Civ. Eng.*, 1895, **123**, 127.

[6] F. F. Lucas, *J. Franklin Inst.*, 1926, **201**, 177; *Bell Techn. J.*, 1930, **9**, 101.

A. Eutectic of white pig iron. × 200

B. Grey phosphoric cast iron. × 350

PLATE XVII

observed in pearlite.[1] The two structures differ only in fineness. Troostite, on this definition, is never a product of the decomposition of martensite, but is derived directly from austenite, the change occurring most readily near 540°.[2]

Sorbite.—The term sorbite has been frequently used to describe the eutectoid constituent of steels which have been cooled too quickly for the development of well-laminated pearlite. It is etched more rapidly than ordinary pearlite, and, like troostite, is a mechanical mixture of ferrite and cementite. It has also been used for the product of decomposition of martensite, in which case the cementite is in the form of small globules. It is doubtful whether the name is required for carbon steels, as the structure containing finely dispersed carbide is more properly described as "tempered martensite." Industrial steels, however, are described as "sorbitic" when their pearlite is so fine as to be resolved with difficulty, this condition giving toughness. In alloy steels, the name sorbite may be conveniently used for the rather obscure mixtures of ferrite and carbide, not necessarily of exact eutectoid composition, which are so often found.

Osmondite.—This name has been used for a stage intermediate between troostite and sorbite, formed at 400°.[3] It does not, however, correspond with any real discontinuity, and the name is now superfluous.

CAST IRON.

White cast iron owes the principal features of its structure to the presence of the austenite-cementite eutectic, the appearance of which is shown in Plate XVIIA. If the proportion of carbon is less than 4·3 per cent., the eutectic is accompanied by crystal skeletons of primary austenite. During cooling, these austenite masses undergo resolution. and generally appear as dark masses of fine pearlite after etching, but their outline remains that of the primary austenite. Needles of secondary cementite, thrown out of solid solution along the curve ES (Fig. 141) are often to be seen in the dark mass of pearlite.

On the other hand, white iron containing more than 4·3 per cent. of carbon shows large plates of primary cementite in addition to the eutectic. An iron containing exactly the eutectic proportion of carbon frequently exhibits a cleavage suggestive of large crystal plates, although free cementite is absent. This effect is due to the tendency of this eutectic already noted (p. 144) to form "colonies" of definite parallel orientation.

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[1] H. C. H. Carpenter and J. M. Robertson, *J. Iron Steel Inst.*, 1932, i, 309.

[2] A useful discussion, by various authors, of the nomenclature of these constituents of hardened steel, with typical photographs of successive stages, is given in *Metal Progress*, August, 1935. Bain prefers to call the nodular constituent "fine pearlite" which is logically correct, but its characteristic darkening on etching, and mode of occurrence, seem to call for a separate name.

[3] E. Heyn and O. Bauer, *J. Iron Steel Inst.*, 1909, i, 109.

Grey cast iron contains as its principal constituents pearlite, graphite, and either ferrite or cementite, according as the proportion of combined carbon is below or above the eutectoid proportion. A further constituent, which is rarely absent from the commercial varieties of grey iron, is the eutectic of iron and iron phosphide, Fe_3P, which forms reticulated masses, brilliantly white in an etched specimen, and appearing as distinct islets of hard material in the softer ground-mass (Plate XVIIB).

The properties of grey cast iron, being a heterogeneous material, depend largely on the size and distribution of the soft graphite flakes, which are a source of weakness. Ordinarily, the crystals of graphite are large unless the proportion of total carbon is low, but they may be kept small by various devices during casting, a fine eutectic-like structure being then obtained.[1] This fine structure is aimed at when improved mechanical properties and resistance to chemical attack are required.

THE INFLUENCE OF OTHER ELEMENTS ON THE IRON-CARBON SYSTEM.

Commercial varieties of iron and steel commonly contain other elements besides iron and carbon, frequently in notable proportions. The addition of a third element may affect the equilibrium of iron and carbon in several ways. In the first place, the tendency of the alloys to assume the metastable (carbide) form rather than the stable (graphitic) form depends to a great extent on the presence of other elements. Silicon and aluminium greatly accelerate the separation of graphite, whilst manganese and sulphur favour the retention of carbon in the combined form.[2] The quantitative relationships have been most fully worked out in the austenite-cementite series, and the conclusion has been reached that two principal types of ternary systems present themselves.[3]

1. The third element forms solid solutions with γ-iron, and also enters into solid solutions with cementite. Equilibria of this kind are obtained with Mn, Si, Cr, and W.

2. The third element forms a compound with iron, which has only a small solubility in solid γ-iron, and is insoluble in cementite. A ternary eutectic is therefore formed. Examples of this type are furnished by P, As, Sb, and Sn.

Manganese may be taken as a typical representative of the first class. Manganese carbide, Mn_3C, is isomorphous with Fe_3C, which it closely resembles. The structure of a white cast-iron is unchanged

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[1] A. L. Norbury and E. Morgan, *J. Iron Steel Inst.*, 1930, ii, 367; 1936, ii, 327; P. Bardenheuer and A. Reinhardt, *Mitt. K.W. Inst. Eisenforsch.*, 1934, 16, 65.

[2] The factors for calculating the displacement of graphite by other elements have been determined by M. Orthey, *Metallurgie*, 1907, 4, 196. See also E. Piwowarsky, *Stahl u. Eisen*, 1925, 45, 1455.

[3] P. Goerens, *Metallurgie*, 1909, 6, 531, 537.

by addition of manganese, and the freezing-point curve is only slightly modified, the general form remaining the same.

In the iron-carbon-silicon alloys, two series of solid solutions are formed, one being an austenite containing carbon and silicon dissolved in γ-iron, and the other a solution of Fe_3C and Fe_2Si.[1]

The behaviour of alloys containing phosphorus is very different.[2] The ternary system Fe-Fe_3C-Fe_3P resembles such a simple system as that of lead, tin, and bismuth. γ-iron dissolves about 2 per cent. C and 2 per cent. P, but iron carbide and phosphide are mutually insoluble. There are thus three binary eutectics (austenite-cementite, austenite-phosphide, and cementite-phosphide) and a ternary eutectic point, at which all three solid phases are in equilibrium. The latter point lies at 953° and 91·3 per cent. Fe, 1·95 per cent. C, and 6·8 per cent. P. Arsenic, antimony, and tin form similar systems.[3]

Sulphur combines with iron to form ferrous sulphide, FeS. The fusible eutectic solidifies in the form of thin, brittle films between the crystal grains (see Chap. VIII). In the presence of manganese, however, the sulphide consists largely of MnS, which collects in drops, but since they are isolated instead of being continuous, their harmful effect is reduced to a minimum. This behaviour of sulphides was first shown by Arnold.[4] Commercial steels should contain sufficient manganese for this purpose.

Small quantities of manganese, silicon, sulphur, and phosphorus are usually present in commercial steels, and very frequently also copper, nickel, and chromium. It is only when other metals are added in quantities exceeding these, mostly belonging to the groups closely related to iron, as a means of improving the properties of steel, that the product is called a " special " or " alloy " steel. Only the briefest reference to the numerous alloy steels can be made in this place. The addition of another metal may affect the metallographic character of steel in four different ways, namely : by entering into solid solution in either α- or γ-iron, thus giving rise to stronger or tougher varieties of ferrite or austenite ; by forming new carbides ; by lowering or raising the temperatures of transformation of carbon steels ; and by retarding molecular change and diffusion. All these factors are present in cases of great technical importance.[5]

The structure of the alloy steels is modified from that of carbon steels. With small additions of foreign elements ferrite and pearlite are found, whilst with larger additions the structure is martensitic with normal rates of cooling but may be made austenitic by quenching, whilst the extreme case is presented by steels which consist of austenite even when slowly cooled.

[1] W. Gontermann, *Z. anorg. Chem.*, 1908, **59**, 373.

[2] J. E. Stead, *J. Iron Steel Inst.*, 1900, ii, 109 ; 1915, i, 140.

[3] P. Goerens and K. Ellingen, *Metallurgie*, 1910, **7**, 72.

[4] J. O. Arnold, *J. Iron Steel Inst.*, 1894, i, 129 ; *Metallographist*, 1900, 273 ; J. O. Arnold and G. R. Bolsover, *J. Iron Steel Inst.*, 1914, i, 396.

[5] For a complete survey of alloy steels, see E. Houdremont, " Sonderstahlkunde," Berlin, 1935.

The specific influence of the added element depends largely on its effect on the allotropic relations of iron, and in this respect the alloying elements fall into two groups. One of these, including C, N, Co, Ni, Au, Cu, Zn, and the platinum metals, has the effect of widening the γ-region, so that in some instances, when a sufficient quantity is present, the alloys are permanently austenitic, or at least remain so down to low temperatures, whilst the other group, including Al, Si, P, Ti, V, Cr, Ge, As, Mo, Sn, Sb, and W, narrows that region, so that when a certain limit is exceeded, the austenitic region disappears entirely, and the α- and δ-regions become continuous. This " closed loop " was first suggested in the system iron-silicon,[1] and has since been found to be of frequent occurrence. It will be noticed that the elements which produce this effect form a compact group in the periodic system.[2] In ternary alloys the loop becomes a closed volume, as in the systems Fe-Al-Si and Fe-Cr-Mo.[3]

B	C		N		O		F						Li
Al	*Si*		*P*		S		Cl						Na
		Ti		*V*		*Cr*		Mn	Fe	Co	Ni	Cu	Zn
		Zr		Nb		*Mo*		Re	Ru	Rh	Pd	Ag	Cd
		Hf		Ta		*W*			Os	Ir	Pt	Au	Hg
		Th		Po		U							

The elements which will form alloys with iron to a useful extent are neighbours in the periodic system, as shown in the table. Elements which close the γ-loop are printed in italics.

Oxygen and sulphur have been enclosed by a dotted line, as they are found in steels, but cannot be regarded as alloying elements. Rhenium has been included on account of its relation to manganese and because it alloys with other heavy metals. Elements which fall outside of the enclosing line either do not alloy with iron, or merely form brittle products without useful metallic character.

Nickel, which has a face-centred cubic lattice like that of γ-iron, alloys with it to form a continuous series of solid solutions. As ordinarily prepared, the alloys are homogeneous. Natural meteoritic irons, however, have a strongly marked structure; the first of the Widmanstätten structures to be discovered (see p. 3).

[1] F. Wever and P. Giani, *Mitt. K.W. Inst. Eisenforsch.*, 1925, 7, 59.

[2] F. Wever, *ibid.*, 1931, 13, 183.

[3] F. Wever and A. Heinzel, *ibid.*, 1931, 13, 193.

When 3 per cent. of nickel is added to a steel containing 0·25 to 0·4 per cent. of carbon, the strength is increased without injury to the ductility. At the same time, on account of the sluggishness of diffusion of nickel, the transformations are slowed down, so that nickel steels allow of greater latitude in heat-treatment than carbon steels. Nickel carbide being very unstable, manganese must be increased in order to prevent the liberation of graphite. From 30 per cent. onwards the alloys are austenitic at ordinary temperatures, and some of these have been mentioned in connection with their magnetic properties (Chap. XIV). With about 36 per cent. of nickel, the carbon being kept low, the coefficient of expansion becomes almost zero, and the steel finds application under the name of *invar.*

Chromium forms very stable carbides, of which Cr_4C and Cr_3C_2 are the most important, together with a double carbide FeCrC. In small quantities it increases the strength of steel without lessening the ductility, but at the same time it assists grain growth, so that a chromium steel requires care in treatment to avoid a coarse structure. With 1 per cent. of carbon and 1·25 per cent. of chromium a steel is obtained which is much used for ball-bearings, and steels with larger quantities are used in the making of dies. Small additions of chromium correct the tendency to form graphite in high carbon steels. Chromium has a marked effect in lowering the quantity of carbon needed to form the eutectoid. Thus with 2·8 per cent. Cr the pearlite point is at 0·62 per cent. C instead of at 0·81 per cent., and with 14 per cent. Cr it is at 0·35 per cent. C.

The nickel-chrome steels form a very large class of engineering steels, and vary widely in composition and in properties. The nickel does not usually exceed 3·5 or the chromium 1·0 per cent. The microstructures are less easy to interpret than those of carbon steels, as the separation of ferrite and pearlite is usually incomplete, and the structures are confused. The tempered martensite which is seen in the heat-treated material does not vary with the conditions in a characteristic way, and it is difficult to draw conclusions as to the properties of the steel from its appearance under the microscope. Thus the defect known as " temper brittleness," a liability to give low resistance to shock if slowly cooled or if tempered within the range 250°-400°, cannot be revealed at present by any known means of etching. The cause of temper-brittleness is still a matter of dispute, each alloying element having been blamed in turn.[1] In order to avoid it, the steels are tempered at 650° and then quenched in oil. On the addition of 0·3 per cent. molybdenum, however, the liability to brittleness disappears.

Manganese.—Manganese is present in nearly all steels, and has the effect of rendering the carbide ($Fe_3C + Mn_3C$) more stable. The structure of the pearlite is minutely lamellar. Up to 1·5 per cent.

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[1] The literature on temper-brittleness is extensive. See R. H. Greaves and J. A. Jones, *J. Iron Steel Inst.*, 1919, ii, 329 ; 1920, ii, 171 ; 1925, i, 231 ; J. H. Andrew and H. A. Dickie, *ibid.*, 1926, ii, 359.

of manganese is now much used, but higher proportions give brittle alloys until the remarkable Hadfield steel is reached, containing 12-13 per cent. of manganese and about 1·2 per cent. of carbon.[1] This is entirely austenitic when quenched from 1000°, and its Brinell hardness is only 200. On attempting to cut or file it, however, the work-hardening of the surface renders it intensely hard, so that it is used where great resistance to abrasion is needed. If slowly cooled it is hard (400 Brinell) and brittle, the structure being then martensitic.

Silicon.—This again is found in small quantities in most steels, and the proportion is increased when higher tensile strength is required. Silicon-iron alloys, almost free from carbon, are used for transformer sheets on account of their low hysteresis loss, the maximum silicon content being 4·0 per cent.[2] This is outside of the γ-loop, so that the alloys have no transformation point, and are permanently ferritic. The structure of an ingot of such an alloy is shown in Plate IXA. It readily forms coarse grains, with a strongly marked cubic cleavage.

A casting alloy of iron with about 16 per cent. of silicon is used in chemical plant, being highly resistant to corrosion.

Tungsten and Molybdenum.—These two metals form very stable carbides, and also double carbides with iron, the compounds W_2C, WC, and Fe_4W_2C having been identified.[3] Both metals also form compounds with iron, and by quenching solid solutions and then tempering, the compounds Fe_3W_2 and Fe_3Mo_2 may be caused to precipitate in such a fine state as to produce age-hardening, the hardened alloys being used as dies for wire-drawing.[4] The heavy tungsten atom has a great effect in lessening mobility in the solid alloy, so that its presence hinders grain growth, retards phase changes, and greatly increases the coercive force. Hence tungsten steels, usually with 6 per cent. W and 0·7 per cent. C, are used in the hardened (martensitic) condition for permanent magnets.[5] Of all engineering steels, the nickel-chrome-molybdenum series provides the best combination of properties, the range of which can be varied by suitable heat-treatment.

Cobalt.—Cobalt carbide decomposes very readily, so that in steels which contain much carbon cobalt is only used in conjunction with chromium. It has a great effect in increasing the coercive force, and permanent magnets with 30-40 per cent. Co are used in the hardened state.[6]

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[1] R. A. Hadfield, *J. Iron Steel Inst.*, 1888, ii, 41 ; *Proc. Inst. Civ. Eng.*, 1888, **93**, iii.

[2] W. Barrett, W. Brown, and R. A. Hadfield, *J. Inst. Elect. Eng.*, 1901-2, **31**, 674 ; T. D. Yensen, *Trans. Amer. Inst. Elec. Eng.*, 1915, **34**, 2601.

[3] A. Westgren and G. Phragmén, *Trans. Amer. Soc. Steel Treat.*, 1928, **13**, 539 ; *Z. anorg. Chem.*, 1926, **156**, 27.

[4] W. P. Sykes, *Trans. Amer. Inst. Min. Met. Eng.*, 1926, **73**, 969 (Fe-W) ; *Trans. Amer. Soc. Steel Treat.*, 1926, **10**, 839 (Fe-Mo).

[5] For heat-treatment, see A. M. Parkin, *Iron Steel Inst.*, *Carnegie Schol. Mem.*, 1924, **13**, 1.

[6] K. Honda and S. Saito, *Sci. Rep. Tôhoku Univ.*, 1920, **8**, 417.

Vanadium.—Vanadium forms a stable carbide, V_4C_3, and is used in small quantities together with other alloying elements, especially chromium. Many other less common elements have been added to steel, for which reference must be made to special works.

High-speed tool steels.—A limit is set to the speed at which a steel cutting tool can be worked on a lathe or other machine by the rise of temperature produced, which causes softening of the martensite by tempering. An improvement was brought about by adding tungsten in sufficient quantity to raise the tempering temperature,[1] and this "Mushet steel" marked a great advance. High-speed steels date from the work of Taylor,[2] and make it possible to use very high speeds of cutting, the tool still retaining its hardness even when the edge is at a dull red heat. The composition of these steels is very various. Tungsten is the most important element, chromium, vanadium, molybdenum, and cobalt being frequent constituents. Although the constitution would seem to be highly complex, it has been pointed out[3] that a generalized diagram represents the facts very closely, Fig. 146. The carbide-forming elements may be regarded as forming a single complex carbide, and a part of the added metals as entering into solid solution in austenite. A typical high-speed steel with 18 per cent. W is indicated by the dotted vertical line. This solidifies as austenite (the small δ-region may be neglected) with some eutectic, one constituent of which is the hard carbide. The network of eutectic must be broken up by annealing for a long time at or over 800°, followed by forging at 1100°. The actual hardening requires a high temperature, usually 1300°, and as this is very close to the solidus care must be taken not to "burn" the steel by melting some of the intergranular eutectic. On account of brittleness, such steels are not quenched in water, but in molten lead or by a blast of air. There is a further appreciable increase of hardness, known as "secondary hardness," when the steel is heated to 600°.

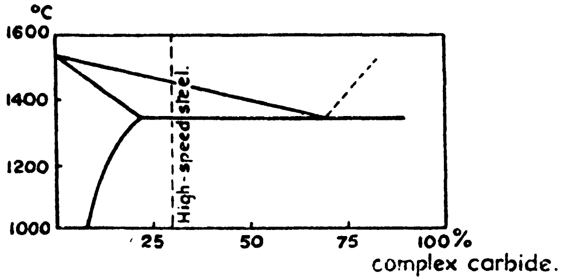

FIG. 146.—High-speed steel diagram.

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[1] R. F. Mushet, Patent, 1856.

[2] F. W. Taylor, *Trans. Amer. Soc. Mech. Eng.*, 1906, **28**, 31; *Rev. Métall.*, 1907, **4**, 58.

[3] M. A. Grossmann and E. C. Bain, *J. Iron Steel Inst.*, 1924, ii, 249.

Stainless steels.—Steels containing large proportions of chromium have a very high resistance to corrosion. The original stainless steel ("non-staining" would have been more accurate) contained 12-14 per cent. Cr and about 0·3 per cent. C.[1] It is near to the eutectoid composition, and must be hardened by quenching to acquire corrosion-resisting properties. On account of the slowness of diffusion, it has to be heated to 900°-950° to dissolve the carbides, and is then quenched. A softer material, sometimes called stainless iron, is obtained with the same chromium content by reducing the carbon as far as possible. With high chromium, the composition falls outside the γ-loop, so that the alloy is permanently ferritic.

An important class of corrosion-resisting alloys is formed by the austenitic steels containing chromium and, usually, nickel.[2] Of these, the most widely used is the alloy containing about 18 per cent. of chromium and 8 per cent. of nickel, known as "18 : 8" and by a variety of trade names. The carbon is less than 0·20 per cent., and for chemical purposes is kept as low as possible, for the reason stated below. In the softest condition, when rapidly cooled from 1100°, these alloys consist of homogeneous austenite, the grains being crossed by characteristic twin bands (Plate XVIB). The steel is rapidly hardened by cold-working, and the grains then show strain markings. If heated in the range 550°-800° carbide is precipitated in the grain boundaries, and the alloy may become brittle, the effect depending both on the temperature and on the time of exposure. On heating more strongly, or even on maintaining the temperature at the upper part of the range for a long time, the carbide re-dissolves. Precipitation in the boundaries greatly reduces the resistance to corrosion, and inter-granular attack takes place readily. It is very liable to occur in welded structures, a zone near to the weld being exposed in the dangerous range of temperature. The cause of the lessened resistance appears to be the withdrawal of chromium from solid solution near the grain boundaries by the precipitation of a carbide rich in chromium, so reducing the chromium content of the austenite below that which gives the resistant properties. It is avoided by (*a*) keeping the carbon content very low, which is not always practicable, and thus preventing precipitation, or (*b*) adding an element, such as titanium, niobium, or molybdenum, which forms a very stable carbide, which is precipitated in preference to chromium carbide. The precipitation then takes place mainly within the grains instead of at the boundaries, and does not lessen the chromium content of the austenite.

The corrosion-resisting steels also have an increased resistance to oxidation at high temperatures. Steels containing nickel, however,

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[1] H. Brearley, Patent, 1916. The high corrosion-resistance of alloys of iron and chromium had been described by P, Monnartz, *Metallurgie*, 1911, 8, 161, but not applied.

[2] W. H. Hatfield, *Engineering*, 1925, 150, 657 ; B. Strauss, *Z. Electrochem.*, 1927, 33, 317.

are susceptible to attack by gases containing sulphur compounds. For very high temperatures, special heat-resisting steels are made containing chromium together with silicon, tungsten, or molybdenum. When the proportion of alloying elements becomes large, the boundary between the steels and certain non-ferrous alloys, such as the nichromes, becomes rather vague. Alloy cast irons, containing nickel, chromium, silicon, or molybdenum, are produced, giving increased resistance to heated gases or to corrosion at atmospheric temperatures, whilst at the same time an increase of strength is usually obtained owing to a reduction in the size of the graphite particles.

THE HEAT TREATMENT OF STEEL.

Owing to the transformations which occur in the iron-carbon system, the properties of steels are greatly affected by the temperature to which they have been heated and the rate at which they have cooled from that temperature. The following terms are used to describe the processes of heat-treatment of steels :

Annealing.—Heating to above Ac_1, maintaining the temperature for a determined time, and cooling slowly. This brings about recrystallization in the austenite region, and time is allowed for the development of pearlite, which is coarser, the slower the cooling. The higher the temperature the coarser the grain, so that over-annealing may produce a brittle metal. Should the solidus line be crossed, so that some of the granular material is actually melted, the steel is said to be burnt. Over-annealed steel may be restored by again heating to a suitable temperature above the critical point, but burnt steel must be re-melted. Should steel be exposed to oxidizing gases during heating, carbon is removed from the outer layers. For proper annealing the steel must be protected against "decarburization," either by wrapping in sheet iron or by maintaining a neutral atmosphere in the furnace.

Normalizing.—This process consists in annealing for a short period as above, but cooling at a rather more rapid rate, usually in air. It aims at producing a fine-grained pearlitic structure, with the constituents in the right proportions for equilibrium.

Hardening.—The hardening of steel depends on the suppression of the normal breaking-up of austenite into ferrite and cementite at the Ar_1 point, and the lowering of the transformation to such a temperature that martensite is produced. There is for each steel a "critical cooling velocity" which is necessary to produce hardening. One of the principal actions of alloying elements is the reduction of this critical rate, either by lowering the critical range or by slowing down the process of diffusion, or both. This is important in the heat-treatment of large masses, such as forgings. With a high critical velocity, the outer zone only is hardened, and the interior does not cool fast enough. With alloy steels the rate may be so slow that uniformity throughout the mass can be attained. Quenching in oil is then employed instead of the more drastic quenching in water, which is liable to cause cracks on account of severe thermal stresses. "Air-hardening" steels are those which have such a low critical rate that they are sufficiently hardened by cooling in air. Such terms are, of course, relative, since the size of the object affects the rate of cooling. A needle of carbon steel, for instance, is hardened merely by cooling in air from above the Ar_1 point, the mass being so small.

Tempering.—Heating the hardened steel to a temperature below the critical point allows the martensite to decompose, liberating cementite in the form of fine particles. This reduces the hardness and relieves the internal stress, so lessening the brittleness to an extent which depends upon the temperature. The desired degree of softness is obtained by controlling the temperature of re-heating, which is determined in practice by the tint produced by the oxidation of the surface. The tints observed correspond with the following temperatures :—

Colour.	° C.
Pale yellow	220
Straw yellow	230
Full yellow	243
Brown	255
Brown and purple	265
Purple	277
Bright blue	288
Deep blue	293
Dark blue, nearly black	316

The tints are interference colours, caused by a transparent film of oxide. In modern practice the use of lead or salt baths, the temperature of which is maintained constant at the required value, is largely superseding the empirical control of the tempering process by observation of the heated surface, but the importance of the temper colours is nevertheless great. The figures given apply only to carbon steels, and the presence of alloying elements alters them greatly. Stainless cutlery steel, for instance, does not show the same colours until much higher temperatures. Pyrometric control is therefore necessary.

By heating to a temperature a little below the critical point the martensite may be completely resolved into ferrite and cementite. The phases present are then exactly the same as if the steel had been slowly cooled, but the structure, and therefore the properties, differ widely. The cementite is liberated in very fine particles instead of forming lamellæ. Such a structure is tough as well as strong, so that quenching, followed by complete tempering, is a means of obtaining improved properties, even from a carbon steel, whilst for many alloy steels it is essential.

CASE-HARDENING AND NITRIDING.

For many engineering parts a hard surface is required to resist wear, whilst the interior or core must be tough in order to resist shock. This combination of qualities is obtained by case-hardening, a process of enriching the surface layer in carbon, so that it will harden on quenching. The object to be hardened is packed in a mixture of carbon with metallic carbonates and heated at about 900°. Sodium cyanide is used for rapid carburization. The steel used must itself be low in carbon, so that its hardness is little affected by quenching. The outer layer or " case " contains about 0·9 per cent. of carbon. As the temperature at which the case is formed is high enough to coarsen the grain of the core considerably, it is advisable to re-heat to above the upper critical point to refine the grain. Quenching from this temperature gives a very coarse martensite, which would be brittle, so the object is again heated, this time to 760° only, in order to bring the case into the austenitic region, and quenched a second time. With a steel containing nickel (3-7 per cent.) although the time taken to introduce carbon is longer, the temperature of quenching is lower, and a single treatment may be enough.

Nitrogen is also used to produce a hard case, harder than that given by carbon.[1] The nitrogen must be supplied in the form of ammonia gas, which dissociates in contact with steel at 500°, and nitrogen is taken up in the form of the nitride Fe_4N, hydrogen being liberated. The layer so formed is thin and, when a plain carbon steel is used, very brittle, but special steels containing aluminium, together with chromium and molybdenum, are more easily carburized and form a thicker case. Since the process of " nitriding " is carried out below the critical temperature, there is no increase of grain size and quenching is unnecessary. The hardness of the nitrided layer is not affected by the rate of cooling. Some of the high-chromium and austenitic steels may also be nitrided.

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[1] A. Fry, *Stahl v. Eisen*, 1923, 43, 1271.

CHAPTER XXII.

NON-FERROUS ALLOYS.

The possible types of structure encountered in the laboratory study of alloys are extremely numerous, but only a limited number of these have properties which render the alloys suitable for technical application. Many structures of metallographic interest are associated with great mechanical weakness, rendering the alloys unfit for any purpose involving resistance to mechanical stress, whether gradually or suddenly applied. Single intermediate phases are in general too hard and brittle to find technical application except in a few special cases, as, for instance, when a brilliant, mirror-like surface is required, as in speculum metal. Occasionally a certain appearance or colour is required for decorative purposes, as in jewellery, and other properties may be comparatively unimportant.

A large proportion of the alloys employed for constructional purposes, and therefore required to possess certain physical and mechanical properties, fall into a few well-defined groups. For instance, amongst the alloys of copper with other metals, the α solid solutions, which consist of copper holding a second metal in solid solution in quantities insufficient to saturate it, are some of the most important of industrial alloys. Whether the second metal be zinc, tin, aluminium, nickel, iron or manganese, the resultant alloys, within certain limits of composition, bear a close resemblance to one another. All have the face-centred cubic lattice. The microscopic structure is in all cases the same, that of polygonal grains which are homogeneous if slowly cooled or annealed, but " cored " if cooled too rapidly for equilibrium. Mechanically, all these alloys are tough and malleable, in degrees which naturally vary with the nature and quantity of the added metal.

A second type of structure, due to the separation of a micrographic constituent from solid solution during cooling, also presents itself in several instances among the copper alloys. This " $\alpha\beta$ " structure is very characteristic, and the resemblance between alloys of this type containing different metals is often very close, so that an alloy of copper containing 8 per cent. of aluminium, for instance, is almost indistinguishable in appearance, so far as the arrangement of the α-and β-phases in the micro-section is concerned from one containing 42 per cent. of zinc. Here, again, the similarity of structure corresponds with a marked similarity of properties.

In this chapter, some of the more important alloys which find industrial application are briefly reviewed. An entirely systematic arrangement has not been adopted, so that whilst the grouping is generally according to chemical composition, alloys of different composition have occasionally been grouped together, if the similarity of their application seemed to render such an arrangement convenient. The list of alloys mentioned below could be extended indefinitely did space permit, but the principal types of structure at least receive mention. Reference must be made to special works for details.

Alloys of copper.—The commercial varieties of copper usually contain a small quantity of oxide, and this is readily seen under the microscope, without etching, as a characteristic eutectic of copper and Cu_2O. The particles of oxide are bright blue under ordinary illumination, but with an immersion objective their true transparent colour, ruby-red, can be made out. Arsenical copper shows a characteristic coreing. Many other elements may be added within the limits of solid solubility: producing changes in the coreing which to the practised eye give indications of the composition, and at the same time the character of the eutectic is changed. The effects of impurities on the properties of copper depend to a large extent on such changes, the balance between the quantity of oxygen and that of such elements as arsenic, antimony, and bismuth being particularly important.[1]

Copper-zinc.—The industrial alloys of copper and zinc fall, with a few unimportant exceptions, into two classes, those composed of the α-solution only, and those built up of the α- and β-phases in conjunction. The first group includes the true brasses, and the second Muntz metal and similar alloys. The equilibrium diagram is shown in Fig. 147.

Of the brasses, an alloy containing 33 per cent. Zn is commonly used for casting purposes, whilst the maximum ductility is possessed by the alloy containing only 30 per cent. Zn. The latter mixture is capable of withstanding extremely severe mechanical deformation, and is therefore employed in the production of tubes and wires by drawing through dies at the ordinary temperature. It is necessary to carry out the reduction in thickness in a number of successive stages, restoring the crystalline structure by annealing after each reduction. Annealing is best performed at 600°-650°, when recrystallization takes place. Twinned α-crystals are abundantly produced, and the size of the crystals increases both with the temperature and with the duration of the annealing process.[2] The "burning" of

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[1] D. Hanson, C. B. Marryat, and G. W. Ford, *J. Inst. Metals*, 1923, **30**, 197; D. Hanson and C. B. Marryat, *ibid.*, 1927, **37**, 121; D. Hanson and G. W. Ford, *ibid.*, 169; S. L. Archbutt and W. E. Prytherch, *ibid.*, 1931, **45**, 265; "Impurities in Copper," London, 1937.

[2] See, for the mechanism of annealing in these and similar alloys, G. D. Bengough and O. F. Hudson, *J. Inst. Metals*, 1909, **1**, 89; W. H. Bassett and C. H. Davis, *Trans. Amer. Inst. Min. Met. Eng.*, 1919, **60**, 428.

brass above 750° is due to volatilization of zinc from the α-phase. The α-crystals are homogeneous throughout, "cores" only being observed in the cast metal, and disappearing completely after working and annealing. Lead is often added to cast brass to render it easier to cut or turn; it is recognizable under the microscope as isolated globules, mechanically retained by the solidifying metal, and not truly alloyed. α-Brasses richer in copper are used for ornamental purposes.

The second group of copper-zinc alloys comprises those containing from 36·5 to 46 per cent. of zinc, and made up, when in a state of equilibrium, of the α- and β-solid solutions. From the diagram, Fig. 147, it will be seen that the β-region is of peculiar form, narrowing

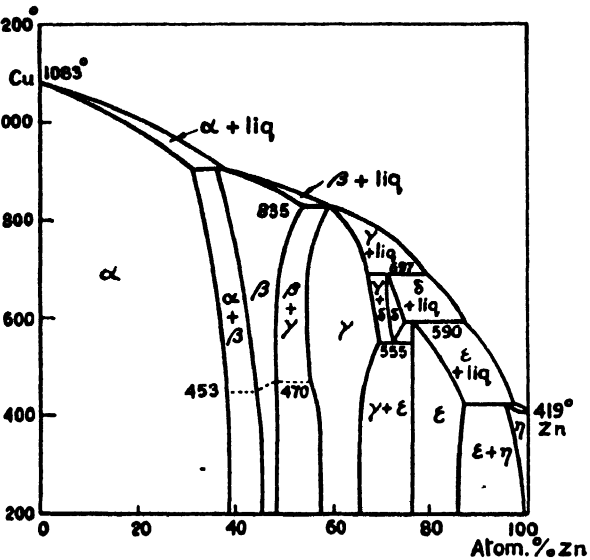

FIG. 147.—Copper-zinc alloys.

considerably as the temperature falls.[1] A number of alloys, therefore, composed after solidification entirely of β-crystals, become heterogeneous at lower temperatures, either the α- or the γ-phase crystallizing out, according to the composition. Alloys containing the γ-phase in excess, even in small quantity, are devoid of technical importance, the γ-crystals, consisting of the compound Cu_5Zn_8, being extremely hard and brittle.

Muntz metal, or 60 : 40 brass, containing 40 per cent. Zn, is composed of α- and β-crystals, but may be obtained in the form of homogeneous β-crystals by quenching from temperatures above 750°, and then forms polygonal grains with straight boundaries. The structure of an annealed specimen is seen in Plate VIB, in which the light areas

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[1] E. S. Shepherd, *J. Physical Chem.*, 1904, 8, 421; V. E. Tafel, *Metallurgie*, 1908, 5, 343.

represent the α-constituent and the dark the more readily etched β-constituent.

The β-constituent gives to alloys in which it occurs the property of being ductile at a higher temperature, so that the 60 : 40 alloy, unlike 70 : 30 brass, may be rolled hot, or formed into rods by the process of extrusion, the metal being forced through dies while in a plastic condition, although much below its melting-point. On the other hand, the β-constituent is less ductile at the ordinary temperature than the α.

Small additions of a third metal are often made. An alloy containing 30 per cent. of zinc and 1 per cent. of tin is known as *Admiralty brass*, and one of 37 per cent. of zinc and 1 per cent. of tin as *Naval brass*, on account of their superior resistance to the corrosive action of sea-water. This quantity of tin is entirely held in solid solution, and is not microscopically recognizable. An alloy of similar structure, containing about 40 per cent. of zinc, and 1 per cent. or rather more of iron in solid solution is used in engineering under the name of *Delta metal.*

Aluminium, silicon, nickel, and manganese are often added to improve the properties of the brasses, leaving the type of structure unchanged. They are known collectively as *high-tensile* or *special brasses*, and separately as aluminium brass, etc., although such erroneous designations as manganese bronze, properly belonging to quite different alloys, are in frequent industrial use. Brass containing 2 per cent. of aluminium resists corrosion owing to the formation of a protective film of alumina, and is used for condenser tubes.[1]

Copper-aluminium.—The α-alloys known as aluminium bronze have a high tensile strength and a high resistance to corrosion. The α-β-structure is seen in Plate VIIB. The β-constituent, like that of the brasses, has good hot-working properties. With 10 per cent. of aluminium the alloy has almost the colour of gold, and is very permanent. It has been used for coinage. It is hardened by quenching from 850°, and then has a martensitic structure, which may be tempered like steel. It should not be cooled so slowly as to allow of the formation of the brittle δ-constituent. This alloy may be further hardened by adding 1-3 per cent. of iron, and in this form is used for die-castings of high strength.

Copper-tin.[2]—Here, again, the first important series of alloys consists of α-solid solutions. If these were to solidify under conditions of perfect equilibrium, those containing up to 14 per cent. of tin would be homogeneous, and their structure would not be affected

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[1] R. Genders, *J. Inst. Metals*, 1930, **43**, 163.

[2] The copper-tin system has been the object of many researches since the classical work of Heycock and Neville, and there is not yet general agreement as to the complex changes in alloys containing from 60 to 80 per cent. of copper. Discussions of the diagram are given in papers by T. Isihara, *J. Inst. Metals*, 1924, **31**, 315; *Sci. Rep. Tôhoku Univ.*, 1928, **17**, 927; O. Bauer and O. Vollenbruck, *Z. Metallk.*, 1923, **15**, 119, 191; T. Matsuda, *Sci. Rep. Tôhoku Univ.*, 1928, **17**, 141.

by quenching. The α-solid solution is seen in Plate IIB. In practice, only alloys up to 6 or 7 per cent. of tin fulfil this condition, and the alloys most generally used, the gun-metals, containing from 8 to 10 per cent. of tin, solidify as two phases. The β-phase breaks up at 510° to form a eutectoid mixture of α and δ, the latter being a hard, brittle substance of bluish-white appearance. It is absorbed on annealing, but the process involves a contraction of volume, so that the annealed castings are porous. Alloys with 12 to 18 per cent. of tin are used in the cast state for bearings. Bell metal may contain up to 25 per cent.

Bronzes containing both tin and zinc find extensive application. Admiralty gun-metal has 10 per cent. Sn and 2 per cent. Zn. Lead, up to 2 per cent., is often added to produce cleaner castings and to give greater facility in machining. In larger quantities it is a source of weakness, remaining undissolved as inter-crystalline material, and thus reducing the strength. For statuary purposes, the percentage of zinc is as high as 5, that of tin being 5-8. The presence of zinc facilitates casting and modifies the colour. Lead is also added, the effect of this being not only to produce a highly fluid alloy, but to modify very greatly the oxidation film, or "patina," which forms on the surface. Some Japanese and Chinese art bronzes, which assume a fine matt black patina, contain as much as 10-16 per cent. of lead, the brittleness thus produced being unimportant for the purpose of statuettes. The production of a patina, either by spontaneous oxidation in the air, or by treatment with oxidizing solutions, is a phenomenon of great interest, which has received very little attention from the scientific point of view. Very small quantities of foreign metals have a marked effect in modifying the colour of this surface layer, as in the case of the Japanese alloy *shakudo*, the fine patina of which is dependent on the presence of gold in quantities varying from 1-4 per cent. The purple or black surface coating is produced by "pickling" with a solution, consisting generally of copper sulphate and acetate. The old Japanese workers excelled in the preparation of this kind of oxidized surface layer.

Bronze coins, which are required to take a sharp impression of the die and to be hard enough to resist the wear and tear of handling, are α-solutions, consisting in this and most other countries of 95 per cent. Cu, 4 per cent. Sn, and 1 per cent. Zn.

Of alloys richer in tin, the only mixture of importance is *speculum metal*, which consists largely of the white, brittle δ-constituent, associated with the α-solution in small quantity, or, if containing more than 32 per cent. Sn, with the compound $Cu_{31}Sn_8$.

Phosphor-bronze.—Phosphorus is added to bronze as a deoxidizer, but small further additions are made for increase of strength, an alloy with 5 per cent. Sn and 0·3 per cent. P standing cold working well. This is an α-solid solution. When the phosphorus exceeds the limit of solid solubility, it forms a hard, white compound, Cu_3P, which appears as a characteristic eutectic. Bearing bronzes may have 10-12 per cent. of tin and 0·5-1·0 per cent. of phosphorus.

Copper-nickel.—Copper and nickel form a continuous series of solid solutions, having the face-centred cubic lattice throughout. They are therefore ductile, the hardness varying with the composition. Small additions of nickel, of the order of 2 per cent., are made to copper for use at high temperatures. The *cupro-nickels*, with 15-25 per cent. of nickel, are strong and capable of severe deformation and chemically resistant. Monel metal, an alloy with about 70 per cent. of nickel, is obtained directly by smelting the mixed copper-nickel ore of Sudbury, Ontario, and is used for its great strength and resistance to corrosion. The alloy with 40 per cent. of nickel has the lowest electrical conductivity and temperature coefficient, and is therefore drawn into wire and used for electrical resistances, under the name of *constantan*.

All copper-nickel alloys, and in fact most alloys which contain nickel, are cored when cast (Plate IIA), and undergo diffusion only slowly, so that prolonged annealing is necessary to obtain a homogeneous α-structure.

An alloy containing 82 per cent. of copper and 15 per cent. of manganese, the remainder being nickel and iron, has a low electrical conductivity and almost zero temperature-coefficient, and is hence used for electrical resistance coils under the name of *manganin*. All the components are in a state of solid solution.

Ternary alloys of copper, zinc, and nickel, forming a single α-solid solution, are much employed under the names of *Nickel silver* (formerly *German silver*) and various other trade designations. The most useful alloys of the series contain 50-60 per cent. Cu, 15-20 per cent. Ni, and 20-30 per cent. Zn, but variations even beyond these limits are found. *Platinoid*, an alloy used in the construction of electrical resistances, is a nickel brass containing small quantities of tungsten.

Copper alloys which are capable of age-hardening are also in use. These include alloys with nickel and silicon, from which a phase containing nickel and silicon in the ratio Ni_2Si, but which appears to contain copper as well, can separate on ageing.[1] Another series of this class consists of copper with nickel and aluminium.[2] High tensile strengths are obtained after suitable treatment.

The remarkable age-hardening properties of " beryllium bronze " have been described earlier (p. 334).

Nickel-chromium alloys.—Alloys consisting mainly of nickel and chromium (nichrome) are exceptionally resistant to oxidation at high temperatures, and are therefore used in the form of resistance wires for heating elements.[3] Ternary solid solution alloys containing iron are

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[1] M. G. Corson, *Trans. Amer. Inst. Min. Met. Eng.*, 1927, **78**, 435 ; D. G. Jones, L. B. Pfeil and W. T. Griffiths, *J. Inst. Metals*, 1931, **46**, 423 ; C. H. M. Jenkins and E. H. Bucknall, *ibid.*, 1935, **57**, 141.

[2] D. G. Jones, L. B. Pfeil and W. T. Griffiths, *ibid.*, 1933, **52**, 139 ; H. W. Brownsdon, M. Cook, and H. J. Miller, *ibid.*, 153.

[3] See, for instance, C. J. Smithells, S. V. Williams, and J. W. Avery, *ibid.*, 1928, **40**, 269.

also used, and the composition may then even approach that of the stainless steels, the boundary between ferrous and non-ferrous alloys thus becoming arbitrary. It is commonly drawn at 50 per cent. of iron. Alloys which have very high resistance to chemical attack have been made by adding copper and molybdenum to the nickel-chromium alloys.

Alloys of nickel with manganese, tungsten, and tantalum have also been described, being mostly designed for resistance to acids. Their constitution has been little investigated.

Alloys of cobalt.—Although the chemical relationship between cobalt and nickel is very close, the two metals may behave very differently in alloys, as is shown by the difference between cobalt and nickel steels. The most important technical alloy of cobalt is *stellite*, containing up to 75 per cent. of cobalt, the remainder being chromium with a smaller proportion of tungsten.[1] Stellite, being intensely hard, is used for high-speed cutting tools, since its structure is not affected by heating to a high temperature; as a hard edging to objects subjected to erosion, such as turbine blades and the wearing parts of machines; and also for its resistance to acids.

Aluminium alloys.—The needs of the aircraft industry have been mainly responsible for the very rapid development of the light alloys of aluminium, bringing them into the first place among non-ferrous metals for constructional purposes. Aluminium is a weak metal, but it may be greatly strengthened by alloying with elements which form solid solutions or hard compounds, and especially by age-hardening. The simple casting alloys contain zinc, copper, and sometimes nickel, in varying proportions. Alloys with 4, 8, or 12 per cent. of copper are used for castings, and one with 13·5 per cent. of zinc and 2·75 per cent. of copper is also popular. These alloys contain eutectics. They may be heat-treated in the same way as wrought alloys, but if so required they should be chill-cast to obtain a fine grain, as with coarse grains the time needed to dissolve the second phase becomes too long. The alloys of aluminium with 10-14 per cent. of silicon form a class by themselves. They have the advantage of giving very clean and sound castings, with small contraction on solidifying. They must be subjected to the process of "modification" before casting (p. 198).

Alloys to be used in the wrought state are essentially those which lend themselves to the process of age-hardening. Duralumin was the first of these, and is widely used. Ordinary duralumin contains about 4 per cent. of copper, 0·5 per cent. of magnesium, and 0·5 per cent. of manganese, but varieties are used with increased manganese or silicon. The process of ageing has been described (p. 332). For bringing the maximum amount of the second phase into solid solution, heat-treatment must be carried out at a temperature as near to the eutectic temperature as possible, great care being taken, however, not to exceed it, as the intercrystalline material would then

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[1] E. Haynes, *J. Ind. Eng. Chem.*, 1913, 5, 189.

melt, and the alloy would become quite brittle. Y-alloy, which contains 4 per cent. of copper, 2 per cent. of nickel, and 1·5 per cent. of magnesium, has a wide range of usefulness, retaining its strength up to high temperatures, so that it may be used for pistons in internal combustion engines.[1] It is used in either the cast or wrought state, and is brought into its best condition by ageing. For this purpose it is quenched from about 500° in boiling water, and either aged spontaneously or by heating to 100° for an hour. An important series of alloys which may be considered as derived from Y-alloy contains a smaller proportion of copper, with added iron and titanium. The iron increases the strength and prevents grain growth during the heat-treatment, whilst titanium has a remarkable effect in keeping the grain size small when casting.

Copper, zinc, magnesium, silicon, manganese, and silver are among the elements which are able to produce age-hardening in aluminium, whilst iron, nickel, and titanium have no such action. The presence of several of these elements in the same alloy leads to complicated effects, of which the inhibition of ageing by iron and its stimulation by magnesium have been mentioned.

All the light alloys of aluminium contain more than one micrographic constituent, and the identification of the phases present in a section is difficult, on account of the very slight differences in etching properties between them, and it is necessary to apply several reagents and to examine under different conditions to arrive at definite conclusions. It is not possible to study these alloys by micrographic methods alone, whilst the X-ray method often fails to give the required information, owing to the small amount of the phase in question. Electrical and hardness measurements must supplement the others in any study of constitution.

Alloys of magnesium.—Magnesium forms hexagonal crystals, but as the basis of alloys it is classed with aluminium rather than with zinc and cadmium, since the alloys are mainly used for constructional purposes in aircraft and other machines in which lightness is of importance. Magnesium has much less capacity for forming solid solutions than aluminium, but age-hardening is sometimes possible, aluminium, zinc, and manganese, for instance, having an appreciable solid solubility at high temperatures, falling practically to zero.[2] In spite of the inflammability of the metal, the alloys are cast without difficulty by using a flux and an atmosphere of sulphur dioxide. Aluminium, zinc, manganese, and cadmium have been mostly used as alloying elements, but calcium, cerium, silver, and cobalt have given promising results.[3]

Alloys of zinc.—Metallic zinc is used mainly in the rolled form,

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[1] W. Rosenhain, S. L. Archbutt, and D. Hanson, *Proc. Inst. Mech. Eng.*, 1921 (11th Report to Alloys Research Committee).

[2] Summarised by E. Schmid, *Z. Elektrochem.*, 1931, **37**, 447.

[3] See the monograph on Magnesium by J. L. Haughton and W. E. Prytherch (H.M. Stationery Office. 1937).

and only in a minor degree as castings. The principal alloys with zinc as a base are those with about 90 per cent. of zinc used for die-casting. As the solid solution range is usually very limited, the alloys of zinc have a duplex or more complicated structure. Copper is always one of the components of the die-casting alloys, together with either aluminium or tin.[1] The ease of casting makes these alloys popular, and the troubles once experienced in respect of instability have been overcome by attention to the purity of the zinc used.

Alloys of tin and lead.—Ordinary plumbers' solder consists of 67 per cent. of lead and 33 per cent. of tin; it is therefore composed of dendrites of lead, surrounded by a eutectic of the two metals. Fine tinman's solder contains 63 per cent. of tin and 37 per cent. of lead, so that it is an almost pure eutectic. *Pewter* is an alloy of very variable composition, tin being the chief constituent, and lead, up to 15 per cent., being a common addition. Copper and antimony were often added. Modern pewter, however, as used for artistic work, contains at least 95 per cent. of tin. Britannia metal is a variety of pewter, free from lead, and having copper and antimony as hardening metals.

Type metals and bearing metals may conveniently be considered together. The type metals are alloys of lead, tin, and antimony, the tin ranging from 2 to 10 per cent. and the antimony from 10 to 20 per cent. according to the requirements of the type-casting process. They contain a ternary eutectic, with embedded crystals of two different antimony-tin phases.[2] Like these alloys, the bearing or anti-friction metals consist of hard crystals embedded in a softer ground-mass. They fall into two main classes: those with a tin base, in which the ground-mass is tin with other elements in solid solution, and those with a lead base, the ground-mass of which is a eutectic. The hard crystals receive the load and resist abrasion, whilst the softer matrix provides the necessary plasticity. The pseudo-cubic crystals of the tin-antimony system (Plate VIA) provide the hard constituent. When the alloy contains much lead, the lightness of the crystals causes them to rise to the top of the melt, so that it is not easy to obtain a homogeneous casting. To check this tendency, small quantities of copper are added, and the ϵ-constituent of the copper-tin series, separating first as six-rayed stars of great hardness, forms a network which entangles the cuboids and prevents segregation.[3] Lead has also been hardened for the purpose of making bearing metals by the addition of sodium, the hard constituent then being the compound Na_2Pb_5, or by calcium or barium, which form similar compounds.[4]

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[1] T. F. Russell, W. E. Goodrich, and N. P. Allen, *J. Inst. Metals*, 1928, **40**, 239.

[2] F. D. Weaver, *ibid.*, 1935, **56**, 209.

[3] G. Charpy, "Étude des Alliages," Paris, 1901, p. 201.

[4] W. A. Cowan, L. D. Simpkins, and G. O. Hiers, *Chem. Met. Eng.*, 1921, **25**, 1181.

An entirely different class of bearing metals is represented by the "plastic bronzes," in which a spongy mass of copper, sometimes hardened by tin, antimony or nickel, has its pores filled with an alloy consisting mainly of lead. The hard and soft constituents in this case bear a different relation to one another. The means by which an even distribution of two phases, which when liquid form an emulsion, is secured has been discussed (p. 58). Microscopically, the spongy structure is clearly seen, the lead being enclosed in the form of globules.

Alloys of silver.—Silver, when employed for the purposes of coinage, or of the manufacture of silver articles, is always alloyed with a metal capable of entering into solid solution with it, in order to give increased hardness and resistance to wear. Sterling silver, used in the British coinage until 1920, and for ornamental and other work bearing the hall-mark, consists of 92·5 per cent. silver and 7·5 per cent. copper. The "fineness" of silver and gold being reckoned in thousandths instead of in percentages, sterling silver is said to be 925 fine. It is not a homogeneous solid solution, but consists of crystals of a solid solution rich in silver, separated by a eutectic (see Plate IIIA). This fact renders the alloys liable to segregate during solidification, so that different portions of the ingot contain different quantities of the eutectic, a fact of great importance to the assayer,[1] and the first observed example of inverse segregation (p. 147). Alloys containing only 90 per cent. Ag and even less, find application in jewellery. Cadmium is sometimes added in small quantities. The standards vary considerably in other countries.

The other alloys of silver are only of limited importance, the solid solutions with platinum and with paladium being the most interesting.

Alloys of gold.—Fine gold, being a very soft metal, is not in general use, and a hardening metal is almost invariably added. The added metal is either copper or silver, both of which form homogeneous solid solutions with gold. British standard gold contains 91·67 per cent. gold and 8·33 per cent. copper ("22 carat" = 22/24 = 91·67 per cent.), and this is the composition employed in coinage, whilst most of the alloys used for the manufacture of jewellery contain larger quantities of the hardening metal. Silver may take the place of copper, yielding alloys of paler colour. In both cases the structure is homogeneous. The old alloy *electrum* contains enough silver to be white.

Amalgams.—The alloys of mercury are known as amalgams. Few of them have much technical importance, the principal being the amalgams of tin and silver used as dental fillings. An alloy having a composition very close to the formula Ag_3Sn, but sometimes with copper replacing a part of the silver, is used in the form of annealed filings, and is mixed with mercury. A reaction occurs slowly,

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[1] W. C. Roberts (afterwards Roberts-Austen), *Proc. Roy. Soc.*, 1875, **23**, 481.

the compound being decomposed with the formation of new solid phases, thus bringing about the "setting" of the amalgam. The proportion of tin in the alloy must be kept within very narrow limits to avoid large changes of volume, an excess causing contraction and a deficiency expansion.[1]

Brittle alloys.—Many alloys are produced commercially for the purpose of adding small quantities of elements to molten metals. They are often made by reducing the mixed oxides by aluminium. Silicon and phosphorus as such are rarely added to metals, rich alloys with iron, copper, or tin being usually employed. These rich alloys, composed principally of intermetallic compounds, or of silicides, phosphides, etc., are commonly highly brittle, which is advantageous when definite small quantities have to be weighed. Their microscopical examination is, however, difficult. Grinding a flat section with emery leads to the breaking out of small particles, producing a rough, pitted surface, on which it is impossible to distinguish structure. Better results may often be obtained by using a smooth carborundum block in place of emery paper.

The technical phosphor-copper, containing 10 per cent. P, consists of crystals of the phosphide, Cu_3P, surrounded by eutectic, and yields good micro-sections (see Plate IVA). Another quality, however, contains practically 15 per cent. P, and consists only of the phosphide, with traces of a second compound richer in phosphorus; it is almost impossible to polish. So, only the lower cupro-silicons lend themselves to microscopical examination. Rich alloys known as "hardeners" are used in the same way. For instance, in the preparation of light aluminium alloys, it is convenient to make up an alloy containing equal weights of aluminium and copper, or one of 20 per cent. of copper, 12 per cent. of nickel and 68 per cent. of aluminium, and to add these to larger quantities of the principal metal. The metallography of these brittle alloys is not usually of great importance, but a micrographic examination will sometimes serve as a means of checking their composition without resort to chemical analysis.

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[1] M. L. V. Gayler, *Brit. Dental J.*, 1936, **60**, 605; *J. Inst. Metals*, 1937, **60**, 407.

APPENDIX.

PAGE 96.

The interpretation of inverse-rate curves is by no means simple, especially for alloys which undergo delayed transformations, such as alloy steels. After a peak has been reached, the curve often swings back beyond the line of simple cooling, as if there had been a thermal change in the opposite direction, whilst the apparent indications of the amount of thermal change may be misleading.[1] The relation between such curves and those showing the true specific heat (p. 95) needs to be further studied.

PAGE 107.

Grey cast iron presents difficulties in polishing, as the graphite flakes are easily torn out in the process, and are only represented in the final specimen by black cavities. With special precautions, using alternate polishing and etching, even the minute structure of the graphite may be preserved and further studied under polarized light.[2] The non-metallic inclusions are also preserved in this way.

A remarkable method of obtaining smooth surfaces without mechanical work, and therefore without producing a flowed Beilby layer, consists in dissolving the surface anodically, using a highly viscous electrolyte.[3] Thus for copper and stainless steel a syrupy solution of phosphoric acid is used, whilst for aluminium and for carbon steels a mixture of perchloric acid and acetic anhydride, made still more viscous by dissolving some aluminium, gives the best results. A very perfect polish is obtained, the surface being quite free from mechanical distortion, and the reflectivity is actually higher than that of a mechanically polished surface. The process should be called " electrolytic smoothing " rather than polishing.

Although an alcoholic solution of nitric acid is most generally used for the etching of steel, better detail is often obtained by using the 4 per cent. solution of picric acid, both for annealed steels and for tempered martensite.[4] For alloy steels a mixture of the two

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[1] See T. F. Russell, *J. Iron Steel Inst.*, 1939, i, 147, and discussion.

[2] H. Morrogh, *ibid.*, 1941, i, 195.

[3] P. Jacquet, *Nature*, 1935, **135**, 1076; *Compt. rend.*, 1936, **202**, 402; *Bull. Soc. chim.*, 1936, [v] **3**, 705; *Trans. Amer. Electrochem. Soc.*, 1936, **69**, 629; P. Jacquet and R. Rocquet, *Compt. rend.*, 1939, **208**, 1012. A tabular review of the procedure for different metals is given by G. E. Pellissier, H. Markus and R. F. Mehl, *Metal Progress*, 1940, 55.

[4] J. R. Vilella, " Metallographic Technique for Steel " (Cleveland, Ohio, 1938).

reagents is often effective. The names "nital" and "picral" are commonly used by American writers.

PAGE 112.

An effective method of revealing the macro-structure of many metals consists in machining a surface with a fine-pointed tool, using a very light cut.[1] The varying hardness of grains along different crystallographic directions leads to differences of level which reproduce the macro-structure with great distinctness. The method was chiefly applied to tin bronzes, but was also successful with other alloys. By using a sharp knife at a suitably controlled angle, the macro-structure of such a soft metal as lead could be brought out clearly.[2]

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The hot oxidation of iron and its alloys leads to the formation of a scale made up of distinct layers, the outermost of which is ferric oxide. A thicker layer of magnetic oxide follows, and the innermost layer is one formed by the decomposition of the ferrous oxide phase stable at high temperatures.[3] An alloying metal, such as nickel, is concentrated at the interface between the scale and the unchanged metal. It is now considered that the growth of scale takes place rather by migration of metallic ions outwards than of oxygen inwards.[4]

PAGES 265-298 (CHAPTERS XVI AND XVII).

The recent literature on the deformation of metals, both as single crystals and as aggregates, is too extensive to be summarized here. Reference may be made to a discussion on internal strains in solids,[5] which includes new experimental work and also a number of theoretical studies which take into account the time factor in the propagation of slip.

PAGE 277.

Direct evidence of the melting of the surface of a metal during abrasion has been obtained by measuring the thermo-electric effect between two rubbing surfaces.[6] The surface in actual contact is small in comparison with the whole, so that high local pressures

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[1] (Sir) J. Dewrance, *J. Inst. Metals*, 1927, **37**, 21. Figs. 3, 6, 12, 13 and 19 of the paper were produced in this way, but the method was not published at the time. See C. H. Desch, *ibid.*, 1940, **66**, 401.

[2] B. O. W. L. Ljunggren, *J. Iron Steel Inst.*, 1940, i, 341.

[3] L. B. Pfeil, *ibid.*, 1929, i, 501; 1931, i, 237. See "Review of Oxidation and Scaling of Heated Solid Metals" (H.M. Stationery Office, 1935).

[4] C. Wagner, *Zeitsch. physikal. Chem.*, 1933, **21**, B, 25; 1936, **32**, B, 447, and later papers; T. P. Hoar and L. E. Price, *Trans. Faraday Soc.*, 1938, **34**, 867.

[5] *Proc. Phys. Soc.*, 1940, **52**, special part.

[6] F. P. Bowden and K. E. W. Ridler, *Proc. Roy. Soc.*, 1936, **154**, A, 640; F. P. Bowden and T. P. Hughes, *ibid.*, 1937, **160**, A, 575.

occur, and the frictional heat increases until the melting-point of the more fusible of the two metals is reached.

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Considerable sensitiveness has been claimed for a mechanical method of determining the solidus temperature for such alloys as can be drawn into wire.[1] This consists in applying stress, preferably in torsion, to a vertically suspended wire which is being heated. An abrupt fall in the resistance to stress occurs at the solidus temperature, even when the quantity of eutectic, for instance, is very small.

The effect of imperfect diffusion in the solid phase during the solidification of an alloy is to widen the interval between the liquidus and the apparent solidus, and to cause eutectic to be present in alloys which if in equilibrium would consist of a single phase. The quantitative relations have been studied.[2]

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Most X-ray workers make use of filings for the determination of phase boundaries. The alloy must be made as homogeneous as possible by annealing before filing, and precautions must be taken to avoid contamination by dust and by particles of steel. This is particularly important for alloys of reactive metals, and special apparatus has been devised for the preparation of filings out of contact with air.[3] Equilibrium in subsequent transformations is more easily reached in filings than in massive specimens, but loss of volatile components from the surface by volatilization is a common source of error.

Whilst the X-ray method is admirable for the mapping of the phase fields at atmospheric temperatures its use for the determination of boundaries at higher temperatures demands caution. In most work of the kind quenched specimens are used, but it is unsafe to conclude that these represent the equilibrium at the temperature of quenching, as transformations often take place very rapidly, especially in filings. The most satisfactory plan is that of using a high temperature X-ray camera, demanding special technique.[4] The filings may be enclosed in a very thin capillary of vitreous silica, the absorptive power of which for X-rays is small. The most difficult part of the operation is usually the determination of the temperature of the very small object under examination.

The advantages of X-ray powder photographs as a method of studying equilibrium diagrams have been shortly summarized.[5] Such

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[1] H. Nipper and E. Lips, *Zeitsch. Metallk.*, 1935, **27**, 242.

[2] G. H. Gulliver, *J. Inst. Metals*, 1913, **9**, 120.

[3] G. V. Raynor and W. Hume-Rothery, *J. Inst. Metals*, 1939, **65**, 379.

[4] Such high temperature cameras have been described by A. H. Jay, *Zeitsch. Krist.*, 1933, **86**, A, 106; W. Schmidt, *Ergebnisse tech. Röntgenkunde*, 1933, **3**, 194; and W. Hume-Rothery and P. W. Reynolds, *Proc. Roy. Soc.*, 1938, **167**, A, 25.

[5] A. J. Bradley, H. J. Goldschmidt, H. Lipson and A. Taylor, *Nature*, 1937, **140**, 543.

a photograph gives (*a*) the number of phases present; (*b*) the crystal type of each phase; (*c*) the lattice spacing of each phase, from which the compositions of the phases can usually be derived; and (*d*) the relative amounts of the several phases derived from the intensities of the lines. In a ternary diagram, an alloy represented by a point in a two-phase area in an isothermal triangle breaks up into two phases of compositions represented by the ends of the tie-line running through that point from one single-phase area to another. Three-phase areas are triangles, the vertices of which are cusps on single-phase areas, and any alloy within them breaks up into three phases of compositions represented by the vertices. Bearing these rules in mind, the investigation of ternary systems is greatly simplified.

Physicists, from Roozeboom onwards, have made much use of the principle of lowest free energy in dealing with equilibrium diagrams. Although it is not possible to measure the free energy directly, the concept has much value in deciding between alternative interpretations of experimental results.[1] It can be shown, for instance, that certain published diagrams are theoretically impossible, and that the boundaries must be differently drawn. The lines bounding any single-phase area, if produced, must lie within two-phase regions, and not in the single-phase field itself. The position of a maximum on the liquidus does not necessarily give the composition of an intermetallic compound if that compound has a range of homogeneity.

PAGE 336.

The view here expressed as to the form of the precipitate which produces hardening is supported by X-ray studies of the initial stages of ageing in alloys of copper containing 4 to 5 per cent. of aluminium. Preston[2] and Guinier[3] independently observed that in the course of ageing in alloys of aluminium containing 4 to 5 per cent. of copper. diagrams, which were interpreted as indicating groups of copper atoms, parallel with the 100 planes of the original lattice, and only a few atoms thick. They are at first of small area, increasing to a radius of perhaps 80 or 100 atomic distances. On heating to 200° they disappear rapidly, the hardness at the same time falling to that of the original quenched alloy, but on continued heating the hardness again increases, and plates are re-formed which are still thin but of larger area. After the maximum hardness has been passed the plates increase in thickness and finally constitute particles of a new phase, which has been identified as an unstable form of $CuAl_2$. There can be little doubt that this represents a very general series of changes in age-hardening systems.

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[1] H. Lipson and A. J. C. Wilson, *J. Iron Steel Inst.*, 1940, ii, 107.

[2] G. D. Preston, *Proc. Roy. Soc.*, 1938, **167**, A, 526; *Phil. Mag.*, 1938 [vii], **26**, 855.

[3] J. Calvet, P. Jacquet and A. Guinier, *Compt. rend.*, 1938, **206**, 1972; *J Inst. Metals*, 1939, **65**, 121; A. Guinier, *Thèse pour le doctorat* (Paris, 1939).

PAGE 352.

The structure of cementite has been determined by X-rays.[1] The iron atoms are nearly closely packed, the carbon atoms being interstitial. The structure is nearer to that of γ-iron than to that of α-iron.

PAGE 357.

The carbon atoms in austenite lie at the centres of unit cells and at the mid-points of the edges, these positions being the centres of the largest spaces between the iron atoms. Even when saturated with carbon, only one possible position in twelve is occupied.[2]

PAGE 359.

Recent X-ray evidence[3] points to the carbon atoms in martensite being interstitial, without their positions indicating any special relation to the cementite molecule. The present X-ray technique, however, does not allow of the direct determination of the positions of the carbon atoms, which are inferred from the displacements of the iron atoms, and the possibility of the arrangement suggested in the text is not entirely ruled out.

The method of transformation at constant temperature has proved to have special value in the investigation of the process of hardening. A steel is brought to such a temperature that it is entirely in the form of homogeneous austenite, cooled rapidly to a pre-determined temperature, allowed to transform isothermally, and then quenched rapidly. Any austenite which was not transformed at the temperature of quenching then becomes martensite, and may be identified microscopically. Taking as an example a carbon steel of eutectoid composition, transformation to pearlite immediately below the equilibrium eutectoid temperature is very slow, but becomes much quicker as the temperature is lowered. A maximum rate is reached at 550-600°, and on lowering the temperature still further the transformation becomes much slower. The product still consists of ferrite and cementite, but the structure becomes finer and finer with falling temperature, being described as sorbite or troostite instead of pearlite. At temperatures below 200° the transformation again becomes very rapid, but the product is now not a form of pearlite but martensite. These observations are summed up graphically in what is now generally known as the S-curve.[4] As the times

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[1] H. Lipson and N. J. Petch, *J. Iron Steel Inst.*, 1940, ii, 95; W. Hume-Rothery, G. V. Raynor and A. T. Little, *ibid.*, 1942, i, 143.

[2] N. J. Petch, *J. Iron Steel Inst.*, 1942, i, 111.

[3] H. Lipson and A. M. P. Parker, *Iron and Steel Inst.*, 1943 (Advance copy).

[4] The literature of this subject is extensive. See, for a general account, E. S. Davenport, *Trans. Amer. Soc. Metals*, 1939, **27**, 837.

of transformation in different parts of the diagram may range from seconds to weeks, it is necessary to plot the logarithm of the time (Fig. 148). The actual position of the curve depends not only on composition but also on grain size, an increase in the size of the grains shifting it somewhat to the right.

As an alternative to quenching and microscopical examination, a continuous record of the magnetic properties of the steel may be made, the appearance of α-iron being clearly indicated.

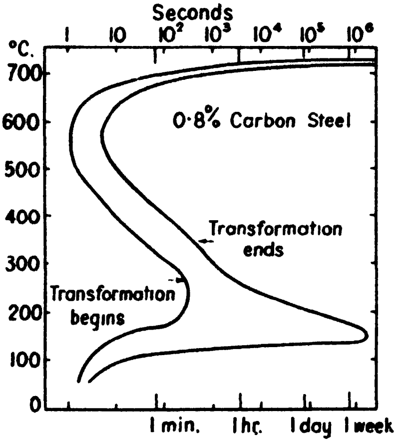

Fig. 148.

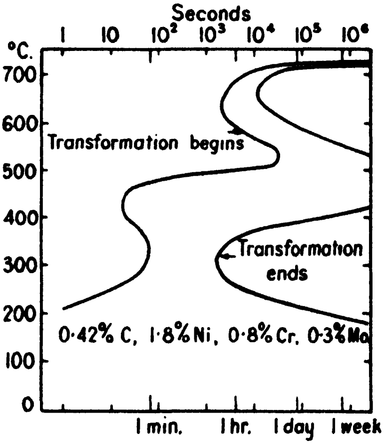

Fig. 149.

The construction of such curves is of particular value in dealing with alloy steels. With many of these, however, the curve takes a more complex form. Fig. 149 shows such a curve for an alloy steel with 0·42 C, 1·8 Ni, 0·8 Cr, and 0·3 Mo. There is an intermediate region of slow transformation between the upper and lower ranges of the carbon steel curve. This breaks up the diagram, and the transformation in the intermediate range assumes greater importance.[1] Although ferrite and carbide separate in this range, the structures produced are quite unlike the normal pearlite or even troostite. The ferrite takes an acicular form, and the term "bainite" has been applied to the structure, which has distinct mechanical properties.

Transformation at constant temperature by quenching from the hardening temperature in a bath of molten metal or salt has found industrial application in the treatment of steel articles of thin section under the name of "austempering," the structures obtained being mostly of the intermediate type.

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[1] See especially W. T. Griffiths, L. B. Pfeil and N. P. Allen, *2nd Report Alloy Steels Com., Iron Steel Inst.*, 1939, 343; N. P. Allen, L. B. Pfeil and W. T. Griffiths, *ibid.*, 369.

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