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CALCIUM METALLURGY AND TECHNOLOGY

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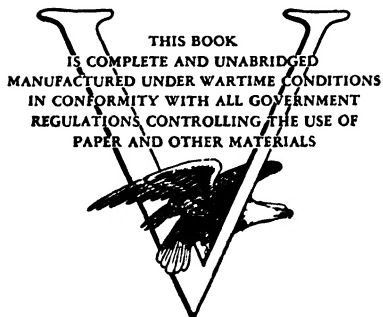


American Chemical Society
Monograph Series

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GENERAL INTRODUCTION

American Chemical Society Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this introduction) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first monograph of the series appeared in 1921. After twenty-three years of experience certain modifications of general policy are indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. This differentiation is fast becoming nebulous. Research in private enterprise has grown apace and not a little of it is pursued on the frontiers of knowledge. Furthermore, most workers in the sciences are coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and now frankly recognize that

their objectives are common, namely the search for new knowledge for the service of man. The officers of the Society therefore have combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the series, it seemed expedient to construe rather broadly the definition of a monograph. Needs of workers had to be recognized. Consequently among the first one hundred monographs appeared works of the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the monograph character, which means more complete and critical treatment of relatively restricted areas, and where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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Preface

Calcium metal has earned a place for itself in the metallurgical world. Although the entire production of calcium is only a fraction of the tonnage of metals like sodium, aluminum, and magnesium, it is still far greater than that of lithium, barium, cesium, and potassium. Extremely small amounts, almost of the order of traces of calcium, exert tremendous influence on the properties of alloys. As an example, 0.03 per cent calcium in alloys of the 80 nickel-20 chromium type employed for high-temperature electrical resistance applications increases the service life many times; but amounts of the order of 0.06 per cent, in contrast to those alloys containing the lower percentage which can readily be hot-rolled, cause difficulties in hot fabrication.

It has been the authors' good fortune to have been associated with the metallurgical development of calcium production, technology, metallurgical use, development of applications, and commercial distribution over the past two decades. During this period there has been a gratifying increase in production and consumption. It is unfortunate perhaps, but certainly to be expected, that many applications of calcium metal are of the secret art or unpublished process variety. They are, therefore, not to be found in this volume.

The authors are indebted to Messrs. J. H. Critchett, G. K. Herzog and A. B. Kinzel of the Electro Metallurgical Co., a unit of Union Carbide and Carbon Corporation, Frederic W. Willard, president of Nassau Smelting & Refining Co., Inc., Dr. E. E. Schumacher, research metallurgist of Bell Telephone Laboratories, Inc., Dr. W. J. Kroll, consulting metallurgist, and Professor C. H. Mathewson, for their helpful criticism of the volume in manuscript form.

An attempt has been made to correlate as much of the

available information, including the alloy systems, as is possible, with the inclusion of as much of the authors' experimental work both in the laboratory and in the field for which release could be obtained. It is hoped that the volume will serve as a collection of information on the properties of this interesting alkaline-earth metal, and that it will suggest many new applications of value in the metallurgical and chemical fields.

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Contents

	Page
GENERAL INTRODUCTION	3
PREFACE	5
Chapter	
I. THE PROPERTIES OF CALCIUM	9
II. THE PRODUCTION OF CALCIUM	21
III. ALUMINUM-CALCIUM ALLOYS	35
IV. COPPER-CALCIUM ALLOYS	47
V. CALCIUM IN FERROUS METALLURGY	54
VI. CALCIUM HYDRIDE	57
VII. GOLD-CALCIUM ALLOYS	64
VIII. LEAD-CALCIUM ALLOYS	66
IX. MAGNESIUM-CALCIUM ALLOYS	95
X. NICKEL-CALCIUM ALLOYS	106
XI. SILICON-CALCIUM ALLOYS	110
XII. SILVER-CALCIUM ALLOYS	117
XIII. TIN-CALCIUM ALLOYS	120
XIV. ZINC-CALCIUM ALLOYS	124
XV. OTHER CALCIUM ALLOYS	126
XVI. PREPARATION OF CHROMIUM, THORIUM, URANIUM AND ZIRCONIUM METAL POWDERS BY THE USE OF CAL- CIUM	137
XVII. CALCIUM IN THE PETROLEUM INDUSTRY	139
AUTHOR INDEX	141
SUBJECT INDEX	144

Chapter I

The Properties of Calcium

Industrial Application

Over a twenty-year period, calcium has shown a consistent growth in usage and has become an important metallurgical raw material. It is not a tonnage product in itself, but relatively small amounts have a great effect on the properties of materials to which it is added. Its physical, chemical, and metallurgical properties have been insufficiently appreciated. Its ramified uses in industry have largely gone unnoticed.

Industrial applications of calcium metal are listed below. These, along with the alloy systems of calcium with other metals, will be separately discussed and constitute the burden of this volume. Calcium is used, for example, as:

An alloy agent for:

Aluminum, bearing metals, beryllium, copper, lead, and magnesium.

A controller for graphitic carbon in cast iron.

A debismuthizer for lead.

A decarburizer and desulfurizer for ferrous metals and alloys.

A dehydrating agent for:

Alcohol, solvents, and organic liquids.

A deoxidizer for:

Chromium-nickel, copper, iron, iron-nickel, nickel, nickel-chromium-iron alloys and steels, nickel-bronzes, steel, tin-bronzes.

A desulfurizer for petroleum fractions.

An evacuating agent for high vacua.

Getter alloys in radio tubes.

A modifying agent for aluminum, beryllium and magnesium alloys.

A reagent in preparation of:

Bearing bronzes of high lead type chromium-nickel to prevent formation of chromium carbide, chromium-nickel steels, copper-calcium alloys, lead alloys, pure nickel castings to reduce defects, 50 nickel-50 iron and other alloys to eliminate cracking during hot working.

A reducing agent in preparation of:

Chromium metal powder, thorium, uranium, and zirconium.

A separator for argon from nitrogen.

Uses of calcium-iron:

Deoxidizer for iron castings in green sand molds.

Uses of calcium-lead:

Battery grids and plates; bearings; debismuthizer for lead; sheathing for telephone, cable and electric lines.

Physical and Chemical Properties of Calcium

In its commercial form, freshly cut calcium is silvery white; fractured surfaces are more brilliant than steel. Such surfaces when exposed to moisture-bearing atmospheres develop thin films of bluish-gray oxide, which protect the metal against further attack. When freshly cut calcium is exposed to moist air, there does not appear to be sufficient heating tendency to create a fire hazard. Unlike sodium or the other alkali metals, calcium may be allowed to come in contact with the skin without danger; it may, in general, be handled like magnesium and aluminum. Calcium is heavier than sodium and the alkali metals, but lighter than beryllium, magnesium, and aluminum. For equal cross-sectional area, its electrical conductivity is exceeded only by that of silver, copper, gold, and aluminum. Thus, for equal weight and length, calcium is among the best available conductors.

Calcium is ductile and malleable. It can be machined in a lathe, turned into shapes, drilled, threaded, sawed, extruded,

pressed, hammered into plates, and drawn into wire. Its commercial forms include chunks, bars, shavings, rods and, very recently, powders.

Calcium is found in the even series of group II of the Periodic Table of the chemical elements, associated with beryllium, magnesium, strontium, barium, and radium. Calcium is often referred to as an alkaline-earth metal. In earlier chemistries all non-metallic substances which were insoluble in water and unchanged by fire were called "earths." Lime (the oxide of calcium) and magnesia (the oxide of magnesium) were found to have an alkaline reaction and were called alkaline earths.

Davy isolated calcium in 1808 by electrolysis. He followed the suggestion of Lavoisier that the earths were like other "bases" and were oxides.

The metals of the alkaline-earth group are all silver white, although whiter than silver, which has a yellow cast, and than tin, which has a bluish tinge. The metals as a group are much less reactive than the alkali metals, such as sodium and potassium, but they do oxidize in air and do decompose water, liberating hydrogen and forming hydroxides. They form basic oxides as CaO , and peroxides without a change of valence

of the metal, as CaO_2 or $\text{Ca} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$. Partington¹ states that

"Calcium peroxide is formed as a hydrate, $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$, by precipitating lime water with hydrogen peroxide (H_2O_2). Calcium peroxide is manufactured for use as an antiseptic by compressing slaked lime and sodium peroxide and washing with ice water." It is not formed directly from lime and oxygen, whereby it differs from the analogous barium peroxide. Calcium forms hydrides as CaH_2 and nitrides as Ca_3N_2 . In volatilizable form, as the chlorides for example, or when a compound is moistened with hydrochloric acid and inserted in a Bunsen burner flame on a platinum support, the alkaline-earth metals color the flame. Calcium gives an orange red color which is distinctive and characteristic of its most prom-

inent spectrum line; strontium a crimson shade; barium apple green; and radium carmine red.

Atomic Weight. The atomic weight of calcium is 40.08 and its atomic number is 20. Its minimum number of isotopes is two; their mass numbers in order of intensities of the mass spectrum lines show values of 40 and 44.²

The electron configuration of the calcium atom is 2—8—8—2, the figures representing the numbers of electrons in the K, L, M, and N shells, respectively. The atomic volume is 25.9.

Crystal Form. From x-ray studies of calcium, Hull,³ found that the crystals are in the cubic system with a face-centered cube lattice, with four atoms per elementary cube, a side of which is 5.56 Å and the smallest interatomic distance 3.93 Å.

Boiling Point. The boiling point⁴ of calcium is 1170°. Pilling⁵ gives the following vapor pressures in millimeters of mercury, calculated from the rate of evaporation in a vacuum:

At 300°	9.6 × 10 ⁻⁸
At 400°	4.2 × 10 ⁻⁶
At 500°	3.7 × 10 ⁻⁴
At 600°	1.2 × 10 ⁻²
At 700°	0.19
At 800°	1.8
At 900°	10.6
At 1000°	47.2

Freezing Point. The freezing point of pure calcium is given in terms of a melting point at 810°. Guertler and Pirani⁶ give a value of 809°. Kroll⁷ states: "The melting point of calcium is considerably influenced by the presence of impurities, especially nitrogen. Antropoff and Falk⁸ found the true melting point of sublimed calcium, free of nitride, at a temperature of 851° ± 1°. A eutectic formed between the metal and the nitride melts at 780°, so that small amounts of nitrogen may reduce the melting point as much as 70°. The boiling point of calcium is given by Hartmann and Schneider⁹ as 1,439°.

Curiously enough, pure calcium can exist in three allotropic modifications.^{10,11} At room temperature the structure of the

alpha calcium is face-centered cube. The heat of formation of the oxide given by Landolt-Börnstein and by the "International Critical Tables" is 151.9 and 151.5 cal. respectively; that of the chloride 190.6 cal. (Landolt-Börnstein), whereas for 2NaCl they give the value of 197.0. Kroll found the Brinell hardness value to be 16.1 (1,000 kg/10-mm ball/1 min), using five times distilled calcium (99.95 per cent pure). Bastien¹¹ gives the following mechanical properties of sublimed calcium: hardness, 13 Brinell (2-mm ball/10-kg load); tensile strength 4.4 kg/mm²; elongation 53 per cent; reduction in area 62 per cent. Barium metal, twice distilled, gives a hardness of 9.9 Brinell (500 kg/10-mm ball/1 min). Calcium can easily be purified by distillation or sublimation.¹² Ca₃N₂ together with silicon, iron, aluminum, and carbon remains in the residue, while H₂Ca is partly decomposed and can be eliminated completely only by repeated treatment. Magnesium and the alkaline metals can be separated by fractionating.

Compressibility. The compressibility or percentage change in volume with unit change in pressure of 1 megabar (0.987 atmosphere; 14.504 psi) of calcium is given as¹³

$$\begin{aligned} \text{Cubical, at } 30^\circ, 0 \text{ atm.} \quad \beta &= 5.885 \times 10^{-6} \\ \text{Cubical, at } 30^\circ, 11,600 \text{ atm.} \quad \beta &= 5.300 \times 10^{-6} \\ \text{Cubical, at } 20^\circ, 99\text{--}493 \text{ atm.} \quad \beta &= 5.8 \times 10^{-6} \end{aligned}$$

$$\text{where } \beta = -\frac{1}{\text{vol cm}} \times \frac{dV_{cc}}{dP_{\text{atm}}}$$

Richards¹⁴ gives the average compressibility of calcium at 20° as 5.7×10^{-6} between 100 and 500 megabars per sq cm. Small amounts of carbides, chlorides, iron, and related substances increase the hardness of commercial calcium.

Density. The specific gravity of calcium is 1.55. Impure material is slightly higher. According to Graf¹⁵ the alpha phase in extruded calcium wire at 450° gives a specific gravity value of 1.48, while the beta phase at 480° gives a value of 1.52.

Thermal Expansivity. The thermal expansion of calcium is given¹⁶ as 0.000025 cm/cm/°C; Bridgman¹⁷ found the coeffi-

cient of cubical expansion from 0 to 21° to be 0.000717. The linear coefficient of expansion of solid calcium between 0 and 300° is given as 220×10^{-7} (Cath and von Steenis³³).

Specific Heat. The specific heat of calcium is 0.157 for the range from -185° to 20°, and 0.149 from 0° to 100°.

The heat of evaporation is given as 4.53×10^4 calories per mole.¹⁸

Entropy. The entropy of calcium is given by Kelley¹⁹ as 9.95 ± 0.1 for the solid and 37.00 ± 0.01 for the vapor at 25° and one atmosphere.

Thermal Conductivity. The thermal conductivity of calcium is low as compared to silver or copper, being of the same order as sodium and the alkali metals.

Electrical Resistance. In comparison with silver and copper, calcium is a poor conductor of electricity. It has an electrical resistance at 0° of 3.43 micro-ohms/cm³, according to Goodwin.²⁰ Its temperature coefficient of electrical resistance is 0.00457. In the case of metal containing 1.08 per cent chlorine, Brace²¹ found an electrical resistance of 6.77 micro-ohms/cm³ at 22°. The pressure coefficient of resistance of calcium increases with rising temperature, while the electrical resistance does likewise. The electrical conductivity of calcium at 20° is 45.1, silver of the same area and length being taken as 100. The conductivity is exceeded only by that of silver, copper, gold, and aluminum. For the same length and weight of metal with calcium taken as 100, silver is 32.5.

Electrochemical Equivalent. Calcium occurs as a bivalent ion in all its compounds. The values in various units for the electrochemical equivalent (defined as the number of grams deposited per second by a current of one ampere) are given below.²²

Mg per coulomb	0.20762
Coulomb per mg	4.81640
Gram per ampere-hr	0.74745
Ampere-hr per g	1.33789
Lb per 1000 ampere-hr	1.64784
Ampere-hr per lb	606.86

Electrolytic Properties. According to the usual terminology, calcium is electronegative to elements it displaces in solution, and electropositive to those which displace it from solution. In simple solutions, calcium is electronegative to all the base metals and the precious metals, and electropositive to the alkali metals. It shows an electrode potential of -2.76 volts.²³

Mechanical Properties. Calcium shows a tensile strength of 8700 psi. Calcium metal is much harder than sodium, but softer than aluminum and magnesium. Its hardness characteristics are much closer to aluminum and magnesium than they are to sodium. Under 500-kg load, sections machined out of the calcium carrot as obtained from the furnace show a Brinell hardness of 17. Under the same conditions, sodium is so soft that measurement cannot be made, the hardness being under 1 on the Brinell scale. Pure aluminum, according to Edwards, Frary, and Jeffries,²⁴ has a Brinell hardness of 25; while magnesium, according to the volume on magnesium published in 1923 by the American Magnesium Corporation, shows a Brinell hardness of 30, and measurements by the Dow Company on Dow magnesium show 32. On the Rockwell B scale, calcium in machined sections shows hardnesses from 36–40. On the Shore scleroscope, calcium shows hardnesses from 7–9 when the normal hammer is used, and 11–12 when the magnifying hammer is employed, as compared to values of 20–23 for magnesium.

Distilled calcium has an elongation of 53 per cent, while extruded wire gives 61 per cent, 98.5 per cent calcium 30.5 per cent, and impure materials (94–96 per cent) show no elongation.²⁵ The tensile strength of distilled calcium is 6,050 psi, its elastic limit 1,465 psi. With the loading speed of 4 mm per minute, distilled calcium is more ductile than aluminum of 99.6 per cent purity and less ductile than lead, but it has a greater elongation than both. The modulus of elasticity of distilled calcium varies between 32×10^5 and 38×10^5 psi. No creep was observed on loading calcium at room temperature with less than 570 psi. Crushing tests showed complete re-

crystallization of calcium at 300° and above during deformation. The pressure required for deformation decreases with the temperature and has a sharp break at 440°, which corresponds to beta-gamma transformation temperature. Gamma calcium deforms plastically under very small loads. Calcium wire could be easily extruded between 420 and 460°. It had an elastic limit of 5,500 psi and a tensile strength of 8,000 psi.

The heat of vaporization of calcium is given as 399 kilojoules per gram atom according to the "International Critical Tables." The same source gives the magnetic susceptibility as 1.10×10^{-6} cgsu at -170° to 18°.

Impure calcium containing 86.7 per cent calcium, 9.1 calcium oxide, 2.7 calcium chloride, 0.35 silicon, 0.88 iron, and 0.2 aluminum, distilled in vacuum and remelted under argon, produced sound metal containing 99.3 per cent calcium, 0.02 iron, 0.14 silicon and traces of chlorine.²⁶ This material showed two transformation points, one at 430° and another at 240°. Graf²⁷, using calcium of 95.4 per cent purity, observed an allotropic transformation at 450°, with a change from face-centered cubic to body-centered cubic lattice; Schulze and Overberg²⁸ also observed a polymorphic transformation between 430 and 450°. The existence of the body-centered lattice seems to depend on impurities, and it is believed that above 450° the lattice of pure calcium is hexagonal close-packed. Despite the evidence of a transformation somewhere between 240 and 300°, the lattice type between 300 and 450° has never been definitely determined. The ductility of calcium is greatly affected by impurities.

The vapor pressure of solid calcium between 500 and 625° was measured by the method of molecular diffusion.²⁹ Microtitration methods were used to determine the amount evaporated, which could be determined within 10^{-6} gram. The results are represented by the empirical equation $\log p$ (in mm) = $8.15 - 9670/T$. The present values for the pressure are about 1/10 of those previously reported by Pilling³⁰ for the same temperature. Because the specific heat of solid calcium is known as a function of T , the "chemical constant" can be

calculated. The new pressure data lead to the correct value for this constant, but the old do not.

Chemical Properties

When heated together calcium and carbon react exothermically to form calcium carbide, CaC_2 , or more truly the acetylide. (The scientifically correct carbide would be the salt of hydrocarbonic acid, H_4C , and would have a theoretical formula of Ca_2C if it existed.) Pure calcium carbide, CaC_2 , is a white solid.

Calcium metal does not react with dry oxygen at room temperatures but does so rapidly at 300° or above. A similar situation exists with nitrogen at ordinary temperatures with slow reaction above 300° and rapid formation of the nitride, Ca_3N_2 , at 900° .

Calcium is not attacked at room temperature by the halogens, chlorine and bromine, if they are dry; attack is marked in the presence of moisture. Violent combination takes place at 400° or above, with the formation of halides. With fluorine, combination takes place readily at room temperature.

The hydride, CaH_2 , is formed with hydrogen at elevated temperatures. This is discussed in a separate chapter.

Calcium reacts slowly with water in comparison to sodium, but impurities and soluble salts markedly accelerate the process.

Calcium cannot be cast by ordinary foundry methods, as it oxidizes readily at elevated temperatures. Oxidation is exceedingly rapid at its melting point, 810° . Melting and casting procedures employing protective fluxes or operations conducted in the presence of non-oxidizing and non-reacting gases allow the production of sound cast forms of the metal. Calcium is heavier than sodium and the alkali metals but lighter than beryllium, magnesium, and aluminum.

Calcium is more active chemically than barium or strontium. On a price basis, it is by far the cheapest of the alkaline-earth metals, but is more expensive than sodium, which is lower in atomic weight and cheaper in cents per pound. In organic syntheses, sodium is in a better competitive position.

However, in metallurgical work, as a deoxidizing agent, reducing agent, degasifier, and alloying metal, the low melting point and high vapor pressure of sodium are disadvantages which cause the more refractory and less volatile calcium to be preferred.

Laboratory applications of calcium metal are well known. It burns brightly in oxygen, combines with sulfur, chlorine, nitrogen, and other elements, and reduces nearly all metallic oxides on heating. Calcium is used in freeing absolute alcohol from the last traces of water. The liquid is digested with calcium turnings, after which the alcohol is distilled. The application of calcium in producing high vacua is common knowledge. If the metal is heated in a tube connected with a vessel at low pressure, it takes up the last traces of air, forming oxides and nitrides, thereby reducing the pressure in the system to very low values.

Calcium does not react with or take up argon. It is therefore employed for the separation of argon from nitrogen. When rapidly heated in CO_2 , the metal is converted to lime and calcium carbide (CaC_2). The hydride, CaH_2 , is formed by passing hydrogen over heated calcium, and in a similar way the nitride, Ca_3N_2 , is produced by passing nitrogen over the metal. When heated in ammonia, calcium forms the hydride and nitrogen; when reacted with steam, the nitride gives off ammonia. Ammonia is absorbed by calcium in the cold with the formation of a compound, $\text{Ca}(\text{NH}_3)_6$ —an exothermic reaction. In the absence of air, this substance is converted to $\text{Ca}(\text{NH}_2)_2$. Laboratory applications in which calcium is employed as an agent for removing small amounts of oxygen, moisture, and other substances with which it reacts readily, the calcium metal meanwhile being in a solid form, are well known.

Calcium alloys with barium, aluminum, and magnesium find application in "getters" in radio and vacuum manufacture, for removing the last traces of objectionable gas from the "vacuum." The metal may also be used by itself for the same application in the form of pellets or as wire, or as wire coated

with magnesium, or in other shapes. A considerable number of these applications of the "secret process" type exist.

Many uses of calcium in conjunction with lithium, lithium and silicon, or other alkali or alkaline-earth metals have been suggested.³¹ For special purposes furnace-quality calcium metal can be distilled and very pure products obtained, or it may be subjected to sublimation without fusion.³²

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³³ Cath, P. G., and von Steenis, O. L., *Z. tech. Physik*, **17**, 239 (1936).

Chapter II

The Production of Calcium

Although many electrothermal compounds of calcium are well known, the properties of the metal itself are not widely appreciated and the metallic form of the element is generally considered a rarity. Calcium carbide, cyanamide, and related products are commonplace materials to many.

Commercial production of calcium metal has been in operation for several decades, but as a result of low labor cost in Continental Europe it was confined to France and Germany. The United States' supply was imported in quantities ranging from ten to twenty-five tons annually from 1920 to 1940. In the summer of 1939, it was realized that calcium metal was essential to American industry and that its use and applications were growing. The United States was completely dependent upon France for its supply, which source might be cut off, or seriously endangered. The Electro Metallurgical Company, a unit of the Union Carbide and Carbon Corp., drew up plans for the production of calcium with a minimum of delay. The plant was built at Sault Ste. Marie, Michigan, and by the winter of 1939 was in regular production.

Many methods have been proposed for the production of calcium and its alloys. Caron¹ used sodium metal which he alloyed with lead and then reacted with molten calcium chloride. Calcium displaces the sodium, and sodium chloride and a calcium lead alloy are formed. It is stated that this procedure was employed by the Metallgesellschaft at Frankfort, Germany. The efficiency of utilization of the sodium is stated

to be of the order of 75 to 80 per cent, and one kilogram of calcium required 6 to 8 kilograms of calcium chloride.

Kroll² reported that calcium compounds can be easily reduced by silicon, titanium, aluminum, and beryllium in the presence of a good vacuum as a function of temperature and pressure. No production methods are based on this, as the reactions are not easily controlled.

The electrolytic separation of calcium from fused calcium chloride was the method first employed by Davy in 1808, and is still the standard procedure. At first glance this would seem to be a simple process, but many factors complicate the situation. It is difficult to prepare pure anhydrous CaCl_2 , owing to hydrolysis. In the presence of impurities, calcium metal is attacked by the melt. The bath thickens, the conductivity decreases, and the yield of calcium falls. Metallic calcium to the extent of 17 per cent can be taken up by the melt, together with several per cent of iron (assuming an iron container); the condition of the electrolyte grows worse with each cooling and reheating. In commercial work the electrolyte must occasionally be completely changed. Calcium oxide is soluble to the extent of several per cent in fused CaCl_2 . When electrolyzed, the oxide content is reduced to zero. Basic salts of a lower oxide of magnesium, CaC_2 , and carbon, all build up in the electrolyte as impurities which necessitate change of electrolyte.

Pure CaCl_2 melts at 780° and impure calcium metal at 800° . The finely divided metal burns in air above 800° and easily forms metal fog in the electrolyte. The range of safe working temperatures is small.

After reasonably pure anhydrous chloride has been produced, there is the problem of collecting the calcium. At the operating temperatures of the cell, calcium reacts with almost all elements, including nitrogen, except the noble or rare gases. The calcium is deposited as a liquid and freezes on the cathode. The cathode must be in motion and adjusted so that the calcium is removed from the bath at the same rate at which it is deposited. The electrolysis causes chlorine to be generated at the anode, and this extremely active agent must be kept

away from the calcium. Since the metal is of lower specific gravity in molten form than the electrolyte, it rises to the top of the bath. Polarization and related electrode effects increase cell voltages; these increases mean raised temperatures which in turn raise the bath or electrolyte temperature and increase the difficulty of collecting the calcium whose melting point, taken at 810° , is only 38° above that of calcium chloride.

Arndt and Willner³ state the decomposition voltage of CaCl_2 at 800° to be 3.24 volts. Arndt and Gessler⁴ give the specific conductivity of the salt at 800° as 1.9.

In 1855 Bunsen and Matthiessen⁵ investigated the electrolysis of calcium chloride as part of their study of molten alkaline-earth salts. Their metal yields were unsatisfactory, as their product, a finely divided metal, burned readily. They tried to overcome this by using mixtures of chlorides to lower the electrolyte melting point but produced only finely divided calcium alloys.

Ruff and Plato⁶ made small quantities of calcium metal using an electrolyte of 100 parts CaCl_2 and 16.5 parts CaF_2 , melting at 660° . The bath temperature was 760° which was raised to 800° in the immediate neighborhood of the cathode, as the result of high cathodic c.d. (3 to 5 amp per mm^2 , or about 1,900 to 3,200 amp per sq in) at 30 volts.

A number of laboratory investigations of calcium metal production have been made. The results are given in Table 1. Frary and his co-workers found that the regular and continuous raising of the cathode rod and the regulation of the cathode temperature were important variables.

In 1904 Rathenau⁷ proposed and successfully employed a cell with an electrode which just touched the surface of the molten electrolyte. He operated this cathode at a sufficiently high current density so that the surface of the calcium in contact with and being deposited from the electrolyte was maintained in a molten form. The cathode was in the shape of a rod which could be raised gradually as the metal accumulated. An irregular form, commercially called a "carrot," was produced. In 1909 Frary and Badger⁸ reported their work on a Rathenau type of cell.

Table 1.

	Wöhler ¹	Goodwin ²	Frary <i>et al.</i> ³	Brace ⁴
Electrolyte				
CaCl ₂	100	100	100	100
CaF ₂	17			
Melting point (°C)	660	780	780	780
Bath temp. (°C)	665-680	800		800
Voltage across cell	38-80	17-18	18-31	25-30
Cathode current density (amp/sq dm)	50-250	3.2-20	9.3	80
Current efficiency (%)	82	26	45-100	
Cathode	Iron			Iron
Anode	Carbon		Graphite	Graphite
Cell Casing	Cast iron		Graphite	

¹ *Z. Elektrochem.*, **11**, 612 (1905).

² *J. Am. Chem. Soc.*, **27**, 1403 (1905).

³ *Trans. Am. Electrochem. Soc.*, **13**, 117 (1910).

⁴ *Trans. Am. Electrochem. Soc.*, **37**, 465 (1920).

Table 2. Operating Details for the Electrolytic Production of Calcium.

Electrolyte	Pure calcium chloride
Temperature (°C)	780-800
Current:	
C.d. (amp per sq in) cathode	650 (100 amp per sq cm)
Energy consumption	30,000 to 50,000 kw-hr per ton, 15-25 kw-hr per lb
Theoretical decomposition voltage of CaCl ₂ at 800°	3.2 ³
Melting point of CaCl ₂ (°C)	780
Specific conductivity of CaCl ₂ at 800°	1.9 ⁴
Pounds CaCl ₂ per pound Ca (theoretical)	2.76
Pounds CaCl ₂ per pound Ca (actual)	4.5
Anodes	Graphite
Cathodes:	
Material	Iron or graphite coated with calcium
Type	Vertical, with surface contact
Cells:	
Lining	Carbon
Casing	Sheet steel

Brace⁹ concluded from his experiments that "Three types of cell were experimented with: (a) the submerged cathode cell described by Goodwin; (b) the moving-cathode type described by Goodwin and others; and (c) a modified form of (b) developed in the course of this investigation. The conclusion reached is that the last mentioned cell is far easier to operate than either of the others, and that the product is much more uniform." Brace states:

"The use of electrolytes containing salts other than calcium chloride was investigated, and the disadvantages of these mixtures are pointed out. It is concluded that pure calcium chloride makes the best electrolyte.

"Proper dehydration of the chloride was found to be essential to the successful production of calcium. A feature of the final process is the elimination of disturbing impurities by treating the electrolyte with metallic calcium just previous to electrolysis.

"Deposits of calcium nearly uniform in cross section were produced. These showed a chlorine content of 1.08 per cent, a resistivity of 6.73 microhms per centimeter cube at 22° C., and a specific gravity of 1.46. The material was easily worked into various forms by the usual metal working processes."

The commercial method for calcium production uses a vertical contact cathode, upon which the calcium is deposited as the cathode is continuously moved upward. The operating details of French practice are given in Table 2.

In reference to the energy consumption figure in Table 2, the variation between 30,000 and 50,000 kw-hr per ton is a function of (1) the size of the furnaces employed, (2) the details of construction and carefulness of insulation of these furnaces, and (3) the length of the operating campaign before changes need to be made either in the electrolyte, in the cell proper, or in the electrical connections. The lower figure is obtainable with large cells and long campaigns, while the higher figure is encountered in connection with small cells either infrequently operated or producing calcium metal for only short periods. Figure 1 shows an early commercial cell for the manufacture of calcium.

A diagrammatic sketch of the cell is shown in Figure 2. The cell *A* is of graphite, water-cooled at the bottom *C*, and



Figure 1. Commercial calcium cell (Courtesy Société d'Electrochimie et d'Electrometallurgie d'Ugine, Jarrie, France).

insulated at *F* on the sides. The electrolyte *B* is in the graphite container, but separated from it by a layer *D* of unmelted or frozen electrolyte. The anodes *G-G* with water-cooled terminals are of graphite and are adjustable sidewise. The cathode *H*, also water-cooled, is adjustable vertically. Operation is so conducted that the surface of the deposited calcium in contact with the electrolyte is kept molten. As the metal accumulates, the cathode is gradually elevated and a rod of calcium of indefinite length is produced. The calcium "car-

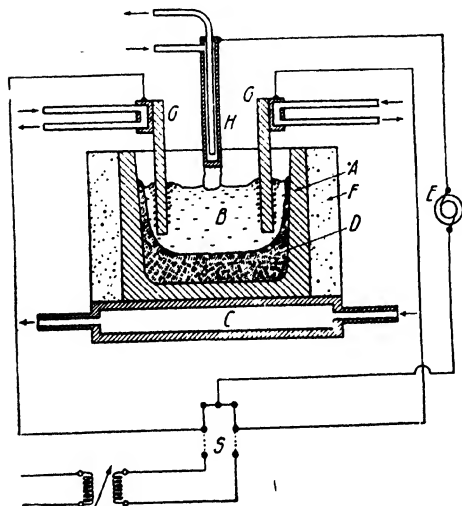


Figure 2. Sketch of cell for manufacturing sticks of calcium metal on rising cathode (H) by electrolysis of fused calcium chloride.

rots" or chunks are of the order of 20 to 30 cm in diameter (Figure 3). The cell is put in operation by melting the electrolyte with alternating current, after which, by proper switching devices, direct current for electrolysis is used. The resistance of the bath is maintained at such a point that the electrolyte is kept molten by the action of the current.

Low recovery values of CaCl_2 in terms of calcium metal are chiefly due to the atomizing effect of the violent chlorine evolution. This causes a fine spray of electrolyte which is carried up the flue of the ventilating system. Other losses are



Figure 3. Two calcium cylinders or rods produced in cell shown in Figure 1. Also a glass jar of calcium metal shavings.

due to the necessary skimming of the bath at intervals and to the layer of chloride formed on the calcium as it is drawn from the bath. Once in operation, the cathode is in effect one of calcium metal. Thin layers of CaCl_2 protect the metal from the air. The commercial metal may contain small quantities of carbon, carbide, and alkali and alkaline-earth metals.

Bagley¹⁰ described the American development and production of calcium.

"In the summer of 1939, the Union Carbide and Carbon Research Laboratories were instructed to design and build a pilot plant consisting of three 2,000-ampere cells using the chloride process. The location chosen was in the hydroelectric plant of the Michigan Northern Power Company at Sault Ste. Marie, Michigan. This company furnishes the power for the adjacent plant of the Union Carbide Company but at one time had also furnished the power for the Sault Ste. Marie street railway system, and the generators were still available to furnish the direct current needed for the calcium cells.

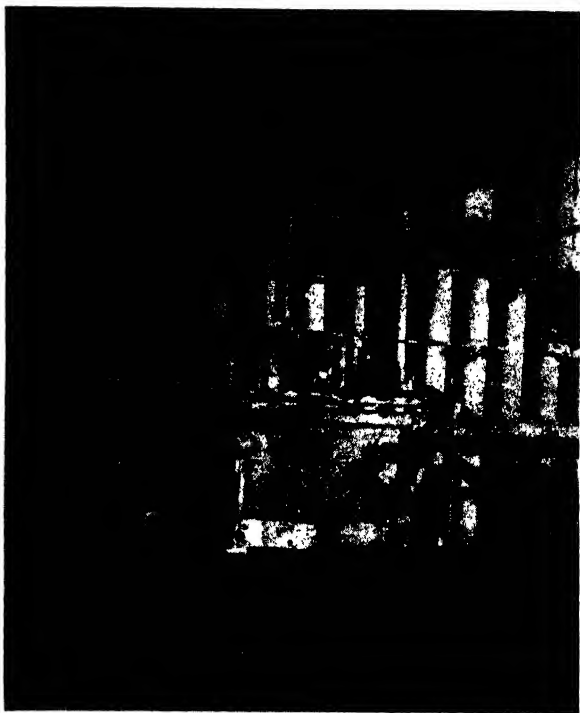


Figure 4. A typical American pilot plant cell for calcium production.

With the help of the Soo organizations the construction was completed and the plant started shortly after the European war began in the fall of that year. In the pilot plant cells, the anode connections project through the side of the cell, and a movable hand-operated cathode is suspended from the frame on top of the cell. [A typical unit is shown in Figure 4.]

"The initiation of the current flow, however, proved to be a long way from the end of the problem. Theoretically all that is required is to pass a certain number of ampere-hours through the cell and a coulomb equivalent

of calcium metal should appear. Actually many ampere-hours were passed before the first calcium was evident. It was found that many factors can operate to prevent results corresponding to the Coulomb law. In the first place, the cell feed must be anhydrous and the commercial calcium chloride must be dehydrated without decomposition. This is difficult, as the chloride tends to hydrolyze with the formation of lime. In the first dehydrating apparatus, this hydrolysis could not be satisfactorily controlled and the chloride produced had a very deleterious effect on the cell performance. Several methods of dehydration were tested in production before one was found that produced a satisfactory dehydrated chloride and was also economical in operation.

"The collection of the calcium metal produced is also more difficult than that of any other metal made commercially by fused salt electrolysis. As in the case of magnesium, calcium is lighter than the bath from which it is made and so floats on top of the bath. Magnesium is not soluble in the electrolyte and is protected by a film of the bath held over the metal by surface tension, so that it can be collected molten and ladled from the cell. Calcium is more active than magnesium and unfortunately cannot be protected in the same way by a molten film of electrolyte. It also has a considerable solubility in the electrolyte and, if allowed to remain in contact with it for any length of time, will all revert to calcium chloride, owing to the rapid circulation of the electrolyte which carries the dissolved calcium into the chlorine-producing area around the anodes. For these reasons it is necessary to use a contact cathode—that is, one that just touches the surface of the electrolyte and is moved up gradually as the calcium is deposited on it in a solid form. This produces a roughly cylindrical piece of calcium that is known in the trade as a 'carrot.'

"The operation of such a cell requires a considerable degree of skill, as the depth of cathode immersion, the cathode current density, the cathode voltage drop, and the bath temperature must be correct in order to obtain a good current efficiency. The growth of the carrot must be controlled in such a way that it emerges from the bath covered with a layer of frozen electrolyte, as the carrot is red hot for some distance above the bath, and without this protection would ignite and burn.

"The training of a sufficient number of operators to the degree of skill required proved to be difficult, and many attempts were made to develop an automatic control apparatus. The early ones were all failures on account of the many requirements that had to be met, but a satisfactory control finally emerged and it is now possible to operate the cells without attention from an operator except for periodic addition of the chloride feed and removal of the carrots.

"The demand for calcium soon exceeded the capacity of the pilot plant, and in 1940 when the Germans overran France and cut off all imports, it was necessary to install new electrical equipment and 4,000-ampere cells, and

as the demand continued to grow, another battery of 5,000-ampere cells was added. This in turn was supplemented with a battery of 10,000-ampere cells. The present productive capacity is sufficient to meet all requirements.

"For some time the output was sold in the form of calcium carrots just as they came from the cells. The metal in these carrots was pure, but their metallic content was only about 85 per cent, owing to the necessity of maintaining a protective layer of chloride around the carrots to prevent burning. For some purposes, this grade of material was suitable, but a demand soon arose for a better grade of metal, and it was necessary to develop means of melting and casting the carrots in order to separate the excess chloride. This presented some difficulty, as calcium is so active that it combines with oxygen, nitrogen, hydrogen, carbon monoxide, and carbon dioxide, but the operation is being satisfactorily carried out in an atmosphere of argon. The cast material contains 95 to 97 per cent calcium and is available in the form of slabs of various sizes, cylinders, and turnings.

"For other important uses a still higher grade of calcium free from all traces of contaminating metals was required. This could be obtained only by distillation, which required both a high temperature and a high vacuum to prevent reaction of the calcium vapors. In addition, the calcium carrots contain sodium which comes from the calcium chloride fed to the electrolytic cells. This also distills and condenses in a very active form which is liable to ignite spontaneously and even explode when the distillation furnace is opened to the air for discharging. The sodium in turn is likely to ignite the calcium, and a calcium fire on a large scale is almost impossible to extinguish. The demand for distilled calcium was met for a time with a 50-pound still operated in the Research Laboratory at Niagara, but this soon proved inadequate and it was necessary to build and install a commercial distillation plant at Sault Ste. Marie. The difficulties experienced on a small scale at Niagara were also encountered on a much larger scale at Sault Ste. Marie, but they were overcome as experience in the operation of the plant was gained, and the production requirements were met.

"New uses for calcium have developed and it is being employed in non-ferrous metallurgy in other than the light metal fields, in ferrous metallurgy for the treatment of ordnance steels, in which it has materially reduced the percentage of rejects in the finished products, and in the pharmaceutical field. Because of its high activity it is not likely to find applications in the structural field although it is lighter than magnesium (density 1.54 as compared with 1.74 for magnesium), but this very activity toward all gases except the noble ones, combined with its other properties such as nonalloyability with steel, have already established calcium as a useful chemical reagent."

Kinzel¹¹ states that from the practice of the American producer, calcium metal is available in a number of forms.

"The crude carrot or lump as produced in the cell is naturally the simplest and cheapest. Due to its annular ridges and conical shape when taken from the cell it was early named a 'carrot,' and this name persists. Carrots are from 7 to 14" in diameter and 7 to 25" long. The calcium metal of the carrot is of high purity, iron and sodium being under the amounts found in calcium manufactured abroad. However, all carrots contain an appreciable amount of entrapped calcium chloride, and the surface is covered with this salt. The carrots may be remelted and cast in molds. Due to the extreme activity of the molten calcium this again is far from a simple operation. Not only must the furnace be of such a nature as to exclude all of the oxygen and nitrogen-bearing gases, but mold design is limited and pouring technique is an art in itself.

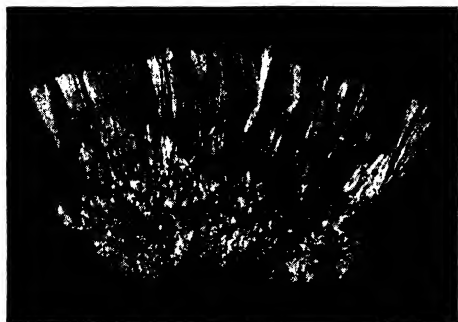


Figure 5. Redistilled crystals of metallic calcium. (Courtesy Electro Metallurgical Co.)

"Two forms of cast slabs are produced as standard. One of these weighs approximately 50 lb and measures about 2½ by 16 by 25"; the other is 1" thick, the 3 by 8" pieces weighing approximately 1½ lb each. Turnings are likewise available. For manufacturing turnings, a cylinder of calcium is cast and turned on a lathe. Obviously the usual cutting fluids cannot be used because of reaction with calcium, and special care is necessary to avoid calcium combustion. Other cylinders are cast for convenience with a center hole through which a rod may be placed. Such cylinders are approximately 25" long and 7" in diameter, the center hole being 2" in diameter. Such cylinders are also available without the center hole. All of the cast calcium is commercially free from chloride. When an extremely high degree of purity is required for limited special purposes, cast calcium may be distilled in high vacuum. The calcium condenses and is available in lumps having much the appearance of cauliflower."

Figure 5 shows redistilled crystals of metallic calcium. Figure 6 shows the improvement in soundness of metallic calcium manufactured over the period of 1935 to 1940. The top

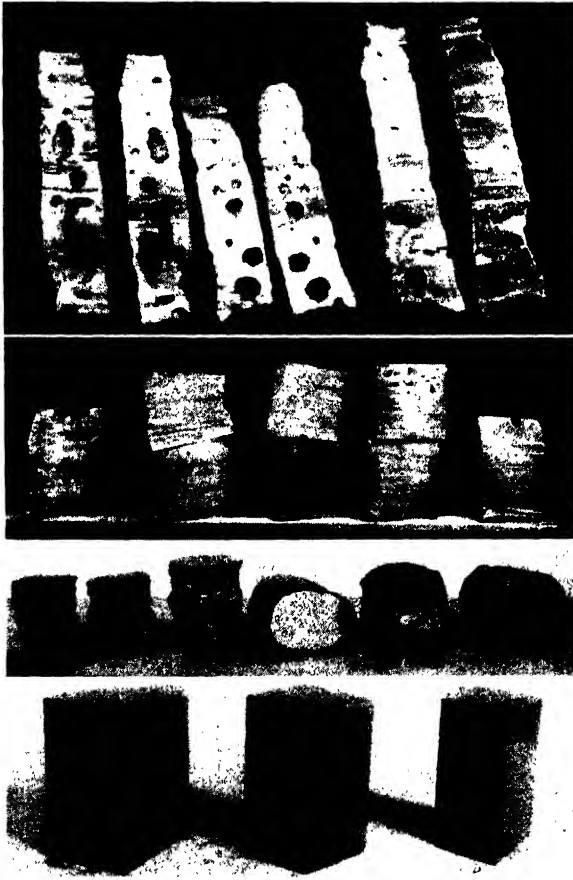


Figure 6. Improvement in the soundness of metallic calcium manufactured in recent years.

Top (1)—Calcium as produced 1935–1936.

Middle (2)—Calcium as produced 1936–1938.

Middle (3)—Calcium as produced 1938–1940.

Bottom (4)—Prisms, blocks, and squares, 1938 on.

(Courtesy Société d'Electrochimie et d'Electrometallurgie d'Ugine, Jarrie, France.)

portion of the figure shows carrots from the production cell; these contained an appreciable number of blow holes throughout their length. Improvement in practice gave much sounder carrots, as shown in the second section of the illustration. Further development of "large pieces of calcium" resulted in

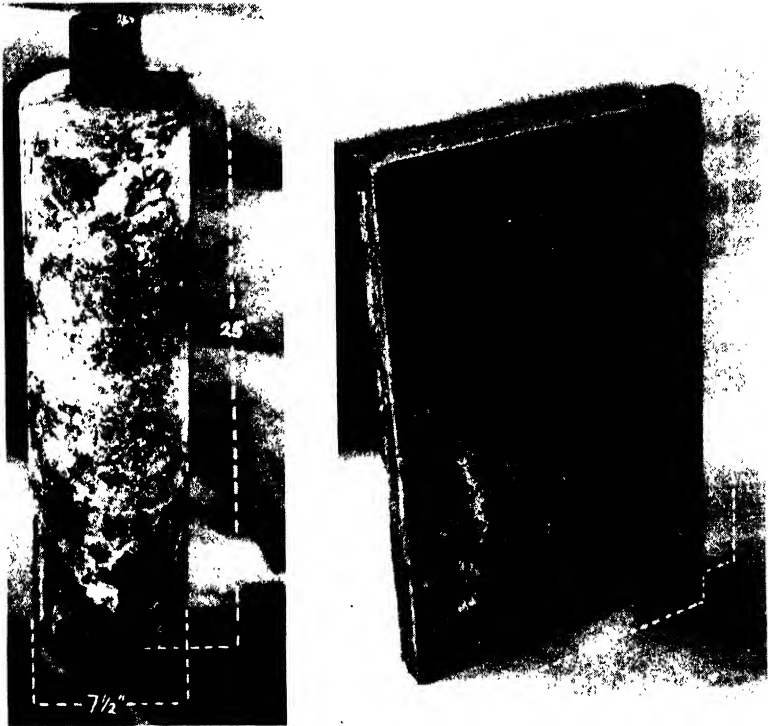


Figure 7. (Left) Cast calcium metal cylinder, with central iron pipe for convenience in adding to molten steel. (Right) Typical slab of calcium metal produced by melting and defluxing "carrots".

material having the characteristics shown in the third portion of the photograph. Further improvement gave prisms, blocks, and squares, illustrated in the bottom portion of Figure 6. Figure 7 shows forms of the American production of calcium. Table 4 indicates the improvement in purities.

Table 3. Approximate Dimensions of Standard Calcium Metal Products.

Form	Shape	Length (in)	Diameter (in)	Cross Section (in)	Weight (lb)
Carrot	Truncated Cone	5 to 20	7 to 14		7 to 25
Slab	Rectangular Round Corners	25		2½ by 16	45 to 50
Cut Slabs	Rectangular	8		1 by 3	1¼+
Cylinder	Cylindrical	25	7		50+
Cored Cylinder	Cylindrical	25	7 O. D. 2 I. D.		45+
Chips	Irregular	¼ to ½		⅙ by ¼ (approx.)	

Table 4.

	1936	1937	1938	Distilled Calcium
Calcium	96.58	97.15	98.65	99.5+
Chlorine	1.95	1.38	0.72
Iron	0.42	0.37	0.2
Aluminum	0.035	0.036	0.03
Silicon	0.012	0.01	0.01
Alkali metals	1.0	0.9	Traces

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Chapter III

Aluminum-Calcium Alloys

The constitution diagram of the aluminum-calcium system is shown in Figure 8. Donski¹ reported the compound Al_3Ca containing 33.02 per cent calcium which forms a eutectic with aluminum with a melting point of 610° at about 8 per cent

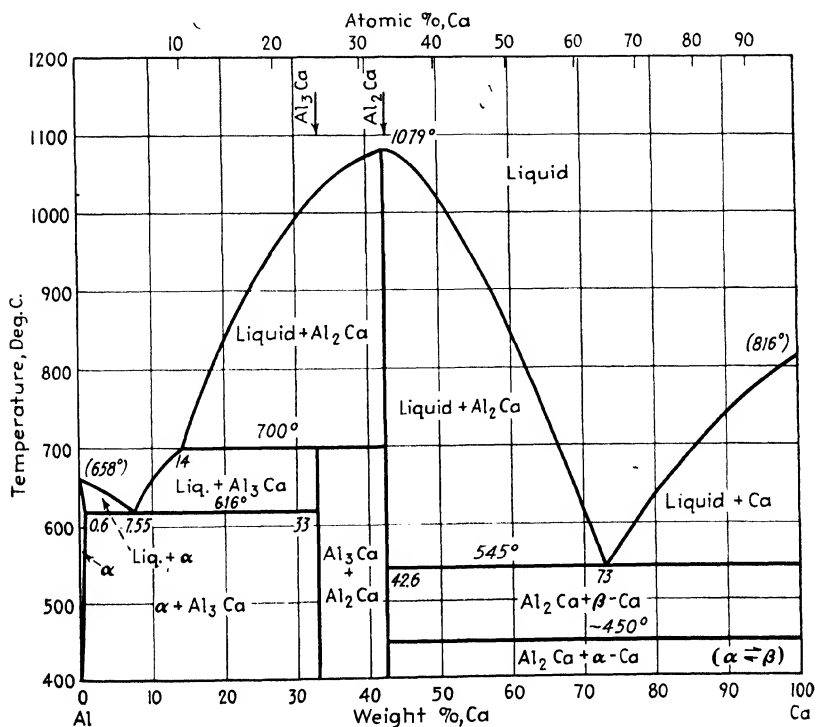


Figure 8. Constitution diagram of aluminum-calcium alloys.

calcium. At 692° he reported two liquid phases and inflection points on the melting point curves at approximately 15 and 43 per cent calcium. He also indicated a eutectic at about 75 per cent calcium, melting at 550°. Later Matsuyama² reinvestigated the system by thermometric analysis and electrical resistance methods. The solubility of calcium in aluminum is small, being 0.6 per cent at 616°. Matsuyama gives a figure of 0.3 per cent calcium at room temperature. Matsuyama stated that the compound Al_2Ca , containing 42.62 per cent calcium, exists, with a melting point at 1079°. At 700° there is a peritectic transformation as shown in the diagram, with a reversible reaction $\text{Al}_2\text{Ca} + \text{melt} \rightleftharpoons \text{Al}_3\text{Ca}$. Donski did not give the purity of his aluminum; his calcium was 99.1 per cent pure. Matsuyama's aluminum contained 0.3 per cent iron and 0.3 per cent silicon, and his calcium 0.14 per cent iron, 0.11 per cent silicon, 0.15 per cent aluminum, and 1.17 per cent magnesium.

Some investigators assume that what is supposed to be Al_3Ca is a peritectically formed mixture of Al_2Ca plus aluminum.³ Einerl and Neurath,⁴ however, report the existence of Al_3Ca , and that it forms with aluminum a eutectic mixture which contains about 8 per cent calcium.

Calcium-aluminum alloys are stated to be extremely stable. An alloy of 60 per cent calcium and 40 per cent aluminum, which otherwise was of no technical value, was so stable that it could not be used for the dehydration of alcohol.⁵

The manufacture of aluminum-calcium alloys is not without difficulties. Aluminum-calcium mixtures have the tendency to oxidize on the surface, and the oxides adsorb gas from the atmosphere. This gas is retained if the oxide particles become mingled with the molten metal, unless the metal is sufficiently liquid to permit the escape of the gas. The bubbles cause the alloy to be of inferior quality. In master alloys this porosity may be imparted to another alloy made by use of the master mix. This difficulty is overcome by the addition of 0.005–0.1 per cent sodium to the alloy, which inhibits oxidation on the surface of the melt.⁶

The effect of calcium on the resistivity of aluminum has been studied by Edwards and Taylor,⁷ who state that the resistivity is proportional to the calcium content in the ranges studied, the resistivity of cast material being higher than for the rolled material. In the former the resistivity rose from 2.988 μ /cm for 0.89 per cent calcium to 3.632 μ for 3.34 per cent calcium, while in rolled material, it rose from 2.742 μ for 0.25 per cent calcium to 3.168 μ for 2.32 per cent calcium. The density of the cast alloys at 20° fell from 2.677 for the 0.89 per cent calcium alloy to 2.636 for the 3.34 per cent calcium alloy, while in the rolled condition the density fell from 2.693 for the 0.25 per cent calcium alloy to 2.658 for the 2.32 per cent calcium alloy.

Calcium used to replace magnesium in duralumin has been studied by Kroll,⁸ who concluded that the calcium addition raised the temperature most favorable for aging duralumin. Meissner⁹ does not agree with these results and believes the higher strength obtained is the result of a favorable aging treatment and has nothing to do with the calcium addition. Grogan¹⁰ states that the solubility of the calcium compound is less than 1 per cent by weight, and that it exerts slight effect on the mechanical properties of aluminum, to which it imparts no hardening properties. The CaSi₂ also produces no hardening.

Although a large number of aluminum-calcium alloys have been developed and manufactured, there is unfortunately not much information available except in patents.

In aluminum alloys calcium has two distinctly different functions. One is to improve the mechanical properties and workability of the alloy, the other to improve its electrical conductivity by removing silicon as calcium silicide, inasmuch as silicon has detrimental effects on the conductivity of aluminum alloys.

For a considerable period calcium has been used in connection with aluminum and aluminum-alloy preparation. In the early development of the strong alloys, calcium was a useful addition in materials which were to be forged or mechanically

shaped. In connection with the aluminum alloys containing copper and magnesium with or without manganese, it eliminated hot shortness during rolling of the ingot into sheet.¹¹ The amount of calcium added is 2 per cent or less, generally of the order of 0.6 to 1 per cent. In Europe and England calcium is used in connection with aluminum containing silicon to precipitate the silicon out of solution and form calcium silicide, with resulting elimination of the deleterious effects of silicon on the electrical conductivity of the aluminum.

Aluminum alloys containing about 4 per cent copper and 0.5 per cent magnesium¹² give a great deal of trouble and much scrap during the hot-rolling of the ingot into slabs, because of the tendency of the metal to crack very badly. The cracks extend from the edge of the slab into the body and necessitate extensive shearing. These alloys are greatly improved by the addition of calcium in amounts of 2 per cent or less. In a number of aluminum-manganese-magnesium alloys, 0.3 to 0.6 per cent of calcium is suggested.

The modification of silicon-aluminum alloys by the addition of calcium and substances of similar properties has been investigated.¹³ Examination of the microstructures of normal and modified alloys shows that calcium and the alkali metals, sodium, potassium and lithium, are very effective as modifying agents. The theory that modification is brought about by volatile elements is disproved by the fact that phosphorus, sulfur, selenium, tellurium, and arsenic give no appreciable effect.

Recently additions of calcium to casting alloys of aluminum have received attention. Tables 5 and 6 give an indication of the extent of these alloys and the amount of calcium employed. Some application of calcium has been extended to the magnesium alloys, examples of which are included in the table.

The addition of 0.01–2.0 per cent calcium and 0.05–0.4 per cent antimony or bismuth, or both, to aluminum alloys that contain 2.0–15.0 per cent magnesium is said to be beneficial.¹⁴ Calcium may likewise be added to improve such alloys when they contain, in addition to magnesium and antimony or bismuth, or all three, one or more of such alloying elements as

Table 5. Aluminum Alloys Containing Calcium.

Composition										Outstanding Property	Chief Application	Reference or Name
Ca	Al	Bi	Cu	Mg	Mn	Ni	Sb	Others				
0.55	Bal.	—	—	—	—	—	—	—	—	corrosion resistance	cladding over dural	Z. Metallkunde, 32, 363 (1940)
0.2	98	—	—	1	—	—	—	0.8 Si	—	high conductivity, strength	high tension lines	German alloy 'Montegal', Chem. Age, 47, 107 (1942)
1.0-1.5	Bal.	—	—	1.4-1.6	2.5-3.2	—	—	0.25-0.40 Cr, 0-0.3 Fe, 2.2-2.7 Si	—	strength after age-hardening	piston forgings	Brit. P. 517,731
0.5-5.0	Bal.	—	0.5-2.0	0.5-3.0	1-7	0-1.7	—	0-0.3 Cr, 0-1.7 Fe, 1-7 Si, 0-0.5 Ti	—	(Cu + Ni < 3%, Ni + Fe or Cr < 2%)	forged pistons	Brit. P. 517,731
0.01-2.0	Bal.	0.05-0.4	—	2-15	—	—	0.05-0.4	—	—	—	—	Can. P. 348,148
0.01-2.0	Bal.	0.05-0.4	—	2-10	—	0.2-5.0	0.05-0.4	—	—	—	—	Can. P. 348,148
0.01-2.0	Bal.	0.05-0.4	—	3-8	0.5-4.0	0.5-4.0	0.05-0.4	—	—	—	—	Can. P. 348,148
0.01-2.0	Bal.	—	—	5-15	—	—	—	0.01-1.25 Pb, 0.01-1.25 Sn.	—	—	—	French P. 790,872
0.1-2.0	Bal.	—	5-20	—	1-3	0.1-3.0	—	1-3 Cr, 1-3 W	—	Ca replaceable by Sn, Ba, Be, Na, K, Li	—	Brit. P. 353,891
0.2-5.0	Bal.	—	—	0.2-10*	0.2-2*	0.2-5*	—	0.2-5 Be, 0.1-1 Cr*, 3-5 Si, 0-3 Sn, 0.3-2 V	—	(*composition includes one or more of these)	—	Ger. P. 535,345
0.01-2.0	Bal.	0.05-0.4	1-6	2-15	0.5-4	—	0.05-0.4	0.5-3 Cr, 0.1-1.0 Mo, 0.1-1 Ti	—	(also contains 0.1-1 V, W and Zr)	—	Brit. P. 428,363

Table 6.

Patent	Date of Issue	Inventor	Type	Al	Ca	Be	Bi	Co	Cr
Ger. 535,345	Dec. 10, 1922	Th. Goldschmidt A. G.	Casting	Balance	0.2-5	0.2-5	0.2-5*	0.1-1*
Brit. 319,967	Oct. 31, 1926	D. R. Tullis	Casting	Balance	0.1-2.0	0.2-3.0
Fr. 729,566	Nov. 9, 1931	Etablissements Emile Louyot	Casting	Balance	0.05
U. S. 1,932,834	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.1-2
U. S. 1,932,836	Oct. 31, 1933	Robert T. Wood and Otto H. Heil to Aluminum Co. of America	Casting	Balance	0.1-2
U. S. 1,932,837	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.2
U. S. 1,932,854	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2
U. S. 1,932,855	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4
U. S. 1,932,856	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2
U. S. 1,932,857	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4
U. S. 1,932,858	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4
U. S. 1,932,859	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	0.5-3.5
U. S. 1,932,860	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-2	0.5-3.5
U. S. 1,932,861	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2
U. S. 1,932,862	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2
U. S. 1,932,863	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4
U. S. 1,932,864	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	0.5-3.5
U. S. 1,932,865	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	0.1-3.5
U. S. 1,932,866	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	0.5-3.5
U. S. 1,932,867	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4	0.5-3.5
U. S. 1,932,868	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4	0.1-3
U. S. 1,932,869	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4	0.1-3.5
U. S. 1,932,870	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	0.5-3.5
U. S. 1,932,871	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	0.1-3.5
U. S. 1,932,872	Oct. 31, 1933	Robert T. Wood to Aluminum Co. of America	Casting	Balance	0.05-2	and/or Sb 0.05-0.4
Fr. 730,088	Dec. 17, 1931	American Magnesium Corp.	Mg alloy	0.1-2
Japan 98,956	Jan. 9, 1933	The Minister of Navy (Buntarō Uani, inventor)	Mg alloy	0.1-0.8
U. S. 1,914,588	June 20, 1933	Robert T. Wood to Magnesium Development Corp.	Mg alloy	0.05-2
U. S. 1,914,589	June 20, 1933	Robert T. Wood to Magnesium Development Corp.	Mg alloy	0.05-2

Table 6.—Continued.

Patent	Cu	Mg	Mn	Ni	Sb	Si	V	Zn	Pb or Sn up to 3	Sn or Pb up to 3	Cd	Remarks
Ger. 535,345	0.2-10*	0.2-2*	0.2-5*	..	3-15	0.3-2	(1)
Brit. 319,967	0.5-5.0	0.2 optional	1
Fr. 729,566	3.5	1	0.5	0.5
U. S. 1,932,834	2-9
U. S. 1,932,836	1-8	5	0.5-6
U. S. 1,932,837	2-10	0.2-5	and/or Bi
U. S. 1,932,854	3-7.5	0.2-2	0.06-0.4
U. S. 1,932,855
U. S. 1,932,856	3-8	0.5-4	0.5-4	and/or Bi
U. S. 1,932,857	3-8	0.5-4	0.5-4	0.06-0.4
U. S. 1,932,858	2-15	0.06-0.4
U. S. 1,932,859	2-10	0.2-5	and/or Bi
U. S. 1,932,860	3-8	0.5-3.5	0.06-0.4
U. S. 1,932,861	1-6	2-10	0.2-5	and/or Bi
U. S. 1,932,862	1-6	3-8	0.2-5	0.06-0.4
U. S. 1,932,863	0.5-5	3-8	0.5-5	(2)
U. S. 1,932,864	3-8	0.2-5
U. S. 1,932,865	1-6	2-10	0.2-5
U. S. 1,932,866	1-6	3-8	and/or Bi
U. S. 1,932,867	1-6	3-8	0.05-0.4
U. S. 1,932,868	3-8	0.5-4	and/or Bi
U. S. 1,932,869	2-15	0.05-0.4
U. S. 1,932,870	3-8	0.5-5	and/or Bi
U. S. 1,932,871	0.5-5	2-15	0.05-0.4
U. S. 1,932,872	2-9	0.1-4	and/or Bi
Fr. 730,088	Balance	0.1-5	0.05-0.4	0.1-5	0.1-15	0.1-10	(3)
Japan 98,956	Less than 2	Balance	0.1-0.8	4-8
U. S. 1,914,588	Balance	2-6	0.1-20
U. S. 1,914,589	Balance	0.1-2.5	0.1-10

(1) *One or more of these metals may be used. (2) 0.1-1 of one or more of W, V, Mo, Ti, and Zr added. (3) Barium, 0.1-2.

cobalt, copper, nickel, manganese, zinc, etc., which may be added to modify or produce a specific property of the alloy. The addition of 0.01 to 2.0 per cent calcium and 0.05 to 0.4 per cent antimony or bismuth, or both, is very beneficial in the case of a series of aluminum alloys which contain as major alloying elements 2.0 to 10.0 per cent magnesium and 0.2 to 5.0 per cent nickel. A useful aluminum alloy contains 3.0 to 8.0 per cent magnesium, 0.5 to 4.0 per cent nickel, 0.5 to 4.0 per cent manganese, 0.01 to 2.0 per cent calcium, and 0.05 to 0.4 per cent antimony or bismuth, or both. Frary¹⁵ states:

“The addition of a few tenths of one per cent of calcium to aluminum has been shown by some English investigators to increase very appreciably the electrical conductivity of aluminum, solely because the calcium combines with a few tenths of a per cent of silicon present in the aluminum, to form insoluble calcium silicide. We find calcium very active in combining with other elements such as silicon or copper, to form these insoluble constituents, and resulting in a decided effect upon the physical properties and behavior of the metal treated.”

Binary aluminum-calcium alloys are but rarely used. In most cases calcium is only one of the various components of the alloy. Bungardt¹⁶ describes a binary aluminum-calcium alloy which contains 0.55 per cent calcium. It was suggested as a protection for an aluminum-copper-magnesium alloy from corrosion. This is done by applying a protective layer of the aluminum-calcium alloy, by means of hot rolling, to the aluminum-copper-magnesium core. The protective layer comprises 5–10 per cent of the thickness of the article. The calcium in the protective layer was to prevent the diffusion of the copper from the core to the protective layer.

Another use for binary aluminum-calcium alloys can be found in the steel industry as a deoxidizing agent. Calloy, Ltd., Avonmouth, England, proposes two different alloys for this purpose, one containing 8–12 per cent calcium and 88–92 per cent aluminum, and another which contains 24–26 per cent calcium and 74–76 per cent aluminum.

One of the functions of calcium in aluminum alloys is the improvement which it affords aluminum-magnesium alloys rich in aluminum. When aluminum-magnesium alloys are

cast into a sand mold, a reaction between the melt and the mold occurs which causes the formation of vapors. If the melt is not liquid enough, bubbles of this vapor are retained, and the cast article is of inferior quality; on the other hand a higher pouring temperature, which is necessary to permit the vapor to escape, also causes an unsound cast. Another difficulty encountered in the casting of aluminum-magnesium alloys is the formation of a heavy, viscous scum which prevents the molten alloy from filling properly the narrower parts of the mold, and prevents the escape of the bubbles of vapor due to the reaction between mold and alloy. These difficulties are to a considerable degree overcome by the addition of a small amount of calcium to the alloy. It prevents the vapor-generating reaction between the mold and the molten alloy, and causes a marked reduction in the volume and viscosity of the scum. The addition of calcium has, furthermore, the advantage of preventing the formation of gas, which takes place during the cooling of aluminum-calcium alloys. It thus makes for sounder castings. The amount of calcium should, however, not exceed 2 per cent, as the mechanical properties of the alloy are disadvantageously influenced by a larger percentage of calcium.¹⁷

The Metallgesellschaft (Frankfurt am Main, Germany) recommends an alloy containing 1 per cent magnesium, 0.8 per cent silicon, 0.2 per cent calcium, and the balance aluminum for high-tension wires ("Magnewin"). In this alloy calcium has the function of depriving the magnesium silicide of its silicon; thus it prevents age-hardening, and prevents the undesired surplus of silicon from forming mixed crystals with aluminum. The electric conductivity increases with the decrease of solid solution of silicon in aluminum.¹⁸

Aluminum-calcium alloys are found in the automotive industry; pistons and crankcases frequently contain calcium. An alloy suggested for pistons contains 2.5–3.2 per cent manganese, 2.2–2.7 per cent silicon, 1.4–1.6 per cent magnesium, 0.25–0.40 per cent chromium, up to 0.3 per cent iron, and 1.0–1.5 per cent calcium. It may be subjected to a solution heat treatment at 520–530° for two hours, followed by quenching,

and then may be given a precipitation heat treatment at 160–170° for 16–20 hours, which is again followed by quenching. The Brinell hardness of this alloy is:

As forged	69
Heat-treated	121–130
Annealed	52–55

For the heat-treated alloy the Brinell hardness at various temperatures is:

250°	40
300°	26
350°	19.5

Generally, aluminum alloys with 1–7 per cent manganese, 1–7 per cent silicon, 0.5–3 per cent magnesium, 0.5–2 per cent copper, 0.5–5 per cent calcium, and optional small amounts of nickel and iron up to 1.7 per cent, chromium up to 0.3 per cent, and titanium up to 0.5 per cent are recommended by Prytherch for pistons in internal combustion engines. Nickel and copper together should not exceed 3 per cent; nickel and iron, or nickel and chromium together should not exceed 2 per cent.¹⁹ Aluminum-calcium alloys are usually produced from lime and aluminum. One method is to heat lime in a bath of molten aluminum at 1500–1600° and to permit the calcium aluminate to collect below the bath of molten alloy.²⁰

It is, however, claimed that this and similar methods cause a preventable loss of metal. It is recommended that intimately mixed briquets of ground burnt lime and aluminum granules be formed and these allowed to react with molten aluminum. Alloys with up to 50 per cent calcium may be made by this method. The mixture in the briquets should be of such proportions that the resulting calcium aluminate slag has the lowest melting point.²¹

A number of alloys were tested by Nowotny and co-workers with regard to their hardness and structure, which was determined by metallographic methods.²² Their results are given in Table 7.

A group of alloys which merits special interest are those between aluminum and silicon-calcium alloys, on account of

their increased hardness, yield, and tensile strength²³ (Table 8).

Aluminum and calcium silicide form a eutectic mixture which contains 4.6 per cent calcium silicide and melts at 637°.²⁴

Frary²⁵ proposed the addition of up to 2 per cent of calcium to aluminum alloys of the type 4 per cent copper, 0.5 per cent magnesium, balance aluminum, to prevent hot shortness. These alloys were used for hot rolling into sheets later to be employed for fabrication of aircraft. The calcium was added in the form of an alloy having a composition of 80 per cent aluminum, 10 per cent copper, and 10 per cent calcium.

Table 7.

Calcium (%)	Heat treatment	Brinell hardness	Structure
0.3	quenched	24.4	homogeneous
1.5	"	45.6	"
1.5	Annealed at 300°C.	52.7	"
2.7	quenched	32.2	heterogeneous
12.3	"	78.8	"
16.5	"	113.8	"

Table 8.

Ca (%)	Si (%)	Brinell hardness	Yield (tons/sq in)	Tensile strength (tons/sq in)	Elongation (% in 2")
0.13	0.13	18.5	1.8	4.6	48.5
0.20	0.35	22.4	2.2	5.6	41.0
0.32	0.54	25.9	2.5	6.3	36.0
0.40	0.71	27.7	3.0	6.9	32.0
0.52	0.95	30.2	3.1	7.5	29.5
0.99	1.35	33.6	3.4	8.2	32.0
1.94	2.67	41.0	4.2	8.6	20.5
1.00	0.12	23.6	2.5	6.0	41.5
2.05	0.10	13.8	3.0	7.2	31.5

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Chapter IV

Copper-Calcium Alloys

The constitution diagram of the copper-calcium system is given in Figure 9. Calcium is only slightly soluble in copper according to the constitution diagram of Baar.¹ A eutectic is formed at a composition of 5.8 per cent calcium having a melting point of 910°. The compound CaCu_4 is formed and has a melting point of 935°. The eutectic is between copper and the compound CaCu_4 . Some solubility of CaCu_4 in copper is indicated in the diagram.

Schumacher, Ellis, and Eckel² showed the presence of the eutectic by metallographic examination of a number of copper-rich copper-calcium alloys. The structure of the eutectic is quite brittle.

As far back as 1907, Pratt³ claimed the use of calcium for deoxidation and degasification of copper. Within recent years studies of this effect have been intensely pursued. Masing⁴ has described the use of calcium in producing deoxidized copper castings of high conductivity. This work was carried forward in the research laboratories of the General Electric Company and the Bell Telephone system by Schumacher, Ellis, and Eckel in a series of papers,⁵ and by Zickrick,⁶ and Wyman,⁷ as well as many others who have not published their work. Schumacher and his co-workers concluded that small additions of calcium in copper effectively deoxidize the metal without materially impairing the mechanical properties and electrical conductivity, provided the residual calcium is kept to a small

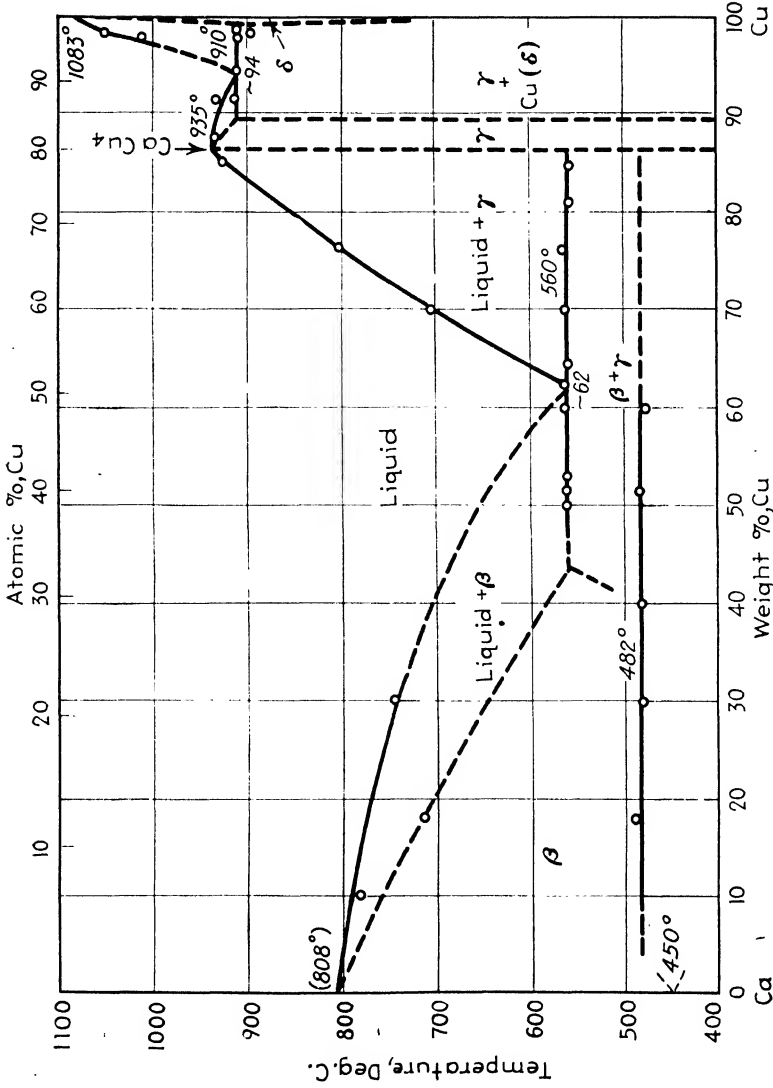


Figure 9. Constitution diagram of copper-calcium alloys.

percentage. The resulting deoxidized copper is not embrittled by annealing and reducing gases.

Brandenberg and Wiens⁸ have described the use of calcium in the casting of sound copper and state that the deoxidation can be carried out without difficulty. The castings that they prepared were sound and sufficiently ductile to permit wire drawing.

Guertler⁹ found that the effect of certain elements in increasing the resistance of copper was as given in Table 9.

Zickrick, in his study of the conductivity of copper castings,¹⁰ concluded that for copper castings the best deoxidizers in reference to their effect on conductivity were calcium, calcium boride, and boron carbide. The calcium was introduced in the form of a copper-calcium alloy. Zickrick used master alloy which contains 4.4 per cent calcium, and which is made by submerging a piece of calcium, wrapped in thin copper sheet, into a melt of copper at 1200°. The alloy is brittle and can be broken easily.

The copper used for the tests originally contained 0.06 per cent oxygen. The samples were annealed at various temperatures for six minutes and tested for their mechanical properties. It was observed that these properties improved with an increasing amount of deoxidizer retained by the copper.

The specially treated sample was annealed for 30 minutes in air at 700° followed by 15 minutes in hydrogen at 800°.

Table 9.

Added element	Increase in resistivity due to 1% added element (microhm cm ²)
Silver	0.10
Calcium (extrapolated)	0.17
Zinc	0.28
Aluminum	1.9
Magnesium	2.0
Silicon	7.0
Phosphorus	10.0

A comparison of copper deoxidized with different deoxidizing agents shows that calcium is to be preferred on account of the comparatively small drop in conductivity it causes. While a remainder of 0.03 per cent calcium caused a drop of conductivity from 101 to 97 per cent, a remainder of 0.03 per cent silicon from the deoxidation with ferro-silicon caused a drop in conductivity from 101 to 75 per cent. Even a remainder of 0.18 per cent calcium caused a drop in conductivity of only 17.3 per cent. While the deoxidizing effect of calcium silicide is satisfactory and the mechanical properties of the copper so treated are only slightly different from copper treated with copper-calcium alloy, the difference in the electrical conductivity of the final product shows that a copper-calcium alloy is to be preferred as a deoxidizer for copper.¹¹

A hard-drawn copper wire which contained 0.4 per cent calcium was found to have a tensile strength of 70,000 psi in comparison to about 62,000 for a wire which is identical except for its lack of calcium.

The increase in tensile strength is nearly directly proportional to the increase of the calcium content between 0 and 0.4 per cent. The elongation decreases from 4.5 to 2 per cent between 0 and 0.4 per cent calcium. The alloys are ductile up to a calcium content of 0.4 per cent; when the calcium content rises to 0.8 per cent they lose their ductility.¹²

Wyman¹³ reports that an addition of 0.037 per cent calcium to copper increases its resistance to embrittlement.

An addition of 1–2 per cent calcium to copper alloys which contain 0.1–5 per cent zirconium and various other components increases the hardness of the alloy.¹⁴

An interesting application of copper-calcium alloys has been found in that the drop in voltage on the electrodes of a spark gap is much reduced when the copper electrodes are replaced by copper-calcium electrodes.¹⁵

Considerable interest was shown and experimental work carried on in connection with over-deoxidized copper which, instead of having little or no residual calcium in the final product, carried a slight excess of calcium to protect the metal and maintain it in a deoxidized condition during further working and fabrication.

Table 10. Melts and Deoxidizers.

Melt No.	Deoxidizer added (%)	Deoxidizer remaining (%)	Copper and silver (%)	Oxygen (%)	Sulfur (%)
1			99.968	0.028	0.0017
2	Ca 0.0375	Trace	99.972	0.002	0.0002
3	Ca 0.075	Ca 0.044	99.928	none	0.0001
4	Ca 0.150	Ca 0.090	99.859	none	0.0001
5	0.250	Ca 0.180	99.786	none	0.0000

Table 11.

Annealing Temp. (°C)	Melt 1 Tensile strength (psi)	Elongation (% in 10")	Melt 2 Tensile strength (psi)	Elongation (% in 10")	Melt 3 Tensile strength (psi)	Elongation (% in 10")
Hard drawn	62,300	1.2	65,200	1.3	66,850	1.4
200	45,370	10.6	60,130	2.4	63,470	1.4
250	36,700	35.2	45,000	10.7	57,700	2.9
300	36,350	37.3	37,200	30.3	43,050	19.4
350	36,350	35.6	37,350	34.6	37,700	33.3
400	36,250	37.4	36,850	34.0	37,000	32.1
special sample	20,530	5.1	36,800	29.4	36,700	29.6

Table 12.

Annealing Temp. (°C)	Melt 4 Tensile strength (psi)	Elongation (% in 10")	Melt 5 Tensile strength (psi)	Elongation (% in 10")
Hard drawn	67,450	1.2	67,600	1.3
200	66,150	2.1	68,150	1.9
250	63,350	2.1	62,300	1.9
300	47,600	7.8	54,600	3.0
350	39,000	28.3	40,850	25.1
400	38,300	32.9	39,350	29.8
special sample	38,500	29.1	38,800	26.3

Calcium has been shown to be preferable as a deoxidizer to other metals of the alkaline and alkaline-earth series. Small amounts of calcium give superior qualities to copper as regards resistance to embrittlement. High-calcium copper alloys are satisfactory deoxidizers. Calcium is preferred to silicon as a deoxidizer for copper, in that it affects the conductivity very little, whereas silicon affects it markedly.

High-calcium copper alloys are now commercially available. They can be produced in brittle forms which are readily powdered or ground. Their manufacture involves the melting of copper and the addition of calcium to the melted copper. Calcium has a lower melting point than copper, and when added to the molten metal readily melts and alloys.

Calcium is an excellent deoxidizer for high-strength tin-copper bronzes. It serves as an effective reagent suppressing lead segregation in the case of the high-leaded bearing bronzes which are tin-free and have lead contents of the order of 30 to 50 per cent, with copper 70 to 50 per cent.¹⁶

Copper and lead do not alloy over a wide range of compositions, but the alloys which they do form are important in certain phases of copper and lead metallurgy. The alloys are presumably solid solutions, occurring on extreme sides of the binary system. On the lead side the maximum solubility is from 0.04 to 0.06 per cent copper in solid solution in lead. This alloy is of considerable importance in the processes of manufacturing cable sheathing, particularly the 99 per cent lead-1 per cent antimony alloy. If the lead used in making this cable sheath alloy contains no copper, the limiting speeds of extrusion of the sheath are greatly reduced. Cable manufacturers specify either Southeastern Missouri chemical lead or a lead bearing a minimum per cent of copper.

On the copper side, the solubility of lead in solid solution is of the order of 0.25 per cent. Secondary copper containing such quantities of lead is not used in the manufacture of commercial bronze or 70-30 brass for hot rolling. The solubility of lead in copper, even in small amounts, introduces a problem in fire-refining of copper and precludes the possibility of using otherwise high-grade secondary copper for phosphor-tin bronzes which are to be subjected to hot and cold working. In copper-lead mixtures where the amount of lead is greater than that of the solid solubility of lead in copper, lead segregation takes place very rapidly and is excessive in alloys containing 30 per cent or more lead. These mixtures are very useful for bearings necessary for engines operating at high speeds and high lubricating-oil temperatures—conditions under which Babbitt,

tin-lead, or related bearing metals fail. Without the use of lead-segregation suppressors, manufacturing practice of copper-lead alloys is very difficult and unsatisfactory.

Calcium has been suggested as an alloying constituent for bearing metals having compositions of the order of copper 62 to 46, tin 4 to 8, zinc 3 to 10, lead 30 to 35, calcium 0.2 to 0.5, and sodium 0.1 to 3 per cent.¹⁷

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Chapter V

Calcium in Ferrous Metallurgy

Quasebart¹ and Watts² were unable, following a variety of practices, to alloy calcium metal with iron in the liquid state. Kroll³ states: "The applicability of calcium as a scavenger for steel is rather doubtful. Calcium does not dissolve in iron, so that the reaction can take place only superficially. Calcium boils at 1,439°, so that in molten steel it can exist only as vapor. In Europe CaPb alloys were tried out for the desulfurization of iron, and during the war Ca-Si compounds were employed for the same purpose, but in either case poor results were obtained."

Industrial plant-scale tests by the authors show considerable commercial divergence from Kroll's views.

Metallic calcium in the form of briquets made with sponge iron has been used as a deoxidizing agent to the extent of 0.5 per cent calcium for iron castings made in green sand molds.⁴ Calcium-treated iron tends to be denser and more uniform in grain structure than ordinary cast iron and to have increased transverse and tensile strength and better impact values (resistance to shock). Further work developed the use of calcium metal alone, additions of which to molten cast iron allowed the regulation of the amount of carbon in graphitic form, causing increase in the strength of the casting and control of the graphitization of the carbon.⁵ Comparative values for ordinary cast iron and calcium-treated cast iron as well as heat-treated cast iron show definite advantages due to calcium additions.⁶

Good results have been obtained with steel,⁷ the calcium functioning as an effective deoxidizer and degasifier, thus producing cleaner steels. It has the advantage over other deoxidizers that practically none of the reagent is left in the metal. Improved characteristics of the steel are shown in higher yield points and greater tensile strength.

Methods had to be developed for introducing the calcium metal into the steel. Briquetting with sponge iron or steel chips gave only partial success. Mechanisms⁸ were finally developed by means of which slugs or pieces of calcium were shot into the ladle of molten metal through an air-pressure gun. Sufficient force can thus be applied to the calcium projectile to shoot it deep into the metal where it reacts, disintegrates, does its deoxidizing, and is converted into lime, which rapidly rises to the slag.

Originally, projectiles of specific shape were employed, but later modifications of the gun use irregular chunks of calcium weighing about 2 oz (57 g) each. By 1940 slugs could be shot at the rate of 120 to 150 per minute when the gun is hand-operated, or 200 to 300 per minute if it is motor-driven, and a 60-ton ladle of steel deoxidized in a period of approximately 5 minutes when 2 lb (0.907 kg) of calcium per ton of steel is used.

Calcium finds commercial application in the manufacture of the 50 nickel-50 iron alloys as a deoxidizer and scavenger. In pure nickel casting and rolling it appears to have some value in reducing internal defects such as seams, and improving malleability. The amount used is of the order of 0.005 to 0.5 per cent.⁹ In the case of the chromium-nickel alloys, it is regularly employed to prevent the formation of chromium carbide. Its use tends to prevent cracking, makes rolling less difficult, and aids when thin sections of the high-chromium high-nickel alloys are cast.

Considerable interest has been shown in the possibility of application of calcium to the making of chromium-nickel steels, particularly of the low-carbon austenitic type, because it gives clean grain boundaries and uniform grain size, and

retards the formation of carbides. The resulting cast forms show no mottling or clouding. These steels include both the ordinary and free-cutting 18-chromium 8-nickel with 0.1 per cent or less carbon; the 18 to 25 per cent chromium with 8 to 10 per cent nickel; the 25 to 31 per cent nickel steels with about 0.3 per cent carbon, 0.9 per cent Mn, and 0.35 per cent maximum silicon; the 34 to 36 per cent nickel steels with manganese of the order of 0.9 to 1.0 per cent; and the 41 to 43 per cent nickel steels. Other ferrous alloys in the manufacture of which calcium is used include the nickel-aluminum-iron alloys, (*e.g.*, 29 nickel, 11 aluminum, 0.9 to 1.1 manganese) as well as a number of magnet steels. In the case of the high-chromium high-nickel iron alloys, such as the 25 per cent chromium 15 per cent nickel, with manganese of the order of 1.0 to 1.2 per cent, some operators claim that the use of calcium enables forgeable materials to be produced, and that if the calcium treatment is omitted, difficulties are met in forging.

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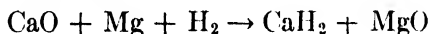
Chapter VI

Calcium Hydride

The technological importance of calcium hydride lies in its ability to decompose at high temperature and to evolve "nascent" hydrogen, which is much more active than the usual molecular hydrogen. This "nascent" hydrogen can be used for the reduction of high-melting metal oxides which do not easily react with other reducing agents.

When hydrogen is passed over calcium metal which is at 400° a reaction between these elements proceeds with evolution of heat. The compound is a crystalline product with a specific gravity and melting point higher than those of calcium metal, and a brittle structure which permits the material to be easily converted to powder form.

Calcium hydride reacts rapidly at room temperatures with water, oxygen or nitrogen even when these are present only as traces. In the absence of water vapor the hydride does not react with oxygen or nitrogen even at dull red heat. Calcium hydride can be produced by two different methods. One of them is to heat calcium oxide and magnesium metal in an atmosphere of hydrogen.



This method has the advantage that cheap lime can be used as starting point.¹

The other method uses metallic calcium as starting point. Commercial calcium has to be distilled before it is used for the production of calcium hydride, to obtain the highest pos-

sible yield. The distilled calcium is stored either in vacuum or in an atmosphere of butane. Metal stored in vacuum starts to react with hydrogen at room temperature, while metal stored under butane needs elevated temperatures before it begins to react. The final yield of calcium hydride is not affected by this fact, however. Table 13 illustrates the course of the reaction for undistilled and distilled calcium.

Table 13.
Per cent CaH₂ formed
Undistilled Calcium (97.17% Ca)

Ca (grams)	Temp. (°C)	Initial Pressure (cm)	Time in minutes					
			5	10	20	30	60	120
1.500	250	67.5	6.6	39.8	63.8	72.9	84.9	87.1
0.6379	270	63.1	3.4	12.7	56.6	75.2	85.0	85.5
1.0178	270	87.6	14.8	48.3	74.2	83.5	89.0	90.0
0.7662	270	69.1	26.4	47.6	75.5	85.3	89.0	89.0

Distilled Calcium (99.51% Ca)

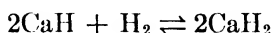
1.4265	230	73.6	23.1	63.8	95.3
1.7631	250	85.0	61.1	93.0
0.7531	250	80.0	76.2	93.0
0.4544	250	50.0	99.2

Attempts to hydrogenate calcium at higher temperatures such as 650–900° never gave a higher yield than 90 per cent. The most favorable temperature for a high yield seems to be around 250°. Calcium is able to absorb 850 times its own volume of hydrogen. The heat necessary for the initiation of the formation of calcium hydride was found to be 7700 ± 500 calories per mol. The dissociation pressure of calcium hydride was found to be:²

	99.2% CaH ₂							
Temperature (°C.)	894	892	884	880	870	855	848	840
Pressure (cm.)	25.31	25.19	21.71	20.93	18.10	14.90	13.20	11.63
Temperature (°C.)	832	823	792	765				
Pressure (cm.)	10.81	9.71	5.64	3.75				
	99.7% CaH ₂							
Temperature (°C.)	894	885	865	849	838	777	750	
Pressure (cm.)	26.15	21.63	16.73	13.91	12.01	4.64	2.90	

While the existence of the compound CaH₂ has been established beyond all doubt, the existence of the half hydride CaH is still disputed.

Kassner and Stempel³ concluded from results of vapor-pressure measurements that an equilibrium exists.



These and similar findings are disputed by Johnson, Stubbs, Sidwell, and Pechukas. The melting point of calcium hydride was found to be 816.15°.⁴

Calcium hydride is used as an intermediary in the production of metal from oxides in a method which consists in treating the oxide with an activated calcium. The calcium lumps are treated with hydrogen, heated to a dull, red glow and the calcium hydride which is formed is crushed and heated to remove the hydrogen. A highly activated calcium metal remains in fine distribution. This metal is used for the reduction of metal oxides of a high melting point, which are difficult to reduce. The saving in metallic calcium amounts to 33 per cent.⁵

The application of calcium hydride has been particularly developed for the treatment of refractory, high melting point oxides which are difficult to reduce by ordinary methods. These specifically are chromium sesqui-oxide (Cr₂O₃), titanium oxide (TiO₂), and uranium oxide (U₃O₈).

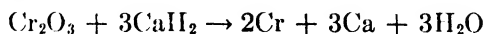
Alexander⁶ has described the application to titanium as follows:

“Since calcium hydride can be easily pulverized in the jaw crusher, it is mixed in the usual tumbling barrel with a refractory oxide such as titanium oxide, and fed into a furnace heated to 900–1000°.

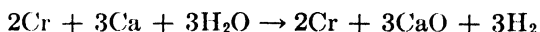
“At a low temperature calcium hydride does not react with the oxide but above red heat it gradually dissociates into nascent hydrogen and nascent calcium with the result that the refractory oxide is completely reduced to metal.

“There is no great excess of heat evolved, and unlike the Thermit Process, the reaction proceeds gradually. The result of such a low temperature reduction is a fine powdered mixture of CaO and TiH₂ which can be degassed and gives pure metal containing only a small amount of hydrogen. The grain size of the produced metal is about 300 mesh.”

In its broader application calcium hydride can easily be pulverized and is intimately mixed with the refractory metal oxide. The mixture is transferred into an electric furnace which is kept under a vacuum of 0.1 mm during the operation. At 675° the calcium hydride starts to evolve hydrogen in the nascent state and the temperature is raised to about 1000°. Since the heats of the different reactions taking place at the same time almost balance one another, the reaction proceeds gradually and the temperature inside the furnace rarely exceeds 1000°. The final product is therefore not a fused mass which would be difficult to handle, but a fine powder which consists of metal hydrides and calcium oxide. The metal can be easily degassed so that it contains only very little hydrogen. If, however, it is necessary to obtain a metal which is completely free of hydrogen, some other method has to be used for the reduction of the oxide. The reaction is characterized by the following equation:



If the water which is formed during this reaction is not quickly removed a secondary reaction takes place:⁷



The best conditions have been determined for the production of a number of metals from their oxides by this process.

	Oxide	Temperature (°C)	Time (min)
Titanium	(TiO ₂)	950–1075°	45–60
Vanadium	(V ₂ O ₃)	1025–1175°	45–60
Niobium	(Nb ₂ O ₅)	950–1075°	45–60
Tantalum	(Ta ₂ O ₅)	1025–1100°	60

The reduction of titanium, vanadium and niobium oxides requires an excess of 50 per cent of 80–90 per cent calcium hydride; tantalum oxide requires a 40 per cent calcium hydride. The hydrogenated metals form 99 per cent of the reaction products under favorable circumstances, and have the following hydrogen content:

Titanium	3% (TiH and TiH ₂)
Vanadium	1.2–2%
Niobium	1.0–1.4%
Tantalum	0.5–1.2%

The calcium oxide which is formed in this reaction can easily be removed with dilute hydrochloric acid.⁸

The Metal Hydrides, Inc., have described their plant practice⁹ for the production of uranium.

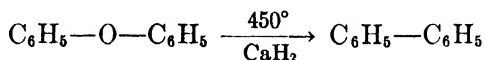
The calcined uranium oxide and powdered calcium hydride are weighed and loaded into a steel tumbling barrel where they are mixed for about half an hour. Then the mixture is loaded into open steel containers, each holding about 20 lbs of the charge. The containers are then placed in a hydrogen furnace of a special type where the charge is heated to about 980°.

At that temperature the calcium hydride gradually dissociates into nascent hydrogen and nascent calcium which, in such a state, are much more reactive than when these elements are merely in a state of high purity but otherwise stable. The reaction proceeds gradually and the temperature of the charge never rises above that of the furnace. In fact, it is constantly under control, and by decreasing or increasing the temperature of the furnace, can be either accelerated or retarded.

After cooling, the resulting material is loaded into a 200-gal tank provided with a mechanical agitator, where it is leached so that it is free from calcium oxide. The powdered uranium is then sluiced into a filter press where it is washed and partly dehydrated. The final drying is carried out in vacuum ovens.

Calcium hydride has frequently been used as reducing agent in organic chemistry, but its use in this field is restricted to the laboratory. Fuchs¹⁰ found that biphenylene changed into

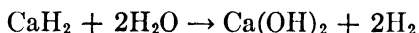
diphenyl, when biphenylene was passed over calcium hydride at 450°. The yield was 12–20 per cent. The reaction is:



Durand and Houghton¹¹ boiled nitrobenzol and calcium hydride in petroleum ether or ligroin (boiling point 75–95°) and obtained either nitrosobenzol or azoxybenzol, according to the length of the time of the reaction. Porlezza and Gatti¹² also describe various reductions in which they used calcium hydride with good effect.

Sulfates and sulfurated oils yield sulfides under treatment with calcium hydride, which can be determined by means of an iodometric titration. For the determination of sulfate by this method it is necessary to treat it with 14 to 28 times its weight of calcium hydride. The determination of sulfur in a sulfurated oil must be made in a bomb.¹³

Another interesting application of calcium hydride is in the determination of water in benzol, toluol, and carbon tetrachloride, which is based on the equation:



One mole of hydrogen is thus liberated for each mole of water dissolved in the organic liquid. The determination is said to be accurate to 0.001 per cent.¹⁴

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Chapter VII

Gold-Calcium Alloys

A thermal investigation of gold-calcium alloys indicated six compounds when gold and calcium are alloyed. The alloys have formulas calculated to be Au_4Ca , Au_2Ca , $\text{AuCa}_{1.11}$, Au_3Ca , $\text{AuCa}_{1.33}$, and AuCa .¹ The constitution diagram as proposed is given in Figure 10. A eutectic is indefinitely indicated at about 87.5 atomic per cent calcium with a melting point of 658° . Additions of calcium to gold lower its melting point and similarly the addition of gold to calcium lowers the melting point of calcium. The calcium metal employed for the work did not have a melting point which agrees with the accepted value. The diagram is therefore only indicative and needs confirmation and revision.

A suggested alloy having the property of hardenability, whose chief application would be in jewelry and in dentistry, contains 5 to 25 per cent platinum and 0 to 10 per cent calcium, the balance being gold.²

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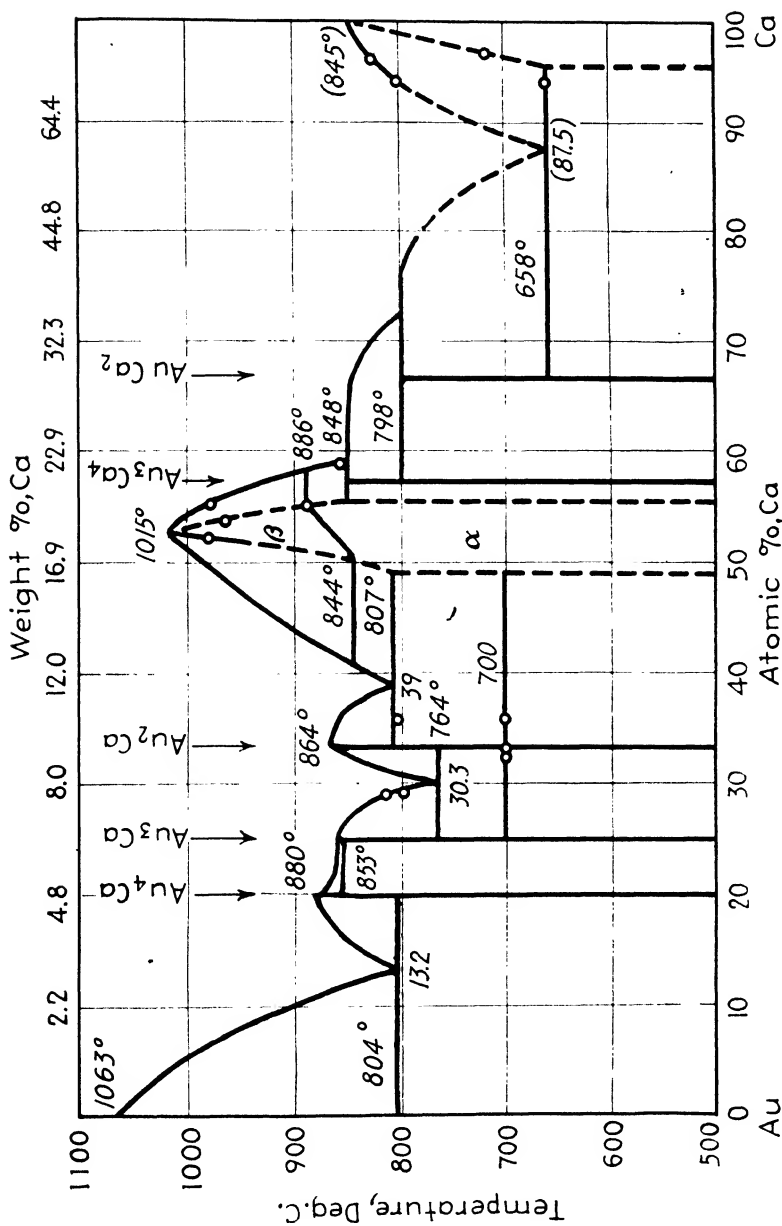


Figure 10. Constitution diagram of gold-calcium alloys.

Chapter VIII

Lead-Calcium Alloys

The age-hardening of lead-calcium alloys has been the subject of a large amount of investigation. The lead-calcium alloy system was studied in considerable detail by Caron,¹ Donski² and Baar.³ The system is characterized by the presence of the compounds Pb_3Ca , $PbCa$, and $PbCa_2$. Only alloys in the range between pure lead and Pb_3Ca are of commercial interest.

The constitution diagram of the lead-calcium system is given in Figure 12, and Figure 11 is an enlargement of this

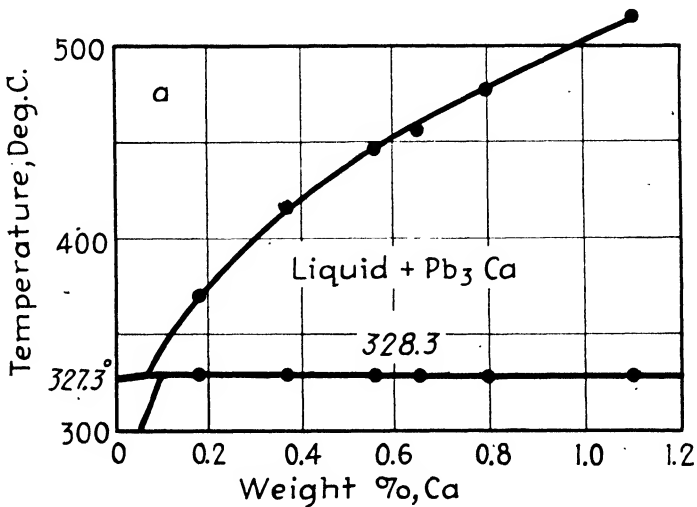


Figure 11. Constitution diagram of lead-calcium alloys, high lead end.

diagram in the range up to 1.2 weight percentage of calcium; Figure 13 a further enlargement in the important area of 0.01 to 0.1 per cent calcium.

The lead-calcium alloys have been subjected to an extended theoretical study, and it has been found that lead and calcium form a number of well defined chemical compounds: Pb_3Ca (freezing point 646°), $PbCa$ (freezing point 928°), and $PbCa_2$ (freezing point 1106°). Pb_3Ca is hard and brittle and not appreciably affected by exposure to air; $PbCa$ and $PbCa_2$

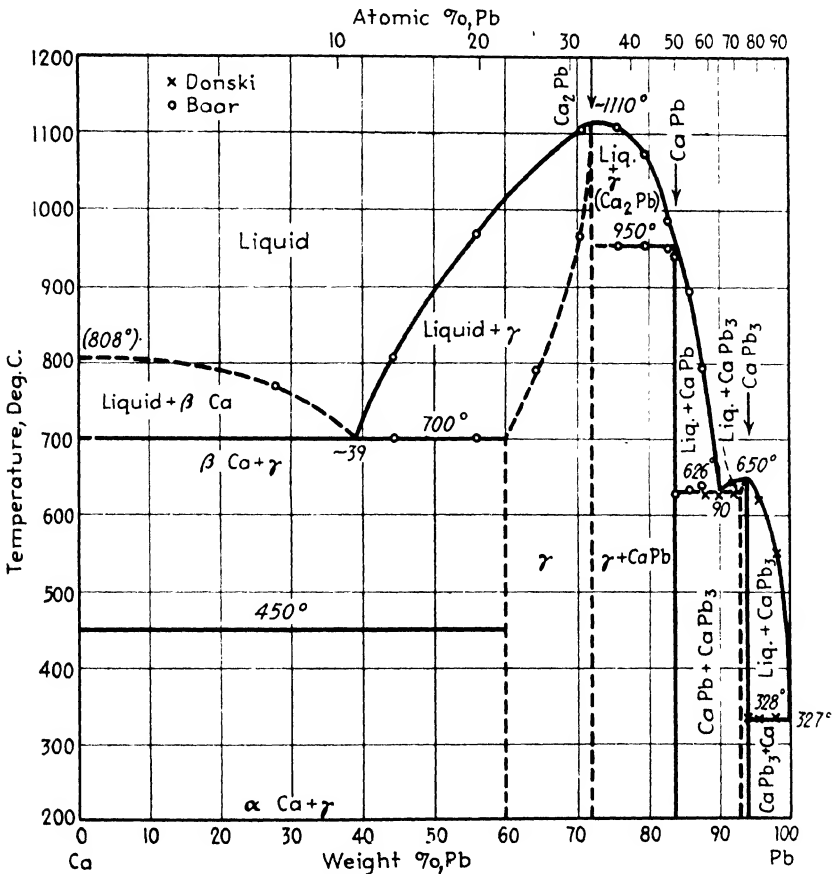


Figure 12. Constitution diagram of lead-calcium alloys.

readily disintegrate in air, especially if any moisture is present.⁴ The crystal structure of the compound Pb_3Ca was determined by Zintl and Neumayr⁵ as being that of a face-centered cube. The lead atoms are on the faces with the calcium atoms at the corners. The dimension of the side of the unit cube is given as 4.891 Å.

Two eutectic mixtures are formed. One of these contains 10 per cent calcium, melts at 620°, and consists of $PbCa$ and a solid solution of $PbCa$ in Pb_3Ca . The other mixture contains approximately 58 per cent calcium and melts at 700°. It

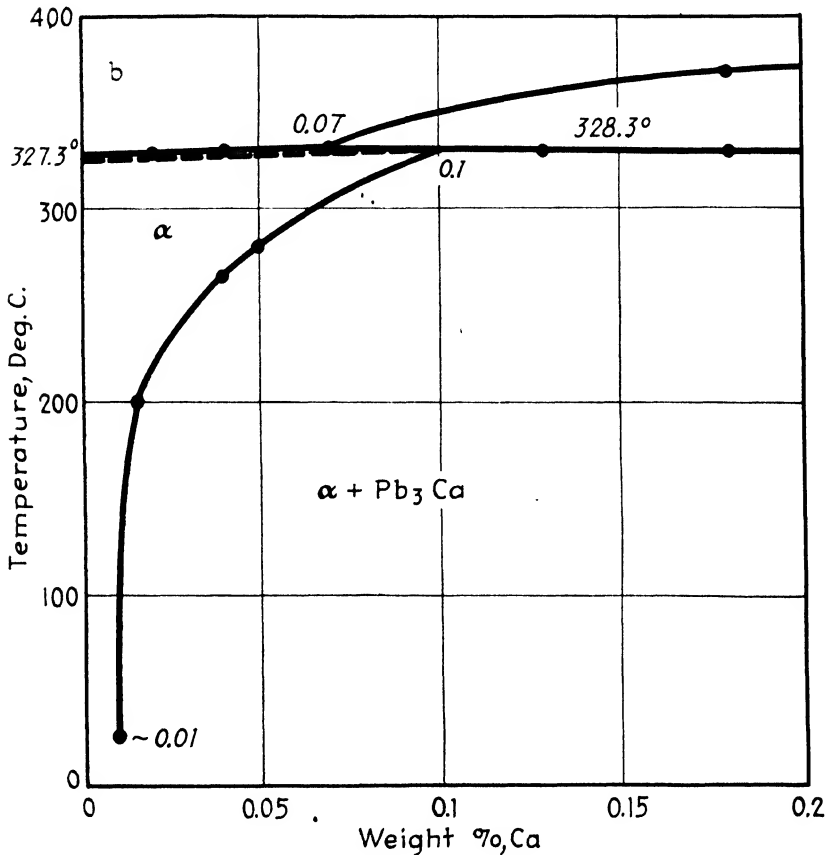


Figure 13. Constitution diagram of lead-calcium alloys, age-hardening area.

consists of calcium and a solid solution of calcium in PbCa_2 .

Kremann, Wostall, and Schöpfer⁶ have also supported the belief that these compounds exist as the result of electrode potential measurements. Ufford⁷ came to the same conclusion by studies of the pressure coefficient of electrical resistance.

Solid solutions exist between 6.1 and 7.6 per cent calcium. No solid solutions have been reported in alloys at the extreme calcium end of the system. Recent investigations of lead-rich alloys show a peritectic reaction and a slight solid solubility of calcium in lead. In Figure 13 is shown a constitution diagram for the lead end of the system, taken from the work of Schumacher and Bouton,⁸ and based on data from thermal analyses, microscopic examination, age-hardening studies, and electrical conductivity measurements. The change in solubility from 0.1 per cent calcium at 327° to 0.01 per cent at 20° makes possible the dispersion-hardening of certain of these alloys by appropriate heat treatment.

Slavinski and Kleiman⁹ report that they isolated Pb_3Ca from a lead-calcium-sodium alloy by filtering the melt through quartz sand; Pb_3Ca remained in the filter. The filtrate was found by chemical testing to be free of calcium.

It is to be appreciated that lead alloys containing calcium are quite susceptible to oxidation in the molten state so that calcium may be lost or drossed out. Ordinarily precautions must be taken to protect the melts from free access of air either by the use of light drosses, charcoal coverings, readily fusible slags, or other protective devices.

In the lead-calcium alloys for cable sheaths it is often difficult to stabilize the calcium properly. Phillips¹⁰ found that magnesium is effective as a stabilizer of lead-calcium alloys but that magnesium itself needs tin as a stabilizer. It was claimed that a new alloy was created whose age-hardening might be caused by a compound of the composition CaMgSn . The new alloy was stated to show greater creep resistance than does chemical lead. It might be possible to reduce the weight of lead pipe or sheathing to somewhat less than its previous weight and yet retain sufficient strength and stability for normal use.

A comparison of creep resistance depends upon conditions under which the observations are made. When different comparison stresses are employed, creep curves very often cross, so that materials may change their relative positions. Some measure of the relative creep resistance of chemical lead and lead-calcium-magnesium-tin alloy was indicated by Moore and Dollins.¹¹ For a fracture time of 10,000 hours, 1300 psi will cause failure in the case of the lead-calcium-magnesium-tin alloy, while a corresponding figure for chemical lead is 700 psi.

The addition of small amounts of calcium to lead produces very interesting effects. The alloys after melting and casting are of the same order of hardness as lead. When they are struck a blow with a peening or ball-headed hammer, a deep impression may be made. They are easily cut with a saw or file. They harden after a period of from several hours to a day at room temperature. Then the same blow with the hammer produces less deformation or indentation. They are not so readily cut with saws or files. Their hardness and stiffness have markedly increased only because they are older, *i.e.*, they have "age hardened."

This age-hardening of the lead-calcium alloys results from the fact that about 0.1 per cent calcium is soluble in lead at the peritectic temperature of 328.3° and only about 0.01 per cent calcium is soluble at room temperature. The constituent CaPb_3 is a submicroscopic dispersed phase which precipitates out below 328.3° and at temperatures below the alpha solubility line in Figure 11.

Schumacher and Bouton¹² determined the existence of a definite range of age-hardening lead-calcium alloys. They state that some of these hardenable alloys possess properties which strongly recommend them for commercial uses. Compared with the lead-1 per cent antimony alloy, which is generally recognized as one of the best telephone cable-sheathing materials, lead-calcium alloys develop greater fatigue resistance, tensile strength and hardness. These properties reach nearly constant values shortly after extrusion because of the rapid rate of precipitation of calcium from solid solution, and the slow

rate of diffusion and agglomeration of calcium, or the molecule Pb_3Ca . The lead-1 per cent antimony alloy continues to change even after a period of years. Experiments on corrosion resistance show lead-calcium alloys to be so little different from the lead-1 per cent antimony alloy as to have no appreciable effect on the life of a cable.

Cables other than those of the telephone type may operate under radically different service conditions and may require sheath properties different from those possessed by lead-1 per cent antimony.

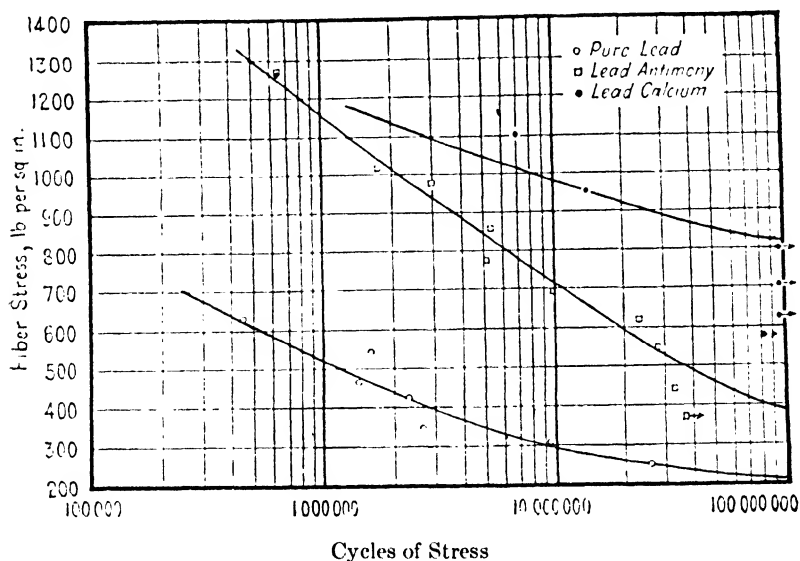


Figure 14. Endurance curves for pure lead, 1 per cent antimony, and 0.04 per cent calcium alloys for cable sheathing according to Townsend and Grenall, A.S.T.M., 1930.

Townsend and Greenall¹³ state that 0.04 per cent calcium-lead alloys show much higher endurance curves and greater fatigue resistance than does 1 per cent antimonial lead. Their curves are given in Figure 14.

Independent investigation by Dean and Ryjord¹⁴ shows that the lead-calcium alloy containing 0.03 to 0.04 per cent calcium and cooled from an extrusion temperature of 225° to 250° has a tensile strength of about 4,000 psi (280 kg/cm²), a dy-

dynamic strength or endurance limit of 1,200 to 1,500 psi (84 to 105 kg/cm²) as determined on the Moore machine at 1,700 rpm, and a static "fatigue" strength or creep resistance markedly superior to the 1 per cent antimony alloy. These properties make this alloy a superior cable sheathing. While 0.02 to 0.1 per cent calcium in a calcium-lead alloy was suggested as sheathing material for electrical cables,¹⁵⁻²¹ calcium contents in the vicinity of 0.03 per cent are at present most commonly used for alloys of this type.

Large-scale field tests of lead-calcium alloys on commercial telephone and cable lines have been conducted since 1930. They will serve as criteria of the commercial usefulness of the alloys. The manufacture of cable sheaths for electrical lines requires so much lead that it is ranked as one of the three major consuming industries.

From the purely metallurgical viewpoint, it might appear that there was little question about the substitution of lead-calcium alloys for the standard lead-antimony alloy for cable sheathing. It appears to date that there has been no important substitution except on what might be considered an experimental basis.²² Substantial quantities of lead-0.03 per cent calcium sheath cable have been under service field tests for some time. The results have not indicated a change from the lead-1 per cent antimony alloy to the lead-0.03-0.04 per cent calcium materials. There is greater difficulty in handling the lead-calcium alloy in the fabrication of cable sheath. This offsets the practical results obtained from certain superior physical properties of the lead-calcium alloys in service.

Very small amounts of calcium slightly increase the deformation pressure of a high-purity lead.²³ It appears that the temperature chosen for the experimental study of the deformation pressures of lead were such that the pressures required to produce deformation are greatly influenced by the previous thermal history of the material. The data might be interpreted as an evaluation of the extrusion characteristics of the various lead alloys. Under actual extrusion conditions the extrusion pressure for the lead-0.03-0.04 per cent calcium would not differ appreciably from that of pure lead.²⁴

Figure 15 shows the electrical conductivity of the lead-calcium alloys of 0.22 per cent or less of calcium as determined by Schumacher and Bouton;²⁵ Figure 16²⁵ shows the hardening

Figure 15. Electrical conductivity of lead-calcium alloys at 30°.

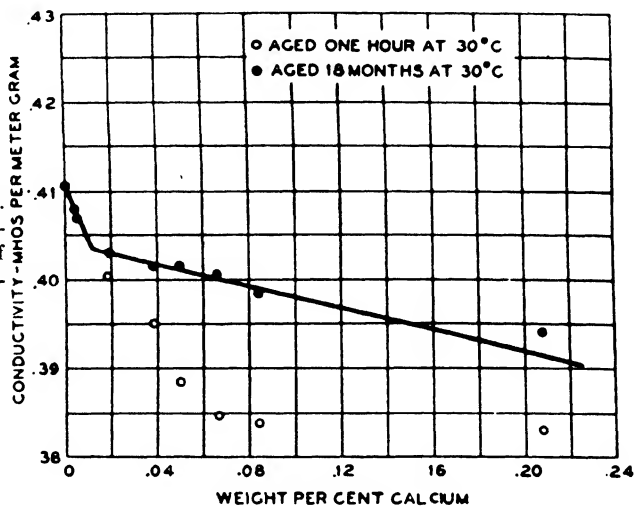
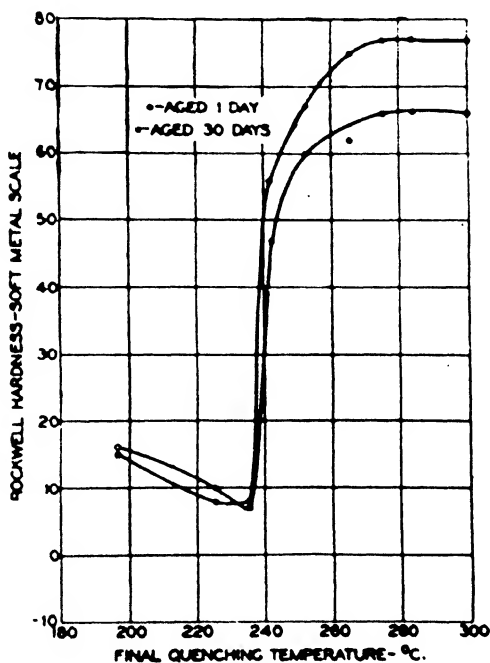


Figure 16. Hardening of a lead-0.04 per cent calcium alloy after quenching from various temperatures.



of a 0.04 per cent calcium lead after quenching from various temperatures; Figure 17²⁶ indicates the effect of percentage of calcium on the tensile strength of aged lead-calcium alloys, and Figure 18²⁷ shows the effect of aging temperature on the hardening of the 0.04 per cent calcium-lead alloy.

The fact that calcium is a highly active metal necessitates careful control of its percentage in lead-calcium alloys. As the traditional analytical methods were too slow for production work, a new, fast but nevertheless reliable method had to be devised. The alloy is melted and cast into an iron mold while it is placed in a cellophane chamber with a controlled humidity of 50 per cent and a content of 0.02 per cent carbon dioxide in the atmosphere. The cooled ingot shows fissures of oxidized material, which increase in proportion to the amount of calcium present and enable an experienced person to make reliable conclusions with regard to the calcium content.²⁸

For the exact analysis of lead-calcium alloys, methods have been devised specifically suited for the determination of small amounts of calcium in calcium-lead alloys. They follow the traditional method: the alloy is dissolved in nitric acid, the lead separated by precipitation as sulfate, and the calcium precipitated as oxalate, which is either heated and weighed as calcium oxide or dissolved in dilute sulfuric acid and titrated with potassium permanganate.²⁹

In the production of extruded and rolled calcium-lead alloys the use of a mixture of graphite and sodium silicate as lubricant is recommended. The mixture forms a hardened lubricating coating when it is dry.³⁰ To assure uniformity of the alloy, the suggestion has been made that the melt be pressed through a perforated plate.³¹ This procedure has not found any appreciable acceptance in the United States. For the "burning" or welding of lead-calcium alloys, it is stated that it is necessary to burn the calcium away, which is done by means of a hydrogen flame and a blow pipe.³² In soldering lead-0.03-0.04 per cent calcium alloys during the installation of hundreds of miles of cable sheath of this material, no difficulty was reported in soldering or similar type of joining.

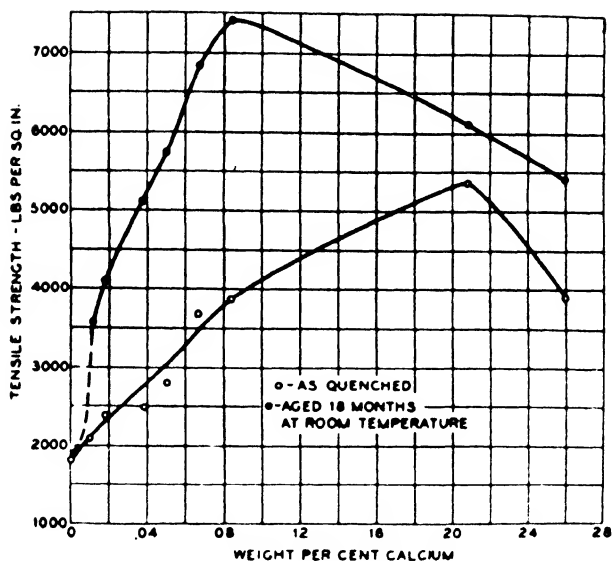


Figure 17. Effect of calcium concentration on the tensile strength of quenched and aged lead-calcium alloys.

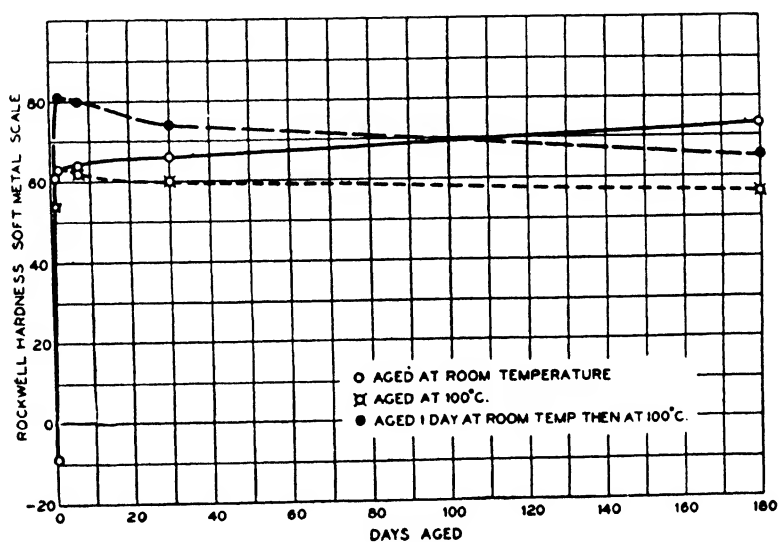


Figure 18. Effect of aging temperature on the hardening of a lead-0.04 per cent calcium-lead alloy.

The material used for cable sheaths is usually a lead-antimony alloy with 1 per cent antimony; a lead-calcium alloy with as little as 0.04 per cent calcium is considerably superior to the lead-antimony alloy with regard to fatigue resistance, tensile strength, and hardness. The best results are achieved when the hot alloy is quenched, permitted to age at room temperature from several days to several months according to the percentage of calcium, and finally is heated for one day to 100°. The latter treatment is important to achieve maximum tensile strength. In the commercial manufacture of lead-calcium cable sheath alloys, no quenching or special heat treatment is required to prepare them for commercial use.

An alloy with 0.11 per cent calcium which was quenched, aged six months, and heat-treated, had a tensile strength of 8200 psi.³³

Table 14 shows the mechanical properties of lead-calcium alloys in comparison with lead-antimony alloys.³⁴

The tensile strength of an alloy of lead-0.04 per cent calcium increased on cold rolling from 5,200 to 6,600 psi; the strength of alloys with 0.08–0.1 per cent calcium decreases. The ductility of lead-calcium alloys is reported to be increased by the addition of tin and magnesium.³⁵ Other investigators apparently do not confirm this statement.

Table 14. Rotating Beam Fatigue Test.

Material	Lowest Break- ing Stress (psi)	Highest Sus- tained Stress (psi)	Properties of extruded tape		
			Tensile Strength (psi)	Elonga- tion (% in 2")	Rockwell hardness soft metal scale
Pb-1% Sb aged 6 months at room temp.	545	466	3000	37	42
Pb-0.040% Ca aged 2 weeks at room temp.	863	784	3470	33	58
Pb-0.040% Ca aged 6 months at room temp.	1101	943	4154	35	64
Pb-0.06% Ca aged 6 months at room temp.	1259	1101	4365	35	65

The second important potential application of lead-calcium alloys is the manufacture of grids for storage batteries for float service. Lead-calcium alloys are not recommended as grids for charge-discharge service. There are, however, large quantities of storage batteries in service on float or reserve type of service for use in emergencies and times of power failure.

The usual material used for this purpose is a lead-antimony alloy containing 9 per cent antimony. A lead-calcium alloy containing but 0.1 per cent calcium proved superior to the antimony alloy. The antimony alloy sulfates in $\frac{1}{10}$ of the time necessary for the sulfation of the calcium alloy, and $\frac{1}{3}$ of the time necessary for the sulfation of pure lead. The calcium alloy retains the electric charges far longer than the antimony alloy, and the corrosion is but slight; its conductivity is about 20 per cent higher than that of the antimony alloy, which is important for a uniform distribution of currents through the grid when large currents are drawn.

The following test may serve as an illustration of the superior properties of the lead-calcium alloys in comparison with the lead-antimony alloys: Lead, lead-antimony alloy, and lead-calcium alloy were subjected for 7 weeks to electrolysis in a bath of 7*N* sulfuric acid. The tensile strength of the samples was then examined and the following decreases were recorded, in comparison with the results given by the samples before the test started.

Lead	19.5%
Lead-1% Calcium	19.3%
Lead-9% Antimony	26.4% ³⁶

Most of the alloys used for storage cells have only small percentages of calcium. It is therefore interesting that an alloy has been developed for this purpose which contains 3 per cent calcium—a comparatively high percentage—and various other components. High hardness and tensile strength are claimed for the alloy.³⁷

It appears that sooner or later lead alloys containing calcium will find a commercial place in the manufacture of batteries. There is some doubt, however, as to whether these

alloys will replace those of the lead-antimony type in part or entirely. It appears that lead-calcium alloys are more difficult to handle under commercial conditions involving the casting of grids. The manufacturing requirements increase the cost, which offsets other advantages. It has not been shown that the lead-calcium alloy has so far been proven on a commercial scale for grids for automotive storage batteries, which is the largest battery use. Under tests where the grids were employed in batteries which float on the line and are not subjected to severe charge and discharge service, there is encouraging evidence of the superiority of the lead-calcium alloy.

For comparative purposes, a number of lead alloys containing calcium are grouped together in Table 16. These are in addition to the ones discussed in the course of this chapter.

Lead-Calcium Alloys for Bearings

During World War I the demand for shrapnel bullets caused a shortage of antimony and antimonial lead, and the lead-barium-calcium alloys known as Ulco³⁸ metal were developed. These hard alloys also found considerable favor for bearings. Investigators have studied the physical properties of lead alloys up to 2 per cent calcium for use as bearing materials. In these, large particles of Pb_3Ca cause hardening and furnish bearing surfaces.

Lead-calcium alloys were introduced for bearings during World War I about the same time in the United States and in Germany. The German alloys were "Lurgi" of a composition of the order of 96.5 per cent lead, 2.8 barium, 0.4 calcium and 0.3 sodium made by the Metallgesellschaft, Frankfurt am Main, or calcium-bismuth-cadmium alloys made by Metallhüttenwerke Schaefer and Schael in Breslau. The first was made by electrolysis of molten chlorides, the second by melting, using calcium carrots as the source of this metal.

The "Lurgi Metall" type alloys were used in the German railroads from 1919 until after the Ruhr occupation. At that time it was found that many locomotives put on side tracks in the non-occupied part of the country could not be moved

after a while due to bad corrosion of the bearings. This was attributed to the presence of the more active barium. "Bahnmetal," widely used as a lining for bearings on German railways, contained about 0.75 per cent calcium with 0.5 per cent sodium and 0.05 per cent lithium. It proved unsuitable on account of its tendency to oxidize and volatilize at the high service temperatures.³⁹ Bahnmetal was the product of chloride electrolysis and reached the stage of being accepted as a standard.

Alloys of lead containing barium and calcium are produced by the electrolysis of fused salts in which fused chlorides of barium and calcium are electrolyzed over a bath of molten lead as a cathode. Calcium-barium-lead alloys are described in the patent literature.⁴⁰ They are suitable for bearing metals. In the commercial manufacture of these alloys, iron pots of about 2 tons capacity each are partially filled with high-quality pig lead. Each pot is set in brickwork over a coal-fired hearth. The lead in the pot is melted by external heat. The molten lead is covered with a layer of a mixture of calcium and barium chlorides of high purity in such proportions as to give a low melting point. The salt layer is usually 3 to 4" thick. Each pot is equipped with a graphite anode at the center, arranged for lowering or raising the electrode. Figure 19 shows a battery of electrolytic pots at the plant of the United Lead Company at Keokuk, Iowa. In starting, the anodes are immersed in the chlorides which have sufficient resistance to the current so that they can be fused directly. External firing is uniform and temperature control is obtained electrically by raising or lowering the anodes. The fused salts are electrolyzed, the resulting barium and calcium being adsorbed in the molten lead cathode. Anode effects, metal fogging and arcing, as well as the formation of calcium and barium carbides, reduce the efficiency of the process. Approximately three days of electrolysis is required to produce a lead alloy containing 2 per cent of the alkaline-earth metals. The molten salts and carbides tend to freeze at the top and around the periphery of the interior of the pot, forming a hard surface. This acts as an insulator and prevents loss of cur-

rent which might pass through the fused electrolyte from the anode directly to the iron pot instead of to the molten lead cathode. If the crust forms too near the anode, it may need to be broken down to give good operating conditions. The rate of adsorption of the calcium and barium by the lead seems to be logarithmic, a condition which is probably due to equilibria set up between the lead and the alkaline-earth metals at one end and the decomposition reactions of the fused electrolyte at the other.

During the course of electrolysis, samples of the molten cathode metal are removed and the alkaline-earth metal



Figure 19. Battery of electrolytic pots at the plant of the United Lead Company, Keokuk, Iowa (Courtesy United Lead Co.).

content determined. When the desired concentration has been reached, current is shut off from the pots. The molten alloy is run out at the bottom into a carrying ladle in which it is conveyed to a large mixing kettle for the production of a uniform batch of considerable tonnage.

A number of lead-calcium alloys suitable as bearing metals have been developed in England and on the Continent. The alloy "Can" contains 1.75 per cent calcium, 1 per cent strontium, 1 per cent barium, 0.1 per cent sodium, and 1.35 per cent copper. Another bearing material of the same make contains 0.35 per cent calcium, 0.3 per cent strontium, 0.5 per cent copper, and 0.4 per cent sodium, the balance in both cases being lead. The "Union Bearing Metal" contains 0.2

per cent calcium, 1.5 per cent magnesium, and 98.3 per cent lead. "Satco Metal" contains 0.6 per cent calcium, 0.15 per cent mercury, 2.5 per cent tin, a little sodium, and the balance lead. The alloys are claimed to give satisfactory service.⁴¹ "Union Metal" is of superior hardness and resistance in comparison with an 80 per cent tin alloy.

A "Union Metal" bearing had to be overloaded 245 per cent before it seized at 760 rotations per minute, which corresponds to a speed of 2.38 meters per second: load, 51 kg per sq cm.⁴²

Table 15.

Temp. (°C)	Brinell Hardness	
	"Union Metal"	80% Tin Metal
20	28-30	30-32
50	25	23
100	20	14
150	15	10.5

Chemical Methods for Producing Lead-Calcium Alloys

As calcium has a high heat of reaction with lead, a somewhat violent reaction takes place when it is introduced into molten lead.

It is often easier and more economical to produce lead-calcium alloys by chemical methods than by the use of calcium metal made by electrolysis. The chemical methods of interest involve the reduction of calcium compounds by aluminum, by sodium, or by lead (as in the carbide procedure).

The aluminum process consists of reducing lime with aluminum and reacting the aluminide with lead. It was suggested by Kirsebom,⁴³ but seems not to have been put into practice on any large scale, probably as the result of the high cost of the reducing agent. The aluminide may be readily made.⁴⁴ The separation of aluminum from lead for reuse may be quite difficult.

Calcium silicide with 22 per cent calcium does not react with lead at temperatures up to 1200°. Under the most favorable conditions, an alloy with 0.3 per cent calcium may be made. The stability of calcium compounds seems to be in the following descending order: Bi_2Ca_3 — Pb_3Ca — CaSi_2 — CaAl_3 — CaC_2 .

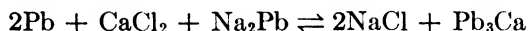
Table 16. Lead Alloys Containing Calcium.

Composition										Outstanding Property	Chief Application	Reference or Name
Ca	Al	Cu	Li	Mg	Na	Pb	Sa	Others				
0.04	—	—	—	—	—	Bal.	—	—	—	good fatigue and tensile strengths	cable sheaths	<i>Metals and Alloys</i> , 1, 405 (1930).
0.10	—	—	—	—	—	Bal.	—	—	—	resistance to sulfating	storage battery grids	<i>Trans. Electrochem. Soc.</i> , 68, 292 (1935).
0.02	—	—	—	0.02	—	Bal.	0.02	—	—	high strength and creep resistance	cable sheaths	"Tubeloy"; <i>Metals and Alloys</i> , 15, 86 (1942).
0.60-0.73	0.1-0.2	—	0.03-0.04	—	0.58-0.62	98.3-98.7	—	—	—	saves tin	railway bearings	German alloy "Bahmetal"
0.03-3.0	—	—	—	0.01-0.03	—	96.7-99.96	—	—	—	3 Ca alloy has high hardness and strength	storage battery grids	Can. P. 384,675
1.0-1.5	—	—	—	—	0.01	99.0-99.5	—	—	—	—	—	French P. 833,471
0.01-0.1	—	—	—	—	—	99.64-98.15	0.35-1.75	—	—	—	—	U. S. P. 2,159,124
2.7-2.9	—	—	—	—	0.45	96.55-96.85	—	—	—	—	—	<i>Z. Metallkunde</i> , 30, 52 (1938).

0.13 0.10	—	—	—	trace	99.87	—	—	—	—	—	—	—	—	—	—	Z. Metallkunde, 30, 52 (1938).
0.10- 10.0	—	6	—	—	Bal.	—	—	—	—	—	—	—	—	—	—	Ger. P. 584,399
0.3- 1.0	0.02- 1.0	—	0.02- 0.22	0.02- 0.22	95.24- 99.07	0.5- 2.0	0.1-0.5 Hg, 0.02-0.22 K	—	—	—	—	—	—	—	—	British P. 374,003
0.02	0.05	—	—	—	98.65	1.0	0.1 Hg	—	—	—	—	—	—	—	—	Can. P. 321,681
0.02- 0.1	—	—	—	—	Bal.	—	—	—	—	—	—	—	—	—	—	British P. 356,801
1.0	—	—	—	—	99.0	—	—	—	—	—	—	—	—	—	—	Can. P. 306,610
0.35	—	0.5	—	0.4	98.45	—	0.3 Sr	—	—	—	—	—	—	—	—	British alloy "Can"
2.0	—	—	—	1.5	96.3	—	—	—	—	—	—	—	—	—	—	"Union Bearing Metal".
0.6	—	—	—	trace	96.75	2.5	2 Ba, 0.15 Hg	—	—	—	—	—	—	—	—	"Sateco Metal"
2	—	—	—	—	—	—	1 Ba	—	—	—	—	—	—	—	—	"Frary Metal"

The Chloride Process. The reactions of sodium alloys with alkaline-earth metal chlorides in the fused state was disclosed by Caron in 1859.⁴⁵ He prepared barium and strontium-tin alloys in this way. The principle was forgotten until 1917⁴⁶ when Kroll used it again to produce lead-calcium-barium from lead-sodium and molten calcium chloride-barium chloride.

The reaction proceeds according to the equation:



This equilibrium has been studied by Lorenz and his students.⁴⁷ Sodium metal reduces molten calcium chloride to a small extent.⁴⁸ A salt with 98 per cent CaCl_2 , balance NaCl , stays in equilibrium with a sodium metal containing about 2 per cent calcium. However, if lead is introduced into this system, the equilibrium is shifted in favor of calcium reduction because the exothermic compound Pb_3Ca is formed. The concentration of the calcium in the alloy is governed by the concentration of CaCl_2 in the salt bath. When a high calcium and low sodium content is desired in the metal, the salts must be rich in CaCl_2 . The production of sodium-free alloys is therefore costly. However, this process is commercial with alloys of fairly low sodium content, of the variety required in bearing alloys, *e.g.*, 0.25 per cent. The salts may be divided into three parts, the final salts running as high as 60 per cent NaCl . Under such conditions the salt consumption is about 8 lb of CaCl_2 per pound of calcium produced in a 2.5 per cent calcium alloy. The waste salts may be reclaimed by wet methods. They are free of lead. The cost of production in the United States, based on 1944 market prices for the reagents, may be about 60 cents per pound, including wages, kettle maintenance, and fuel.

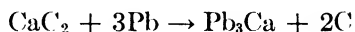
The operation is as follows: Lead is poured into the molten CaCl_2 - NaCl salts of a previous batch, supplemented with fresh salts if necessary. The melting point of the salts is below 780° . This permits operation at a fairly low temperature and reduces the cost of kettle maintenance. Sodium in the form of two-pound ingots is rapidly plunged into the lead through the molten salt layer. The sodium must be dry. The work-

men are protected from splashes by iron plates covering the kettle. The reaction is extremely rapid. When liquid sodium is injected, the end point is reached within two minutes. The sodium seems to disperse rapidly in the lead bath since the temperature is not far from the boiling point of sodium. Little stirring is required. The salts are removed and the treatment repeated with two additional portions of salts. The two final salt additions are saved for reuse. With plain calcium alloys, the finished metal is spooned out, since it has a fairly high melting point when high in calcium. A special overflow ladle is used for the separation of metal and slag. The ladle can be moved in front of the molds. The calcium-barium alloy is usually tapped through a stopcock. The slag operation takes about 8 hours; one batch can be made in 24 hours. The usual kettle size is 10 tons. The metal should be covered with dry sand, after the removal of the salts, if the product is to stand in the open for a period of time. The salts are hygroscopic and react with moisture of the air. The metal fog reacts with moisture, producing hydrogen which pops up and burns at the surface. The composition of the alloy is generally obtained with some accuracy. The sodium efficiency is of the order of 75 per cent. Adjustments are made either with sodium or with master alloys of known composition, on the basis of a rapid analysis while the metal is held in the molten state. The salts must be free of phosphorus and arsenic; these form phosphides and arsenides of calcium and sodium and, consequently, arsine and phosphine by contact with the moisture of the air. The poisonous character of these compounds is well known.

Chloride equilibrium reactions are not limited to lead alloys, as Caron has already shown, but other heavy- and light-metal alloys with alkaline-earth metals can be made by a similar procedure. The alkaline-earth and the alkali metals are mutually interchangeable. For instance, strontium-lead can be made by reacting calcium-lead with molten strontium chloride. Lithium can be introduced into many metals in this way. The incentive for the use of this method is limited by the necessity of reclaiming waste salts containing valuable chlorides.

Magnesium-lead does not react with either sodium or calcium chloride since the affinity of magnesium for chlorine is too low. However, sodium-lead or calcium-lead reacts quantitatively with magnesium chloride.

Carbide Process. Reactions of PbO and PbCl_2 with CaC_2 in the presence of other chlorides yield calcium-lead alloys. Moissan,⁴⁹ Bullier,⁵⁰ von Kugelchen, Pring, and Tarugi⁵¹ operated along such lines. However, these investigators apparently overlooked the fact that CaC_2 reacts directly with lead according to the equation:



This reaction, which Kroll states he discovered in 1916, is the basis of the carbide process.⁵² Other alkaline-earth carbides work in the same manner. Barium-lead can be made by heating BaC_2 with lead. The lead-alkaline earth metal alloys can be produced by reducing CaO or BaO with carbon in the presence of lead at about 1500° , preferably in a carbon resistor furnace. Lead volatilization is a limiting factor. A number of heavy-metal alloys have been made by the carbide reaction.

Calcium carbide reacts readily when heated in open air. When finely divided it burns easily. The flux and the gas processes have evolved from the necessity of keeping air out. The flux process⁵³ as developed by Betterton consists of dropping pea-size carbide into a kettle containing molten CaCl_2 - NaCl and lead while stirring at a rate of about 200 reversals per minute. The NaCl addition is small and functions mostly as a fluxing agent to keep the temperature low in the interest of kettle preservation. The operation is conducted at 750° . Calcium chloride is a good solvent for CaO . Carbide contains up to 20 per cent CaO , which obstructs the path of the lead. The mixer tears off the skins of CaO and free graphite and the flux brings the former into solution. The process lasts 6-10 hours for the production of a 3.5 per cent calcium alloy. The salt consumption is about 1.7 pounds per pound of calcium in the alloy. The carbide efficiency may be as high as 75 per

cent. High-grade carbide is used. The salts, after the run, are free of lead. Molten CaCl_2 retains some water in chemical combination. This water reacts with the carbide to produce acetylene.

A modification of this process has been patented by Siegens.⁵⁴ A flux of $\text{CaCl}_2\text{-CaF}_2$ is used and 1 per cent aluminum is added to the salts. A 6 per cent-calcium alloy is made in 3 to 4 hours with a salt consumption of 2.5 pounds per pound of calcium introduced into the lead. The CaC_2 efficiency is said to be almost theoretical.

In combination with the debismuthizing process, the salts can be supplied from the chlorination phase. The cost of production per pound of calcium in the alloy, based on 1944 prices for carbide and chloride, including wages, kettle maintenance and fuel, may be of the order of 30 cents.

When more NaCl is used in the flux, all kinds of sodium-bearing lead-calcium alloys can be made at temperatures as low as 600° . Pure lead-sodium alloys have been produced in this way.⁵¹ This is a combination of the chloride method with the carbide process, since there are reverse reactions between calcium-sodium in the alloy and $\text{CaCl}_2\text{-NaCl}$ in the salts. Such a combined process has not found application, as there is little use for high-sodium lead-calcium alloys.

The carbide "gas" process,⁵⁵ according to the patent description, consists of heating lead with high-grade carbide powder in heat-resisting steel containers to a temperature between 1100° and 1200° under a non-oxidizing or reducing atmosphere. Nitrogen cannot be used, as calcium rapidly reacts to form nitrides. The carbide is stirred into the lead. After cooling, the lead-calcium is poured off, the dry dross removed and reprocessed for lead recovery.

The basic "carbide" process for lead-calcium alloys which was discovered by Kroll and his associates in 1916 and patented⁵⁶ in Germany but not in the United States, was tried on a small scale. In the laboratory, alloys up to 5 per cent calcium or barium were easily made. Operations were carried out under a gas seal. This proved successful in 1928 and was

patented in the United States.⁵⁷ The flux method, developed in 1925, was not accepted by German manufacturers until 1936. It had been put into practice independently by Betterton⁵⁸ in the United States. Kroll introduced this practice in Europe.

Debismuthizing of Lead

The debismuthizing of lead was discovered in 1917 when it was found that on the addition of bismuth to a lead which contained calcium, bad liquation took place. German and American patents were granted.⁵⁸ The first laboratory experiments resulted in a bismuth content of 0.05 per cent in the purified alloy, starting from any bismuth content in the raw lead. A number of commercial runs were made in the Norddeutsche Affinerie in Hamburg in 1922, using lead with bismuth contents up to 3 per cent. No improvement in reference to the purified lead could be found as far as the 0.05 per cent bismuth limit is concerned. The process was abandoned in Europe, since the maximum bismuth content tolerated in soft refined lead is below 0.01 per cent. This limit is unobtainable by the calcium process. The quantities of bismuth-bearing lead available in Europe are too small to permit operation of a plant of economic size. In the United States large quantities of lead with about 0.3 per cent bismuth, mainly of Mexican origin, had to be treated. A bismuth content of 0.05 per cent is tolerated in American corroding lead. A.S.T.M. specification B 29-40T gives the chemical requirements for pig lead as shown in Table 17. Chemical lead is shown in this specification as tolerating a maximum of 0.005 per cent bismuth, while acid lead tolerates a maximum of 0.025 per cent, and a soft undesilverized lead a maximum of 0.005 per cent. While the A.S.T.M. specification indicates a tolerance of 0.05 per cent maximum for bismuth in corroding grades, it appears that the corrodors actually prefer a lead with substantially lower bismuth content.

Betterton developed a commercial process on the principle of the calcium liquation. His work on the debismuthizing process was to a considerable extent motivated by the desire to increase

Table 17. Chemical Requirements

	Corroding Lead*	Chemical Lead*	Acid Lead*	Copper Lead*	Common Desilverized Lead A*	Common Desilverized Lead B*	Soft Undesilverized Lead*
Silver, max. (%)	0.0015	0.020	0.002	0.020	0.002	0.002	0.002
Silver, min. (%)	0.002
Copper, max. (%)	0.0015	0.080	0.080	0.080	0.0025	0.0025	0.04
Copper, min. (%)	0.040	0.040	0.040
Silver + copper, max. (%)	0.0025
Arsenic, max. (%)	0.0015
Antimony + tin, max. (%)	0.0095
Arsenic + antimony + tin, max. (%)	0.002	0.002	0.015	0.015	0.015	0.015
Zinc, max. (%)	0.0015	0.001	0.001	0.002	0.002	0.002	0.002
Iron, max. (%)	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Bismuth, max. (%)	0.05	0.005	0.025	0.10	0.15	0.25	0.005
Lead (by diff.), min. (%)	99.94	99.90	99.90	99.85	99.85	99.73	99.93

* *Explanatory Note:*

Corroding lead is a designation that has been used for many years in the trade to describe lead which has been refined to a high degree of purity.

Chemical lead has been used for many years in the trade to describe the undesilverized lead produced from Southeastern Missouri ores.

Acid lead is made by adding copper to fully refined lead.

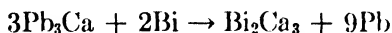
Copper lead is made by adding copper to fully refined lead.

Common desilverized leads A and B are designations that are used to describe fully refined desilverized lead.

Soft undesilverized lead is used in the trade to describe the type of lead produced from ores of the Joplin, Mo., district.

the amount of lead of the chemical lead specification because there have been periods when the supply of chemical lead from its particular mineral resources has been quite inadequate for American requirements, and it has generally commanded a premium over common and ordinary desilverized leads. The main improvements were: The simultaneous use of magnesium and calcium which brings the bismuth limit down below 0.02 per cent, chlorination to eliminate residual calcium, the use of a suitable machinery to handle the drosses, and the production of high-purity lead with less than 0.001 per cent bismuth by the antimony method. The debismuthizing process with calcium and magnesium is said to be used today on the basis of 300,000 tons of lead per year. Some authorities state it to be the greatest improvement in lead refining since the desilverization process with zinc was put into practice by Parkes. The American patent rights were bought by the American Smelting and Refining Company in 1931.

Alkaline-earth and alkali metals form stable compounds with most metals of the antimony group. These have high melting points and are only slightly soluble in the base metal. Sodium, calcium and magnesium, which must be considered as alkaline-earth metals, can therefore be used as cleansers for alloys containing antimony, arsenic, tellurium, selenium, and bismuth. This principle has been described in the basic patents and in an early publication.⁵⁹ When using calcium, antimony and arsenic can be separated from tin. Bismuth can be removed from lead by the use of calcium. The reaction is:



Bismuth contained in lead is therefore first tied up with calcium when calcium metal is added to the molten lead. There is a slight solubility of the compound Bi_2Ca_3 in lead at its melting point, which amounts to 0.048 per cent residual bismuth. Only after all the bismuth has been combined with calcium can lead react to form Pb_3Ca . The equilibrium diagram, bismuth-lead, shows no compound. The main compound in the series, bismuth-calcium, as shown by Kurzyniec⁶⁰

is Bi_3Ca_2 . The melting points of a number of compounds of bismuth with alkali and alkaline-earth metals are as follows: Bi_2Ca_3 928°; K_3Bi 671°; Li_3Bi 1145°; Bi_2Mg_3 823°; Na_3Bi 775°. Any one of the additions, potassium, sodium, lithium, or magnesium, produces liquation in lead containing bismuth, but only with alloys fairly high in bismuth. The debismuthizing effect is low, as far as the final bismuth content is concerned. However, Betterton found that the good debismuthizing action of calcium can be improved by adding magnesium plus calcium. It has also been proposed to use combinations of calcium with alkali metals. These metals reduce the solubility of Bi_2Ca_3 in lead.

Betterton⁶¹ summarized the major factors as follows: It is important to operate at a minimum temperature with a minimum calcium addition. The calcium requirements depend on the bismuth content. They are of the order of 0.6 lb per ton for a 0.1 per cent-bismuth lead and 1 lb per ton for a 0.5 per cent-bismuth lead, which is relatively less for higher bismuth contents. In debismuthizing with calcium plus magnesium, equal amounts of these metals are most efficient. To obtain a bismuth content of 0.02 per cent in the final lead, the requirements are for a 0.1 per cent-bismuth lead, 1.3 lb calcium and 1.3 lb magnesium per ton; for a 0.5 per cent-bismuth lead, 2.15 lb calcium and 2.15 lb magnesium per ton. Again the consumption of reagent is relatively smaller for higher bismuth contents. Zinc, up to 0.3 per cent, does not interfere, but arsenic and antimony above 0.01 per cent use up calcium and magnesium. Copper and silver in the usually low amounts present in lead do not react.

The operation is described by Betterton: Soft, desilverized lead with less than 0.01 per cent antimony plus arsenic is melted and heated to 750°F. Dross-carrying bismuth and calcium with less than 20 per cent bismuth from previous batches are added, reacted with the bath, and skimmed off. The dross then contains more than 20 per cent bismuth and goes to the dross treatment for bismuth recovery. Lead-calcium alloy and magnesium are added and rapidly dissolved,

using a lead pump. The bath is mixed for 30 minutes at 680°F and the dross is removed for treatment with the next batch. The mixture is cooled close to the melting point of lead while the dross is skimmed off. Reheating eliminates 0.02 per cent bismuth and 0.05 per cent calcium. The latter is eliminated either by a chlorine or lead chloride cleansing.⁶²

The dross with more than 20 per cent bismuth is liquated under salts and brought up to at least 50 per cent bismuth and 5 per cent calcium plus 5 per cent magnesium. A liquated metal with little bismuth is brought back for renewed treatment with calcium-magnesium. The recycled bismuth amounts to 8 per cent of the total. Betterton does not give details as to the method for producing bismuth metal from the rich dross. The compound Bi_2Ca_3 theoretically contains 77.6 per cent bismuth which could be approached by careful liquation. The calcium-magnesium content is eliminated with chlorine, leaving bismuth behind, contaminated with fairly large amounts of lead. It is claimed⁶³ that lead may be eliminated from bismuth with chlorine or bismuth chloride since lead has a higher chlorine affinity than bismuth. Raw bismuth with more than 90 per cent bismuth can be refined by aqueous electrolysis in $\text{BiCl}_3\text{-HCl}$ solution.⁶⁴

To produce a lead with less than 0.005 per cent bismuth, Betterton recontaminates the lead with antimony after normal debismuthizing.⁶⁵ In this way, the bulk of calcium-magnesium antimonide is produced, which collects the highly dispersed bismuthide and brings it to the bath surface.

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Chapter IX

Magnesium-Calcium Alloys

Stockem¹ showed that calcium and magnesium alloy in all proportions. Baar² studied its constitution by the freezing point method. Baar's calcium contained 0.55 per cent aluminum and iron plus 0.28 per cent silicon, with an unknown amount of nitrogen. Kremann, Wostall, and Schöpfer³ studied the system by electrical resistance methods with particular reference to the compound Ca_3Mg_4 . The constitution diagram is given in Figure 20. There are two eutectics, one at 21.5 per cent by weight of magnesium with a melting point of 450° and the other at 82 per cent magnesium and 18 per cent calcium with a melting point of 516° . Magnesium dissolves in calcium and lowers the melting point; calcium dissolves in magnesium and lowers its melting point. The intermetallic compound, Ca_3Mg_4 , is approximately 44 per cent magnesium and melts at 720° . The addition of calcium or magnesium lowers the melting point, as each dissolves in the compound.

Magnesium alloys have increased in industrial importance in that magnesium has become much more easily available and cheaper than previously. The use of magnesium and its alloys, especially in the construction of aircraft, has increased many times.

Calcium is one of various components used in the manufacture of magnesium alloys. There are only a few cases on record where a binary magnesium-calcium alloy has been used in practice. A binary magnesium-calcium alloy with 18-23 per cent calcium is employed for storage purposes be-

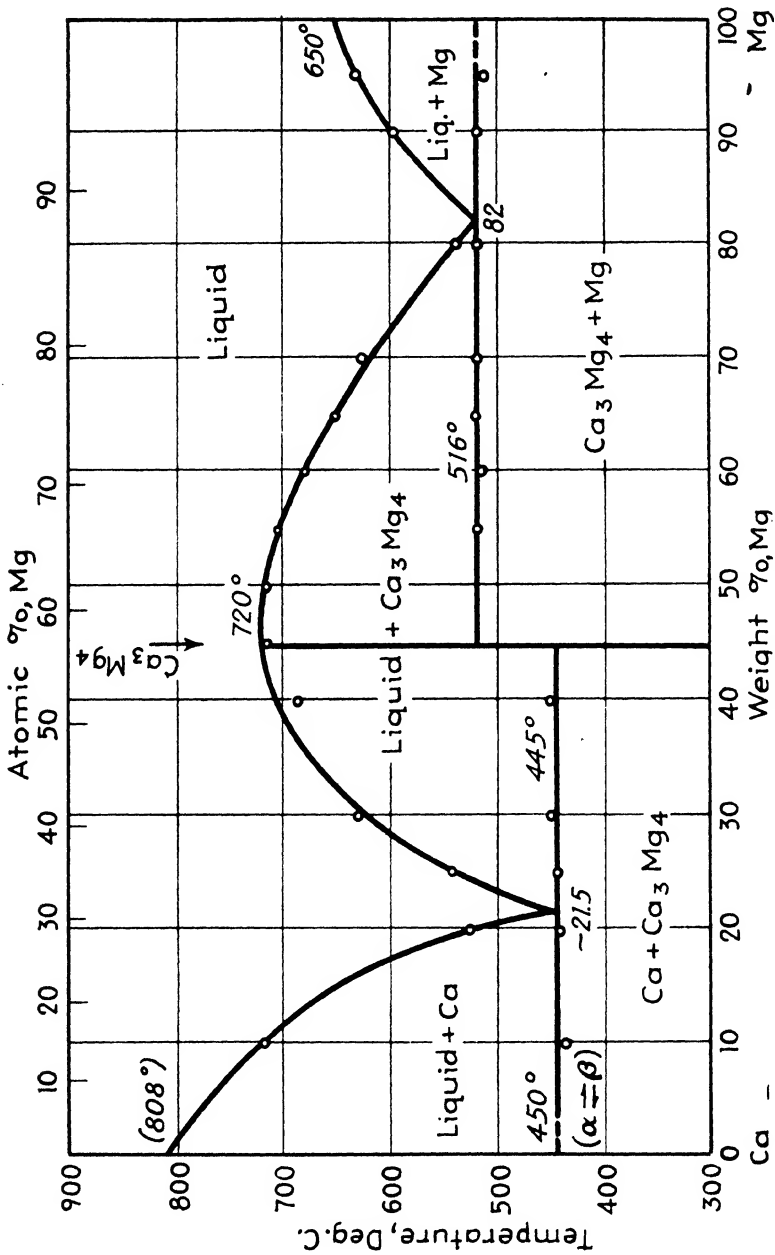


Figure 20. Constitution diagram of magnesium-calcium alloys.

cause calcium in this form is less subject to deterioration by atmospheric influences than in its pure form, probably on account of extremely good stability of the alloy. This material is also applied as a master alloy in the production of magnesium-calcium alloys.⁴

It is stated that the addition of calcium to magnesium alloys contributes a considerable improvement in their mechanical properties, and has the additional advantage of decreasing the inflammability of the magnesium metal. The improvement in the mechanical properties caused by the addition of calcium to a magnesium alloy is illustrated in Table 18.

Sheet metals with 2 per cent manganese and 0.14 per cent calcium showed an elongation of 18–25 per cent at the breaking point.

Table 18. "Magnewin."

	2% Mn, 3% Al, bal. Mg	2% Mn, 3% Al, 0.13% Ca, bal. Mg
Tensile strength (kg/mm)	24	27
Yield point (kg/mm)	15	21
Elongation (%)	1.5	3

Magnesium alloys to which as little as 0.15 per cent calcium has been added show much finer grain structure than the original alloy free of calcium. The difference of grain size between alloys with and without an addition of calcium is of the order of 1:500. It is reported that addition of calcium in the order of 0.45 per cent calcium to magnesium and magnesium alloys, although hardening the alloys somewhat, improves the rollability, extrusion and drawing by both hot- and cold-fabrication procedures.

The fine grain of calcium-containing magnesium-manganese alloys might be explained by the formation of small microspherulitic crystals which consist either of manganese or of the compound Mg_2Ca , depending on whether calcium causes coagulation of the finely divided manganese or the high manganese content reduces the solubility of calcium in magnesium. The small crystals are clearly visible in the calcium-containing alloy.

Bulian⁵ states: "It is important that the addition of calcium to the magnesium-manganese alloys does not impair the high corrosion resistance of the alloy."

The use of magnesium metal as a structural material for aircraft makes it necessary to know how the corrosive effect of sea water can be best counteracted, especially in the case of flying boats.

Obinata and Hayasi⁶ tested a number of magnesium alloys and found that magnesium-calcium alloys containing 0.5–2 per cent calcium were among those showing the highest relative corrosion resistance. During testing the alloys were submerged for sixty days in a 2.5 per cent aqueous sodium chloride solution.

The same investigators studied the effect of calcium on a magnesium-3 per cent cadmium alloy and found the same improved corrosion resistance toward a 2.5 per cent aqueous sodium chloride solution. Although no high tensile strength can be expected from these alloys, the addition of 0.2–0.8 per cent calcium increases the hardness of the alloys. The increasing hardness, on account of the addition of calcium, is accompanied by a decrease in electrical resistance, which might result from the action of calcium as a refining agent.⁷

Einerl and Neurath⁸ have reported that the addition of calcium to magnesium alloys permits high temperatures in the heat treatment and a shortening of the time of treatment. A heat-treated quenched and aged magnesium alloy containing 8–8.5 per cent aluminum, 2.5–3 per cent silver, 0.4 per cent manganese, and 0.2 per cent calcium had a yield point of 17 tons/sq in, a tensile strength of 25 tons/sq in, and 4 per cent elongation.

Magnesium-calcium alloys are suggested as ingredients in the manufacture of porous cement (gas concrete). The pulverized alloy is intimately mixed with the other components of the concrete and reacts slowly with the alkaline concrete mass, leaving large numbers of fine pores.⁹

Ternary magnesium-rich alloys with calcium and zinc have been made by Paris.¹⁰ Among the best of these alloys are

Table 19. Corrosion of Magnesium-Calcium Alloys.*

Corroding liquid	Loss of weight in grams per sq cm per day			
	pure Mg	Mg plus 0-1.35% Ca	Mg plus 1.45-9% Ca	Mg plus 17-26% Ca
Sea water	770	127	370	4500
0.1 N HCl	815	330	700
.01 N HCl	16	2	10	875
.01 N NaOH	0.40	0.35	0.40

* Novotny, Wormnes, and Mohrheim, "Untersuchungen in den Systemen Aluminium-Kalzium, Magnesium-Kalzium, und Magnesium-Zircon," *Metallkunde*, **32**, 39 (1940).

Table 20.

	1% Ca, 1% Zn, Bal. Mg	2% Ca, 2% Zn, Bal. Mg
Density	1.748	1.766
Hardness (Brinell)	59	48
Charpy impact (kg/sq in)	0.64	0.073

Table 21.*

	Tensile strength (kg/ mm ²)	Resili- ence (kg/ mm ²)	Brinell hardness		Sp. gr.
			edge	center	
98% Mg, 1% Ca, 1% Zn	5.6	0.64	63	54	1.74
96% Mg, 2% Ca, 2% Zn	11	0.73	52	44	1.77

* Mondain-Monval and Paris, 14me Congr. Chim. Ind. Paris (October, 1934).

Table 22.¹⁵

	Mg ₃ Ca ₃	Mg ₄ Ca ₃	Mg ₂ Ca
Melting point (°C)	725	715	714
Melting point eutectic with Ca(°C)	460	446	
Ca in eutectic with Ca(%)	82	78.7	
Melting point eutectic with Mg (°C)	525	516	516
Ca in eutectic with Mg(%)	17	18.7	16.3

those which contain 1 per cent calcium and 1 per cent zinc, balance magnesium, or 2 per cent calcium and 2 per cent zinc, balance magnesium.

An addition of 1 per cent calcium to a magnesium-aluminum alloy with 8 per cent aluminum is reported to eliminate the

difficulties which usually accompany the casting of this alloy and causes only a small lowering of the strength of the alloy.¹¹

McDonald¹² claims that an addition of calcium up to 0.13 per cent improves the ductility of magnesium, from 0.13 to 0.3 per cent an addition of calcium gives a slight increase in the ductility, and above 0.3 per cent an addition of calcium causes a decrease in the ductility of a magnesium-calcium alloy.

Alloys with high calcium or zinc content have no valuable properties, according to Paris.¹⁰ The properties of the magnesium-zinc-calcium alloys are given in Table 21.

Magnesium-calcium alloys may be made with master alloys of high calcium content or by inserting a piece of metallic calcium wrapped in a metal screen in the molten metal. Another method is the electrolysis of a mixture of fused magnesium and calcium salts. Du Bellay¹³ treats dolomite with dilute sulfuric acid, mixes the blended sulfates with carbon, and reduces them to sulfides in an atmosphere of sulfur vapor. The mixed sulfides are then electrolyzed in a bath of fused halogen salts. This method can also be used for the individual production of calcium and magnesium, which can be separated on account of their different solubilities in dilute sulfuric acid, in which magnesium dissolves, but not calcium sulfate. This method seems very attractive, but it proved very dangerous in operation, and caused numerous fatal accidents. Furthermore, its operating costs are too high.

Haughton¹⁴ made an interesting observation when he melted magnesium in stainless steel crucibles and added calcium in the form of borings. When he analyzed the alloy he found that unpredictable losses of metal had occurred, and that the loss of calcium was usually much higher than that of magnesium. Alloys made up to contain 18 per cent calcium actually contained only 14.42, 14.70, and 12.98 per cent; others which should have contained 10 per cent calcium had only 8.49, 8.31, and 6.82 per cent.

A number of compounds of magnesium and calcium have been found and investigated, but no complete agreement has been reached about their composition. Various investigators

have found the compounds Mg_5Ca_3 , Mg_4Ca_3 , and Mg_2Ca . The melting points of Mg_4Ca_3 , Mg_2Ca and their eutectic mixtures are so close that it is very likely that these formulas are different expressions for the same compound; for example, the melting point of Mg_5Ca_3 and its eutectic mixture with magnesium is close enough to the other melting points to suggest that the difference is caused by an experimental error.

Paris¹⁰ found in the ternary system magnesium-zinc-calcium the compound $Mg_5Zn_6Ca_2$, which has a melting point of 492–495°.

The solubility of calcium in magnesium is given in Table 23, the results of thermal analysis of magnesium-calcium alloys in Table 26, the electrical conductivities in Table 24, and the thermal conductivities in Table 27.

For comparative purposes a number of magnesium alloys containing calcium are tabulated, with their properties and applications, in Table 25.

Table 23.¹⁵ Solubility of Calcium in Magnesium.

Temperature (°C)	Calcium (%)
516	0.78
500	0.66
450	0.42
400	0.29
350	0.21
300	0.18

Table 24. Electrical Conductivity of a Magnesium-Calcium Alloy.¹⁶

Temp. (°C)	Conductivity (ohm ⁻¹ × cm ⁻¹)	Resistivity (ohm × cm)
20	20.6 × 10 ⁴	4.85 × 10 ⁻⁶
50	18.7 × 10 ⁴	5.35 × 10 ⁻⁶
150	14.2 × 10 ⁴	7.05 × 10 ⁻⁶
250	10.5 × 10 ⁴	8.75 × 10 ⁻⁶

Table 25. Magnesium Alloys Containing Calcium.

Composition										Outstanding Property	Chief Application	Reference or Name
Ca	Ag	Al	Cd	Ce	Mg	Mn	Zn	Others				
0.1-0.2	—	0.3	—	—	97.7	2	—	—	—	increased strength, lower inflammability	aircraft parts	"Magnewin," <i>Z. Metallkunde</i> , 31, 302 (1939).
0.5-1	—	—	3	—	96-96.5	—	—	0.5-1 Hg* 0.5-1 Sn* 0.5-1 Sr* 0.5-1 Te*	—	improved corrosion resistance	*(present singly or in pairs)	<i>Tetsu-to-Hagane</i> , 24, 34 (1938).
0.2	2.5-3	8-8.5	—	—	Bal.	0.4	—	—	—	high strength; better heat treating properties	Precipitation-hardened parts	<i>Chem. Age</i> , 47, 107 (1942).
1	—	8	—	—	Bal.	—	—	—	—	better casting properties	strong castings	<i>Eng. & Tek. (Russ.)</i> , p. 670 (1936).
0.1-2	—	—	0.1-10	—	Bal.	—	0.1-10	0.1-5 Pb	—	good hot workability	rolled shapes, sheets and extrusions	F.P. 730,088
0.05-1.0	0.3-10	—	—	—	Bal.	—	0.1-4	—	—	—	—	B.P. 544,350
0.05-0.5	—	—	3-7	0.1-0.7	Bal.	1.5-2.5	—	—	—	good workability *(present in 2.-286,866)	sheet products	U.S.P. 2,286,866,-867
0.01-1.0	—	—	—	0.01-0.1	Bal.	—	—	1-15 Tl	—	good workability	sheet products	U.S.P. 2,286,870
0.05-1.0	—	—	—	—	Bal.	—	—	0.5-12 Cu	—	good workability	sheet products	U.S.P. 2,221,245
0.05-1.0	0.3-8	—	—	—	Bal.	0.1-3.0	0.1*-8	0.1-S Sn	—	(* present in 2,221,248 only)	properties and applications same as above	U.S.P. 2,221,248 and -249

0.05-1.0	—	—	—	Bal.	—	—	0.1-10 Ti	good workability	sheet products	U.S.P. 2,221,250
0.01-1.0	0.1-2	—	—	Bal.	—	—	—	good workability	sheet products	U.S.P. 2,232,922
0.01-1.0	—	—	—	Bal.	—	—	1-10 Ni	good workability	sheet products	U.S.P. 2,233,008
0.01-1.0	0.3-10	0.3-10	1-15	Bal.	—	—	—	good workability	sheet products	U.S.P. 2,233,265
0.01-1.0	—	0.3-12	—	Bal.	—	—	1-20 Ti	good workability	sheet products	U.S.P. 2,233,953
0.01-1.0	—	—	—	Bal.	—	0.3-8	1-20 Ti	good workability	sheet products	U.S.P. 2,233,959
0.05-1.0	0.3-12	—	—	Bal.	0.1*-3 0.1*-10	—	—	*Zn and Mn present together only in 2,221,247 and -239	properties and applications: as above	U.S.P. 2,221,243, -245, -247, -251, -252, -256, -259
0.1-5	—	—	—	Bal.	0.1-4	—	1-4 Co (optional), 1-4 Ni	—	—	B.P. 472,771
4-6	1.5-3	6-8	—	Bal.	4-6	4-6	—	good tensile properties	—	U.S.P. 2,126,010
0.1-2	—	1-15	—	Bal.	0.1-1	—	0.5-22 Pb	good corrosion resistance	—	U.S.P. 2,026,592
0.1-2	—	—	1-10*	Bal.	—	1-10*	0.5-22 Pb	good casting, heat treating behavior	*(Zn in 2,045,237, Cd in -239)	U.S.P. 2,045,237 and -239
0.05-2	—	—	—	Bal.	—	2-6	4-8 Sn	good workability	heat treated parts	U.S.P. 1,914,588
0.05-2	—	—	—	Bal.	0.1-2.5	0.1-10	0.1-20 Sb	good workability	heat treated parts	U.S.P. 1,914,589

Table 26. Results of Thermal Analysis of Magnesium-Calcium Alloys.¹⁵

Calcium (%)	Primary solidification (°C)	Eutectic solidification (°C)	Eutectic halting time (minutes)
3.7	624	514	100
7.3	602	517	170
11.8	557	515	230
17.4	528	517	330
19.5	562	515	320
23.2	608	515	250
30.2	661	517	140
34.1	685	515	100
39.5	702	505	60
43.0	709	502	20
44.3	713
45.3	714
46.4	711
47.7	706
47.9	707	444	20
48.4	705	444	44
49.7	703	444	44
50.0	703	448	30
54.0	680	445	80
54.6	676	445	100

Table 27. Thermal Conductivity of a Magnesium-Calcium Alloy.¹⁶

Temp. (°C)	Thermal Conductivity <i>K</i> (gm cal/cm/sec/°C)
50	0.33
150	0.34
200	0.34

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Chapter X

Nickel-Calcium Alloys

Information on the nickel-calcium system is incomplete. It is probable that the nickel-calcium relationship in reference to solubility is similar to that of iron and calcium.

In nickel-chromium alloys and nickel-chromium-iron alloys used for high-temperature electrical resistances, the oxides or sulfides, according to Hunter,¹ that collect along the grain boundaries are points of attack, and their elimination by the use of a deoxidizer such as calcium, with the retention of definite amounts of the deoxidizer, markedly improves the useful life of these alloys. Hunter specifically refers to alloys of the 80 per cent nickel—20 per cent chromium type, with 0.03 to 0.2 per cent calcium.

Lohr² in a number of patents claims that the use of calcium with other elements, particularly zirconium and aluminum, notably increases their useful life as determined by the standard A.S.T.M. procedure for high-resistance, high-temperature alloys. The analyses of the alloys covered by these patents are given in Table 28.

The effect of small amounts of calcium on the grain structure, heat resistance, and service life of nickel alloys used for electrical heating elements and other applications has been exploited by manufacturers of such materials to produce resistance elements having several times the service life of electrical heating alloys available from 1928 to 1932.

The nickel-calcium and the iron-nickel-calcium groups of alloys are discussed together because there are few nickel-calcium alloys which have been proposed for industrial use.

Table 28

U. S. Patent	Nickel	Chromium	Iron	Composition (%)			Calcium
				Molybdenum	Zirconium	Aluminum	
2,005,430	Bal.	15-25	..	1-20	0.1-1.0	..	0.01-0.20
2,005,430	Bal.	15-25	..	2-10	0.1-0.3	..	0.02-0.05
2,005,430	Bal.	20	..	5	0.2	..	0.02
2,005,431	Bal.	15-25	0.01-0.50	0.01-1	0.01-0.20
2,005,431	Bal.	15-25	0.20	0.07-0.38	0.03
2,005,432	Bal.	10-15	25-30	1-20	0.1-1.0	..	0.01-0.20
2,005,432	Bal.	10 15	25-30	2-10	0.1-0.3	..	0.02-0.05
2,005,432	Bal.	15	25	5	0.2	..	0.02
2,005,432	Bal.	10-18	17-30	2-10	0.1-0.3	..	0.02-0.05
2,005,432	Bal.	10-18	17-30	1-20	0.1-1.0	..	0.01-0.2
2,005,433	Bal.	10-15	25-30	..	0.01-0.50	0.01-1.0	0.01-0.20
2,005,433	Bal.	10-15	25-30	..	0.20	0.07-0.38	0.03
2,005,433	Bal.	10-18	17-30	..	0.01-0.50	0.01-0.10	0.01-0.20

It has been found that the heat resistance of alloys used for resistance elements was increased by the addition of rare-earth metals like cerium. If thorium is added, the effect is greater than the sum of the improvements caused by the individual additions. The rare-earth metals are expensive. It was discovered that they can be replaced by calcium and other alkaline-earth metals, whose addition causes a similar increase in the heat resistance of the alloy. If thorium is retained, its effect with calcium, or any other alkaline-earth metal, is similar to that with cerium or other rare-earth metals. The amount of calcium or other alkaline-earth metals is 0.02-2 per cent in addition to other components. One proposed composition contains 0.5-2 per cent calcium, strontium, or barium, tungsten, molybdenum, cobalt and manganese, which together should not amount to more than 20 per cent, 13-32 per cent nickel, and the balance iron. Another alloy contains 0.02-1.2 per cent alkaline-earth metals such as calcium, 10-30 per cent chromium, 0-50 per cent iron, tungsten and molybdenum up to 20 per cent, 0.01-6 per cent thorium and at least 20 per cent nickel.³

Kroll (despite lack of certainty as to whether nickel and calcium alloy) stated that nickel-calcium alloys have properties which make them of interest in the manufacture of high-speed tools. A nickel "alloy" which contains 1 per cent calcium is heated to 1050°, quenched to 500° and heat-treated

at this temperature for 12 hours. The increase in hardness is 40 Brinell in comparison with an alloy which is identical except that it does not contain calcium. The alloy may contain 0.5–10 per cent calcium, the balance being substantially nickel.⁴ Other investigators do not confirm these statements.

In a modification of this alloy the presence of one or more of the elements (aluminum, chromium, cobalt, iron, copper, manganese, silicon, tantalum, titanium, vanadium, tungsten, boron, cerium, molybdenum, zinc, or tin,) up to a total amount of not more than 45 per cent is suggested.⁵

Petersen⁶ described an alloy which contains 5–45 per cent iron, 5–30 per cent aluminum, and 0.1–2.0 per cent calcium with or without cobalt, chromium, copper, manganese, molybdenum, titanium, vanadium, tungsten and zirconium, as well as carbon, silicon, phosphorus, and lead, and suggests it for a permanent magnet. An alloy composition suggested contains 24 per cent nickel, 14.5 per cent aluminum, 1 per cent copper, 1 per cent calcium and the balance iron.

Calcium is useful as a deoxidizing agent for nickel. A silicon-calcium alloy which contains 25 per cent calcium was patented to deoxidize and purify nickel and to alloy calcium with nickel after the deoxidizing is finished. Of the silicon-calcium alloy 0.5 per cent is used as deoxidizer and an additional 0.2 per cent is added as an alloying agent. If the melt is likely to be exposed unduly to the atmosphere, 0.15 per cent cerium is recommended by Pfeil⁷ to act as protection against oxidation.

Pfeil further proposes the removal of excess calcium (after the deoxidation is finished) by treating the melt with arsenic, by which means the excess calcium is removed as calcium arsenate. Calcium-silicon alloy is added to produce a nickel-calcium alloy.⁸

Moore⁹ suggests a nickel-chromium-calcium alloy for the manufacture of stainless steel. It may contain 33.3–95 per cent nickel, 2.5–33.3 per cent chromium and 2.5–33.3 per cent calcium. The alloy is introduced into the molten steel by an air-pressure gun. The calcium functions as a deoxidizing and

purifying agent. The calcium oxide formed rises to the slag, while nickel and chromium are distributed through the whole melt.

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Chapter XI

Silicon-Calcium Alloys

The silicon-calcium alloys have no mechanical properties which make them particularly interesting and attractive. Their deoxidizing qualities, however, make them very important materials for the metallurgical industry.

To prevent the formation of carbon monoxide during the solidification of cast steel it is necessary to deoxidize ("kill") the steel before it is poured. The deoxidizing agents most frequently used are manganese, silicon, ferrosilicon, and aluminum. It has been found that 0.12 per cent calcium silicide is in most cases sufficient, while 0.5 per cent manganese or 0.22 per cent silicon are usually necessary for the "killing" of steel. The use of silicon-calcium alloys as deoxidizing agents has the advantage that the steel and the slag become more liquid. This prevents the inclusion of aluminum oxide in the steel in those cases where an additional charge of aluminum as deoxidizing agent is necessary.¹

A deoxidizing agent which contains 41.67 per cent calcium, 0-1.2 per cent carbon and the balance silicon, besides a small amount of impurities, is said to form a very fusible slag which separates much better than that formed when aluminum is used as a deoxidizing agent.²

Hurst³ made a number of experiments on the influence of silicon-calcium compounds on alloys of pig iron with molybdenum, tungsten, and titanium. Ordinarily these alloys are made by addition of ferro-molybdenum, ferro-tungsten, or ferro-titanium to the molten iron. The alloy yield is low, as a

result of the lower melting point and pouring temperature of the pig iron. Hurst tried to overcome these difficulties by using the oxides of the alloying metals in the place of their ferro alloys, and to reduce the oxides with silicon-calcium alloys which contain 62 per cent silicon. The alloys were stated to show high tensile strength, and in some cases a reduction in the sulfur content of the alloy.

The metal oxides were mixed with the calcium-silicon alloy and distributed through the melt of pig iron by stirring. Results for several alloys made with silicon-calcium compounds as reducing agents are given in Table 29.

Thirty-three to 76 per cent of the silicon added as silicon-calcium alloys was recovered by the analysis of a large series of alloys made by this method, as were 55–100 per cent of the molybdenum. The sulfur content of the alloys falls to 0.054

Table 29.

Alloy	Load (lbs)	Transverse Strength		Tensile strength (tons/sq in)	
		Deflection (inch)	Modulus of rupture (tons/sq in)		
0.2% Ca-Si					
1.1% MoO ₃	3808	0.31	37.5	17	
2% Ca-Si					
1.5% MoO ₃	3606	0.30	41.3	26.5	
2% Ca-Si					
1.5% MoO ₃	5130	0.41	54.8	25.9	
2% Ca-Si					
1.5% MoO ₃	3830	0.4	43.75	25.4	
		Brinell hardness		Analysis	
		edge	center	% Si	% Mo
0.2% Ca-Si					
1.1% MoO ₃		207	217	1.1	0.5
2% Ca-Si					
1.5% MoO ₃		255	196	1.67	1.07
2% Ca-Si					
1.5% MoO ₃		286	277
2% Ca-Si					
1.5% MoO ₃		217	217	1.54

per cent in comparison with 0.1 per cent for original pig iron. A number of tests were made with tungsten oxide and titanium oxide (Table 30).

The tests for transverse strength were made with bars supported 18 inches apart. The tensile strength tests were made with the broken halves of the test bars which were machined down to 0.798 inch in diameter. The Brinell hardness was tested with a 10-mm ball and a 3000-kg load.

Silicon-calcium compounds are in a somewhat negative way important components of alloys used for high-tension power lines, as pointed out in the chapter which deals with aluminum-calcium alloys. Calcium metal is added to those alloys to prevent the formation of age-hardening magnesium-silicon compound ($MgSi_2$) and to prevent the formation of mixed aluminum-silicon crystals, which have a detrimental effect upon the electric conductivity of the alloys.

Table 30.

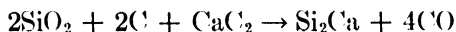
	Load (lbs)	Deflection (inch)	Transverse Strength Modulus of rupture (tons/sq in)	Brinell hardness		Sulfur (%)
				edge	center	
2.3% Ca-Si						
1.2% WO_3	3425	0.31	36.9	207	217	0.02
2.6% Ca-Si						
1.4% WO_3	3630	0.30	39.0	241	228	0.02
3.2% Ca-Si						
1.5% TiO_2	3360	0.30	33.9	207	196	0.031
3.5% Ca-Si						
3.0% TiO_2	2910	0.27	31.35	228	218	0.026

Recovery of components of alloy by analysis (%)

	Recovery of components of alloy by analysis (%)		
	Si	W	Ti
2.3% Ca-Si			
1.2% WO_3	22	33	..
2.6% Ca-Si			
1.4% WO_3	46	60	..
3.2% Ca-Si			
1.5% TiO_2	17	..	10
3.5% Ca-Si			
3.0% TiO_2	39	..	18

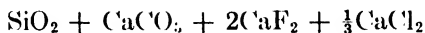
The low specific weight of calcium makes it difficult to retain the calcium silicide below the surface of the molten slag on top of the steel, which has to be oxidized. It has therefore been suggested to replace a part of the calcium with barium in the deoxidizing compound.⁴

A number of various methods are used to produce silicon-calcium alloys, all of which have, however, the common characteristic that they do not use calcium metal as a basic material. One method described is based on the following reaction:



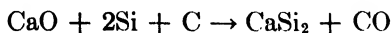
The reaction takes place in a single-phase furnace.² The energy consumption is stated to be 6000 kw-hours per ton, and the energy efficiency, 45 per cent.

Dodero⁵ recommends the melting of silicon dioxide with the oxides of alkaline-earth metals as a way to produce mixtures of silicon and metal-silicon compounds of the general formula MeSi_2 . The same investigator reports that he melted the mixture



at 1000–1200° for 2 to 2½ hours in a carbon crucible, which served at the same time as anode, and an iron rod as cathode with a current density of 20 to 30 amps per sq cm. The product contained 0.66 per cent silicon, 17.1 to 56.2 per cent silicon combined with calcium, and 1.3 to 3.2 per cent silicon combined with iron. The proportion of free silicon was found to rise with the temperature; at 1000° almost pure calcium silicide was obtained.⁶

The production of silicon-calcium alloys from calcium oxide, quartz and coke is another procedure:



This method requires control of the conditions while the reaction is taking place. Weiner⁷ states that the best results are achieved when a current of 500 amperes and 40 volts is used. The product of this reaction is reported to decompose

after a few days in the air, or in water, into crystals of different size. The presence of silicon hydrides and acetylene was determined by their smell. This is explained by the dissolution of the rest of the carbide which has not reacted in the silicide during the reaction. This carbide then causes decomposition of the reaction product. Others proposed that the calcium oxide be replaced by carbonate.⁸

Varzanov⁹ stated that the melting of 20 per cent silicon carbide, 46 per cent calcium carbide and 34 per cent quartz in an electric furnace resulted in the formation of a silicon-calcium alloy which contained 32–37 per cent calcium and less than 1.5 per cent iron, the balance silicon.

Another method proposes the reduction of alkaline-earth oxides with an alloy which contains 35 per cent silicon and 50 per cent aluminum. An excess of molten aluminum-silicon alloy must be used in the process. When 100 grams of calcium oxide are added to 1000 grams of molten aluminum-silicon alloy a ternary alloy is stated to be formed which contains 29 per cent calcium, 22 per cent aluminum, and the balance silicon.¹⁰

The calcium-silicon system is given in Figure 21. According to the diagram two compounds exist: CaSi and CaSi_2 . The eutectic of the system of 61 per cent silicon has a melting point of 980° .

Three different calcium silicides have been found and their composition has been confirmed. Calcium monosilicide (CaSi) or Ca_2Si_2 is prepared by heating pure calcium and silicon at 1050° in an electric furnace in an atmosphere of carbon dioxide. The Debye-Scherrer diagram shows that two modifications of this compound exist. Calcium disilicide (CaSi_2) can be obtained in its pure form by heating calcium hydride (CaH_2) and silicon in an atmosphere of hydrogen or by heating Ca_2Si_2 . In the second reaction the initial presence of 20 per cent CaSi_2 is necessary.

Dicalcium monosilicide (Ca_2Si) has been reported as being made by heating a finely powdered mixture of calcium and silicon in the proportion 1:4 for 1 to 2 minutes at 1100° in an atmosphere of carbon dioxide, hydrogen, or nitrogen. It is

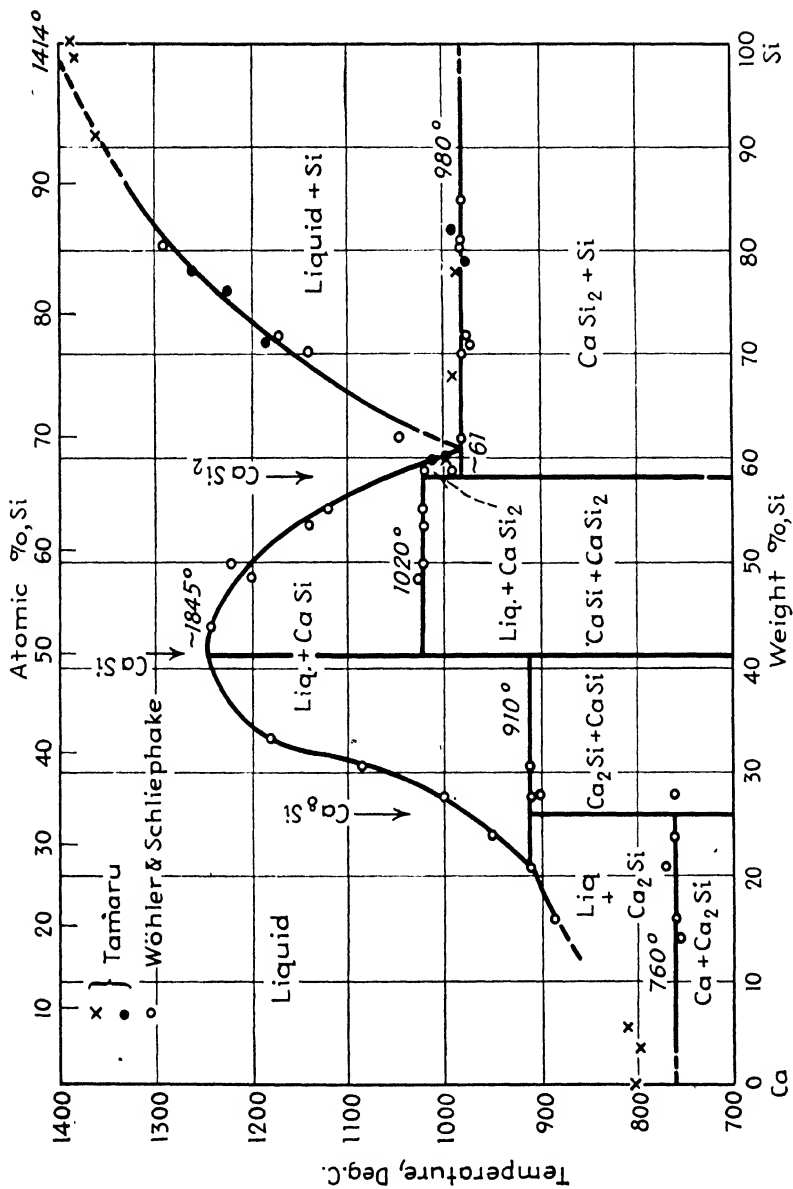
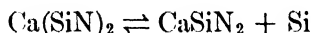
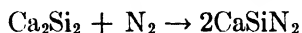


Figure 21. Constitution diagram of silicon-calcium alloys.

slowly decomposed by air, quickly by ethyl alcohol or water, and instantaneously by 2*N* hydrochloric acid, and leaves a residue of hydrated silicic acid. When heated in hydrogen atmosphere, Ca₂Si decomposes at 800°, yielding Ca₂Si₂ and calcium hydride. The silicides are insoluble in each other. CaSi₂ has the property of combining with nitrogen to form a calcium silicocyanide, Ca(SiN)₂, which then forms an equilibrium with calcium silicocyanamide (CaSiN₂) and silicon.



Pure monosilicide forms calcium silicocyanamide at once.¹¹



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Chapter XII

Silver-Calcium Alloys

The constitution diagram of the silver-calcium system is shown in Figure 22. The compounds Ag_4Ca , Ag_3Ca , Ag_2Ca and AgCa are reported by Kremann, Wostall and Schöpfer¹ from potential measurements. Additions of calcium to silver

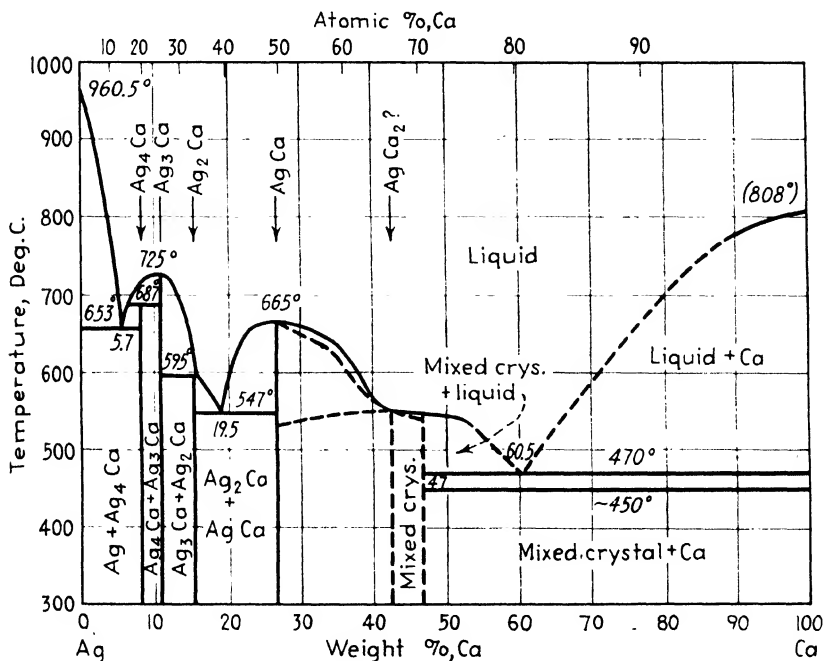


Figure 22. Constitution diagram of silver-calcium alloys.

lower its melting point, and the same holds true for additions of silver to calcium. There appear to be indications of a eutectic at about 61.5 per cent silver with a melting point of 470°.

An x-ray study of the silver-calcium system² gave no indication of the compounds AgCa_2 , Ag_2Ca , or Ag_3Ca . The compounds AgCa (face-centered cubic, with $a = 9.07 \text{ \AA}$) and Ag_3Ca (tetragonal, with $c/a = 0.88$ and $c = 9.96 \text{ \AA}$) were found.

It is reported that a contact made of silver-calcium alloy which contains 2.5 per cent calcium is able to withstand a 25 per cent heavier current load than a similar contact made of fine silver. Where a fine silver contact fails by welding at 12 amperes, a silver-2.5 per cent calcium alloy was found to carry a current of 15 amperes, and a silver-3 per cent calcium alloy one of 17 amperes, before failure occurred.

The silver-calcium alloys have a hardness of 90 to 95 Rockwell F. They can be made harder by adding up to 1 per cent nickel, cobalt, or manganese. To restrain the growth of the grain and to prevent the softening of the alloy at high temperatures, up to 10 per cent copper may be added.

Silver-calcium alloys are much more resistant to tarnishing by hydrogen sulfide than is pure silver. A silver-calcium alloy and a similar piece of pure silver were simultaneously exposed to an atmosphere of hydrogen sulfide. The fine silver was heavily tarnished after 24 hours, but the alloy showed only a slight film of tarnish after 72 hours.

Silver-calcium alloys containing up to 5 per cent calcium are made by incorporation of master alloys in fine silver melts. A typical master alloy is made in disc or pellet form by compression of silver powder and calcium chips at elevated temperatures. It is said that this method prevents undue oxidation of the calcium. The alloy should be poured at 960° or a slightly lower temperature; if the pouring temperature is higher, a porous cast is obtained. Magnesium metal is recommended as deoxidizer for this process, but if the melting is done in a hydrogen atmosphere no deoxidizer is necessary. The alloying should be done above 700° in this case to prevent the formation of calcium hydride. A compound of the formula Ag_3Ca has been found in silver-calcium alloys.³

The deoxidation of commercial silver alloys was studied⁴

by determining the amount of oxygen present after deoxidation and by microscopic and macroscopic examination of the deoxidized alloys. The use of calcium, magnesium, lithium, beryllium, aluminum, silicon, manganese, boron, zinc, phosphorus, tin, and cadmium was investigated in preliminary experiments. The elements are considered in two groups. The oxides of the elements from calcium to boron in the above list have a heat of formation greater than 45 kg-cal per equivalent and the elements can react completely with an equivalent amount of oxygen; the last four elements are only partial deoxidizers. In the first group the deoxidation rate is determined by the melting point of the elements. Those with a melting point below 1000° react nearly completely in 1 minute. If the melting point is from 1000 to 1500°, deoxidation requires from 3 to 5 minutes. If the melting point is very high, solution of the deoxidizer is slow and the reaction is incomplete even after 5 minutes. Calcium was found to have commercial possibilities in this application.

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Chapter XIII

Tin-Calcium Alloys

There has been considerable study of the tin-calcium alloys. Moissan¹ stated that when tin is heated to temperatures above its boiling point, it unites with calcium to form a crystalline alloy. Donski² found that tin dissolved calcium at 650°.

The constitution diagram of the system is given in Figure 23. The addition of calcium to tin produces a sharp rise in the freezing point. The liquidus curve rises from the melting point of pure tin (232°) to a maximum of 627°, corresponding to the compound Sn_3Ca , or 10.1 per cent by weight of calcium. From here the liquidus falls slightly to a eutectic point (between Sn_3Ca and SnCa) at 609°. This corresponds to 31.2 atomic per cent calcium. The horizontal line at 609° is part of the solidus line of the system. From the eutectic, the liquidus curve rises to 987°, the melting point of the SnCa compound. This corresponds to a slight break in the curve which, however, is not the maximum. The liquidus continues to rise to a maximum at 1122°, corresponding to the compound SnCa_2 . The remainder of the diagram is of the eutectic type, the constituents being SnCa_2 and pure calcium. From the maximum, the curve drops to a eutectic at 759°, of 81.41 atomic per cent calcium. The liquidus then rises to 820°, the melting point of pure calcium.

No evidence of solid solution has been found in the study of the system. As a result, the solidus is simple. All the tin-calcium compounds are readily acted upon by water and

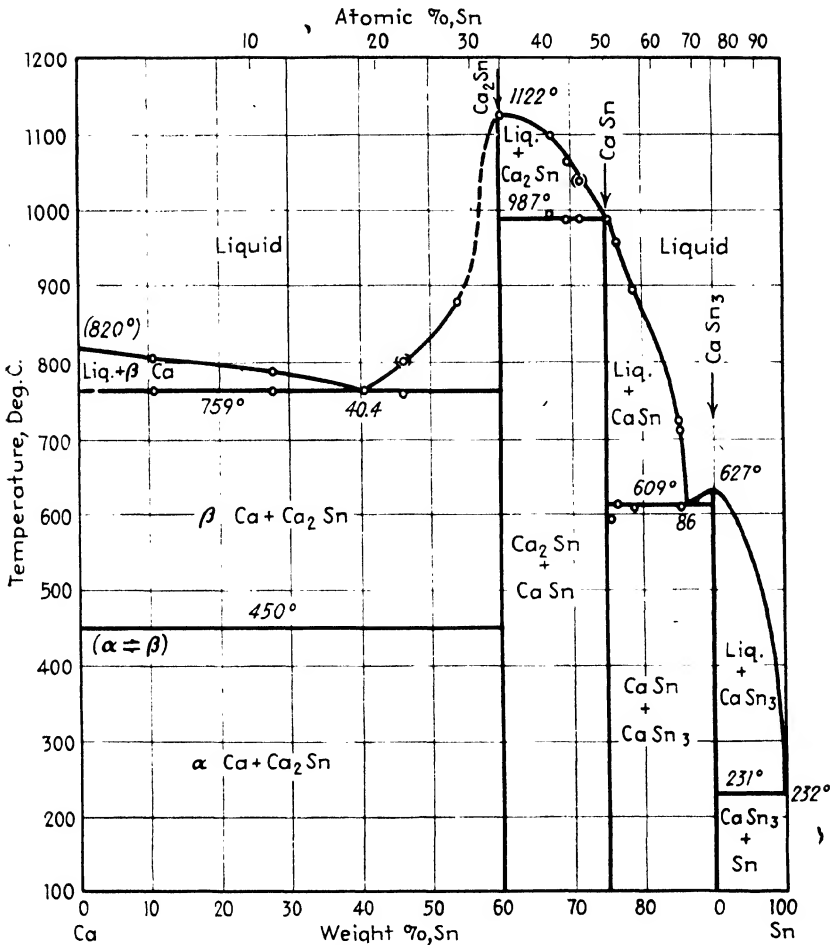


Figure 23. Constitution diagram of tin-calcium alloys.

atmospheric influences. The alloys are all white. The crystals of the tin-calcium compound cleave into thin plates a little paler in color than mercury. The alloys containing up to 4 per cent calcium are harder than tin and fairly tough. With further increase of calcium they become brittle. Tin-calcium alloys have been proposed for use as aluminum solders.

The tin-calcium alloys in general are rapidly attacked by water, air, and dilute acids. The alloys at present have prac-

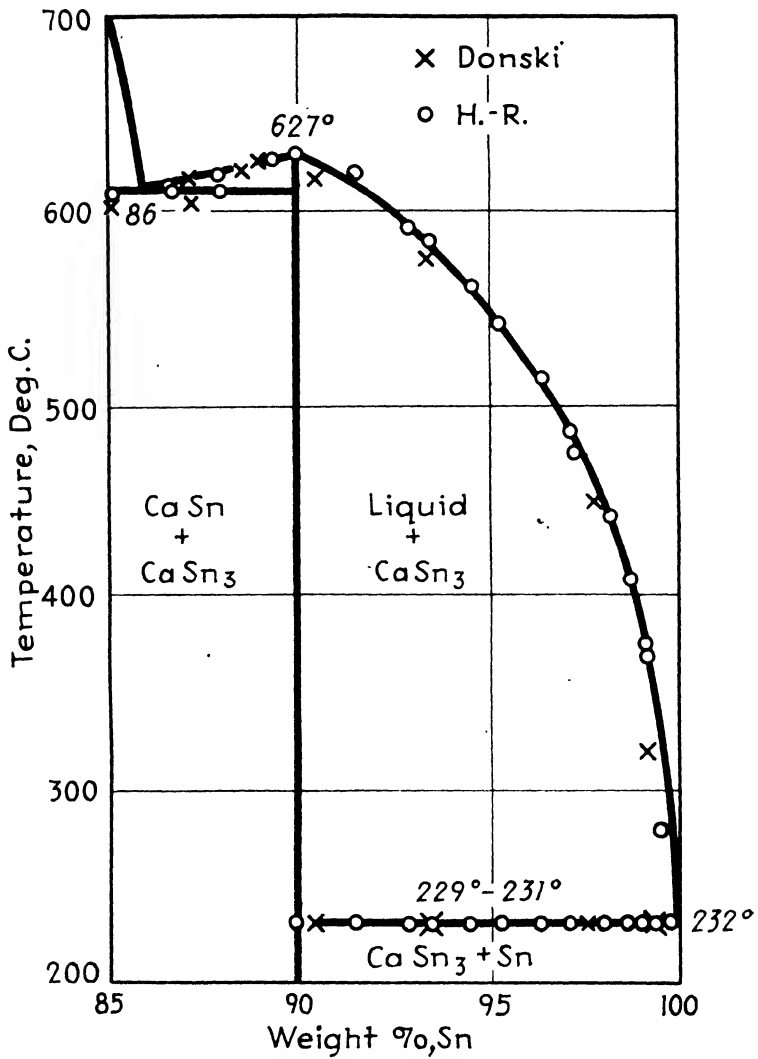


Figure 24. Constitution diagram of tin-calcium alloys, high tin end.

tically no industrial applications as binary alloys, but are of considerable theoretical interest.

The effect of small amounts of calcium on the melting point of tin was studied by Heycock Neville,³ Donski,⁴ and Hume-Rothery.⁵ This is illustrated in Figure 24. Their work also indicated the compounds CaSn_3 and CaSn .

Derge and Markus⁶ report that an addition of 0.1 per cent calcium to tin causes a corrosion at a pH of 11.2 which is markedly stronger than that which pure tin undergoes under the same conditions. However, that some practical application of tin-calcium alloy exists is illustrated by the fact that a patent has been taken for the removal of plating by electrolysis which, among other sorts of plating, specifically refers to tin-calcium plating as especially suitable for being subjected to the process. The method consists of electrolysis of the plated material in an alkaline bath which contains nitrate and a reducing agent. Alkali sulfite or bisulfite, a solution of sulfur dioxide, and a grape sugar solution are recommended as reducing agents.⁷

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Chapter XIV

Zinc-Calcium Alloys

The constitution diagram as proposed from the work of Donski is shown in Figure 25.¹ Further experimental work is needed on the system.

Zinc-calcium alloys and zinc-magnesium-calcium alloys are suggested for the production of porous concrete (gas cement). A 50-50 per cent zinc-calcium alloy and a 15 per cent-zinc, 15 per cent-magnesium, 70 per cent-calcium alloy have been stated to be most suitable. The alloys are very brittle, highly reactive and spontaneously combustible.²

An addition of calcium is said to improve the mechanical properties and increase the hardness of zinc-aluminum, zinc-magnesium and zinc-lithium alloys.³

The ternary alloys of magnesium, zinc and calcium have been investigated.⁴ The compounds in the system include Ca_3Mg_5 , Ca_5Zn_2 , and $\text{Ca}_2\text{Mg}_5\text{Zn}_5$. The last exists as large polyhedral crystals, insoluble in nitric acid, melting without decomposition at 495° . Alloys containing 30 per cent or more of calcium oxidize readily; alloys rich in zinc oxidize slightly, are hard, break easily and are difficult to work; alloys rich in magnesium are light, oxidize but slightly, and are easily worked.

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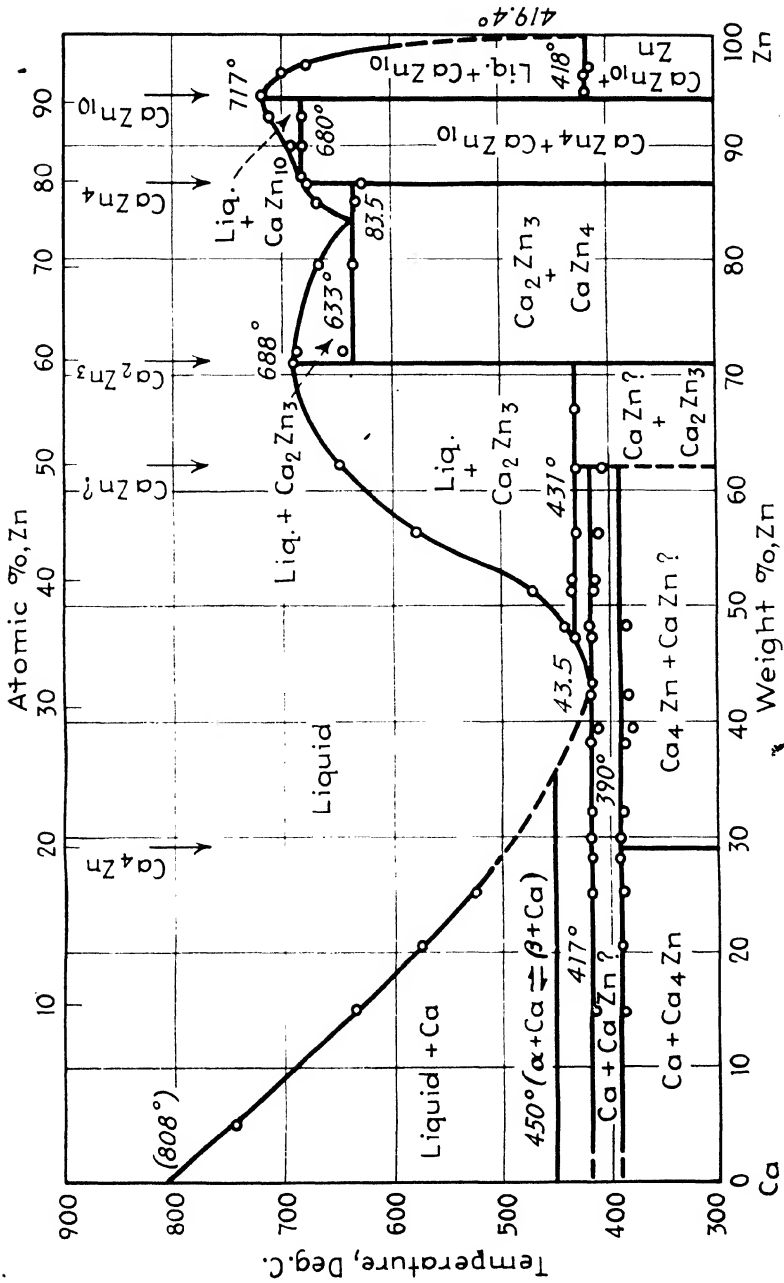


Figure 25. Constitution diagram of zinc-calcium alloys.

Chapter XV

Other Calcium Alloys

Antimony-Calcium

This system, shown in Figure 26, is of only limited interest as a result of the low solubility of calcium in antimony and lack of reliable experimental work on the system. It is claimed that in the debismuthing of lead by calcium or its alloys, calcium-antimony compounds are formed and that these enter the slags of the operation.

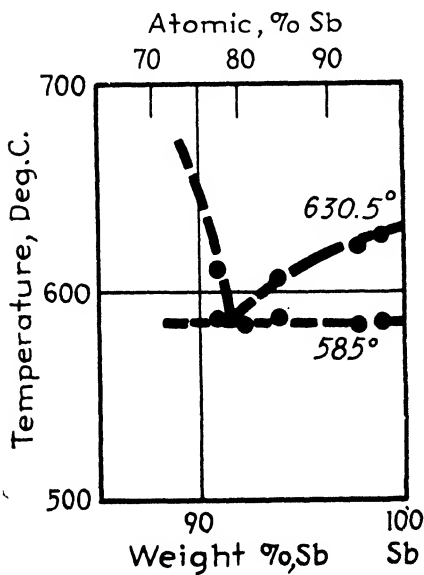


Figure 26. Constitution diagram of antimony-calcium alloys.

Beryllium-Calcium

A binary beryllium-calcium alloy has been made by dissolving beryllium in boiling calcium. The mass was found to have a core of pure beryllium and 29 per cent calcium. Up to now no practical application has been found for beryllium-calcium alloys.

Beryllium oxides (with iron) can be reduced to form beryllium-iron alloys only with calcium, or reducing agents containing calcium.¹ Magnesium, aluminum, silicon, lithium and cerium did not so function. Iron-beryllium alloys with up to 10 per cent beryllium may be formed by reacting beryllium oxide with a magnesium-calcium alloy containing 40 to 60 per cent calcium in the presence of Fe_2O_3 . The beryllium and iron compounds are reduced and alloyed.² Boiling magnesium does not dissolve beryllium, but in boiling calcium an alloy of approximately 71 per cent beryllium and 27 per cent calcium is formed.³

Bismuth-Calcium

The solubility of calcium in bismuth is low, as is also the solubility of bismuth in calcium, as shown in Figure 27. The removal of bismuth from lead is an industrial use of calcium discussed under lead.

Boron-Calcium

Boron-calcium alloys are used in the manufacture of steel, copper, and their alloys as deoxidants.

Calcium boride is an effective deoxidizer, Osborg⁴ stating that 106 grams of it are equal in effect to 180 grams of aluminum or 400 grams of pure calcium. It forms an easily fusible slag.

Calcium boride does not react with water, hydrochloric or hydrofluoric acid, but is decomposed slowly by concentrated sulfuric acid and energetically by nitric acid, melted alkali carbonates, bicarbonate and caustic alkali. Its melting point is about 2000° .

Calcium boride may be produced by electrolysis of calcium tetraborate (CaB_4O_7) which can be considered as a solution of

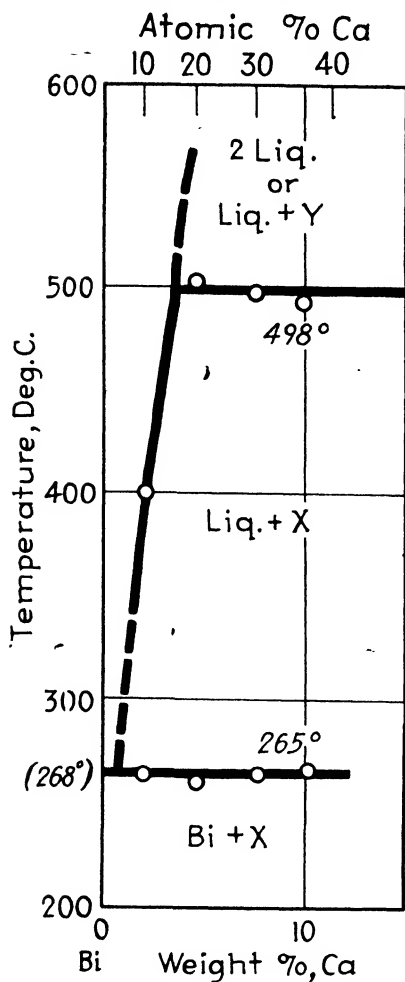
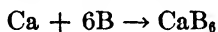
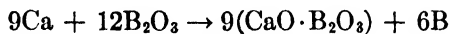
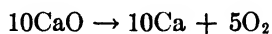


Figure 27. Constitution diagram of bismuth-calcium alloys.

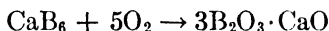
calcium oxide in boron oxide ($\text{CaO} + \text{B}_2\text{O}_3$). The electrolytic process can be explained by the following sequence of reactions:



A mixture of CaB_6 and amorphous boron is deposited on the

walls of the carbon crucible which acts simultaneously as the cathode. The anode is a ring of carbon in the axis of the crucible. Pure CaB_6 is made by electrolyzing the mixture $3\text{B}_2\text{O}_3 + \text{CaO} + 10\text{CaCl}_2$. Kroll and Jensen⁵ state that it has nearly the theoretical composition of 61.84 per cent boron and 38.16 per cent calcium; its density is 2.42. It scratches quartz easily and is just able to scratch rubies.

The deoxidizing effect of CaB_6 is illustrated by the equation⁶



Cadmium-Calcium

The addition of calcium to cadmium raises the melting point of cadmium. The system is somewhat complex as shown in the provisional constitution diagram from the work of Donski and others, in Figure 28. Apparently two compounds, CaCd_2 and CaCd , are formed. The combinations of calcium and cadmium have not as yet evoked any industrial interest.

Lithium-Calcium

The lithium-calcium alloys of which the 50 per cent lithium-50 per cent calcium and 30 per cent lithium-70 per cent calcium are produced in commercial quantities, are in many instances more effective than lithium or calcium alone, according to Osborg.⁷ The lithium-calcium alloys may be made in high purity, are more convenient to handle than lithium, and cost less than lithium. Their major uses are as refining, degasifying, deoxidizing and scavenging agents, inasmuch as they combine with oxygen, sulfur, hydrogen, nitrogen, oxides of carbon and silicates. Osborg⁸ recommends that the treatment of molten metals and alloys with lithium and lithium-calcium alloys be carried out in the furnace or in the ladle. In applying the treatment, it should be borne in mind that the specific gravity of lithium is as low as 0.5, so care should be taken to prevent the lithium or lithium-calcium alloy from rising to the surface of the molten mass. In the case of chromium alloys, the ladle should be covered, as the reaction is rather violent. In practically all other instances the treatment, properly applied, is

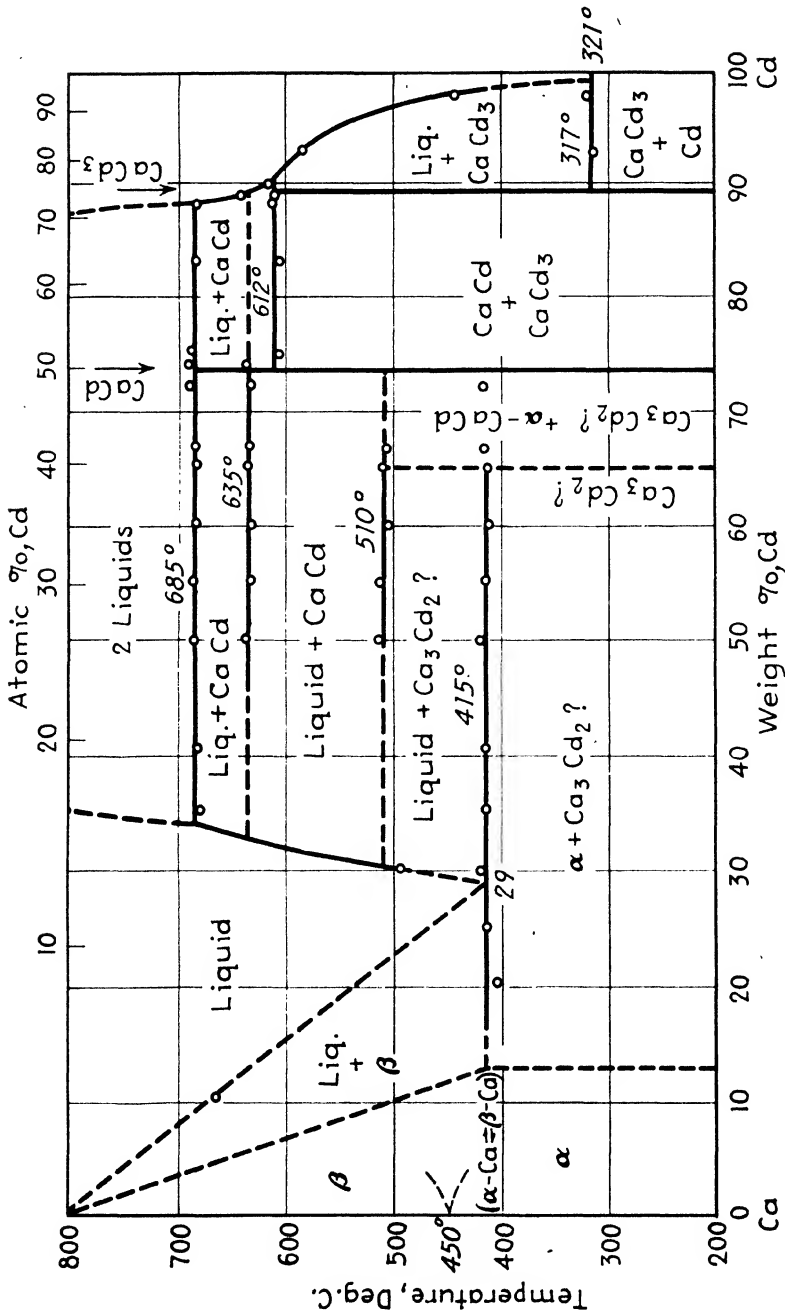


Figure 28. Constitution diagram of cadmium-calcium alloys.

carried out with convenience and in a simple manner similar to the application of the conventional phosphorizer in treating copper and copper alloys.

Due to the low equivalent weight of lithium (6.94), the amount of lithium or lithium-calcium alloys sufficient for the treatment is often as low as 0.005 per cent lithium. Of course, the percentage required for the treatment will depend on the degree of purity of the metal or alloy to be treated.

Lithium-calcium alloys are used in the manufacture of steel, copper, nickel and their alloys as deoxidizers.⁹ They can be produced by the electrolysis of a mixture of molten calcium and lithium chloride. Ternary lithium-sodium-calcium alloys are made by the same method.¹⁰ The alloys are silvery white and brittle if they contain 50 per cent calcium or more. The 25 per cent lithium-75 per cent calcium alloy is as brittle as glass and can be finely ground (under oil). It must be kept in an air-tight container or under kerosene. Lithium-calcium alloys react more slowly with the atmosphere than does lithium.

Mercury-Calcium

The constitution diagrams are shown in Figure 29, resulting from the work of Cambi and Speroni¹¹ and of Eilert.¹² Calcium shows only slight solubility in mercury with a range of compound formation.

Nitrogen-Calcium

A fragmentary diagram of the system is shown in Figure 30. A definite chemical compound, Ca_3N_2 , calcium nitride has been well studied. On treatment with water ammonia is formed. Calcium metal is often used for the elimination of nitrogen in molten metals.

Platinum-Calcium

Insufficient data exist on the platinum-calcium system to justify a constitutional diagram. Vines and Wise¹³ state:

“Although this system has not been investigated in detail, the fact that platinum melted in lime crucibles under reducing conditions is difficult to

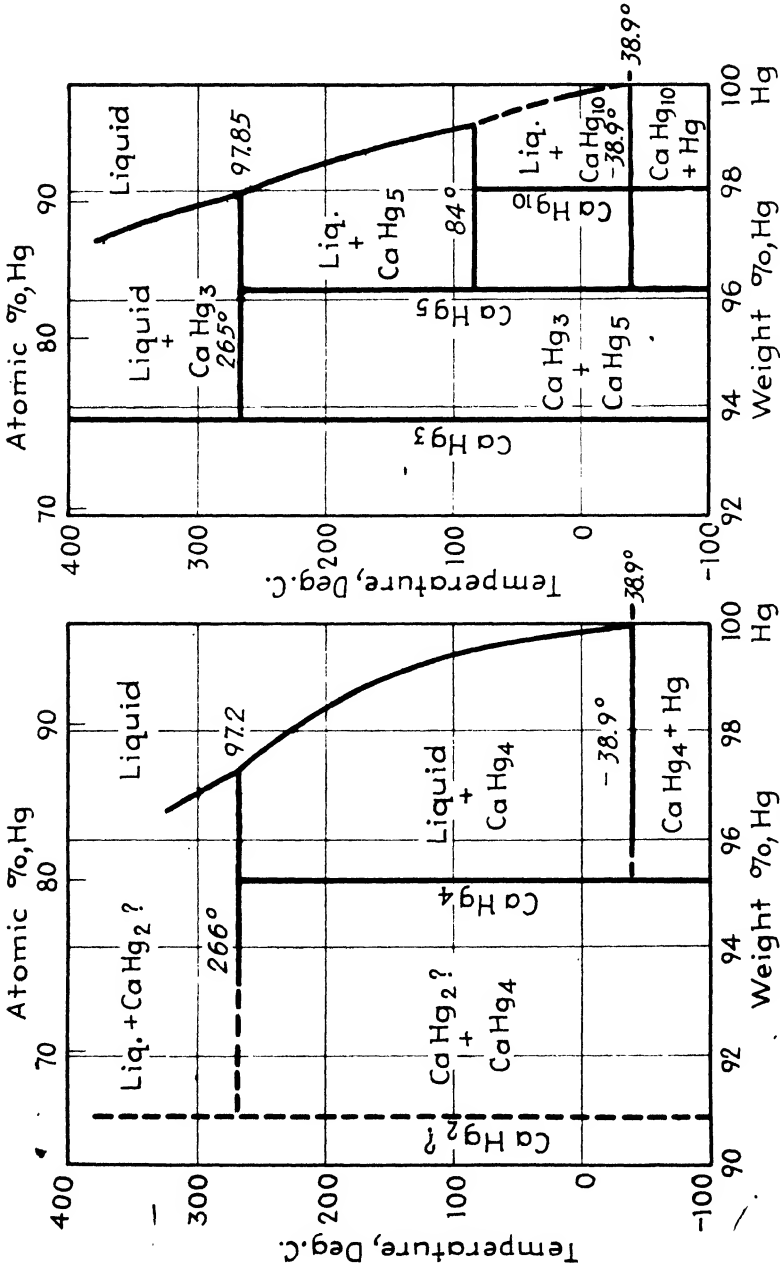


Figure 20. Constitution diagram of mercury-calcium alloys.

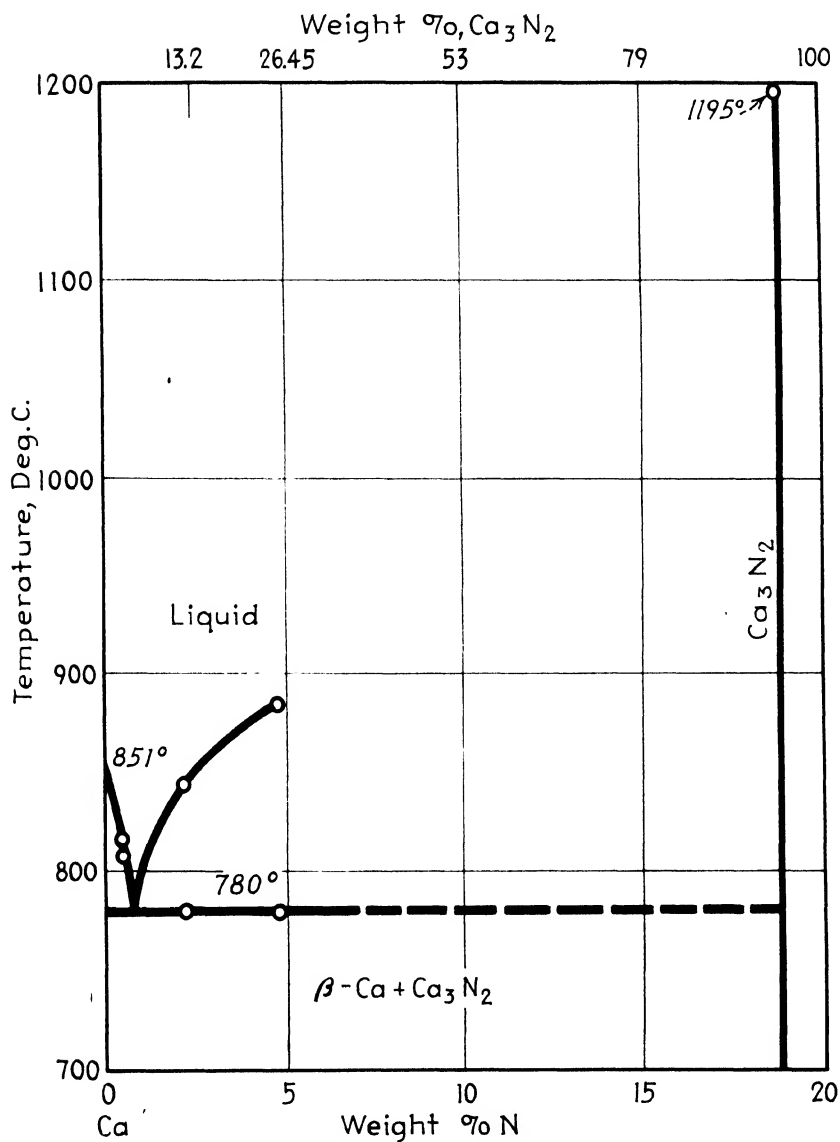


Figure 30. Constitution diagram of nitrogen-calcium compounds.

work, indicates that even small amounts of calcium form an insoluble low melting or brittle compound with platinum. Age-hardening of low calcium content platinum alloys, observed by Sivil¹⁴ confirms the suspected low solid solubility of calcium. Small amounts, of the order of 0.01 per cent, of calcium increase the tensile strength and markedly raise the annealing temperature of platinum, according to Carter¹⁴ and Sivil. As previously noted the low calcium content alloys may be age-hardened."

Interesting products are obtained by adding calcium to platinum and metals of the platinum group which are to be used for resistance elements. The claim is made that these alloys are less volatile at high temperatures than pure platinum metals.¹⁵

In the case of platinum alloys containing up to 10 per cent nickel, iron, chromium, aluminum, tantalum or tungsten, and gold alloys which contain 5-25 per cent platinum, calcium in amounts up to 10 per cent may be added. These alloys are said to be further improved by heating them to 800°, chilling, and reheating at 450°.¹⁶

Sodium-Calcium

This system, shown in Figure 31, indicates solubility of calcium in sodium and sodium in calcium. Some of these alloys are by-products of alumina electrolysis, being found in the cell linings, and of sodium production and calcium manufacture. Ordinarily sodium impurity in calcium metal does not affect its use, and in a similar manner calcium impurity in sodium is not a deterrent in the applications of that metal.

Thallium-Calcium

The constitution diagram from the work of Donski¹⁷ and of Baar¹⁸ is given in Figure 32. The alloys have not as yet aroused industrial interest.

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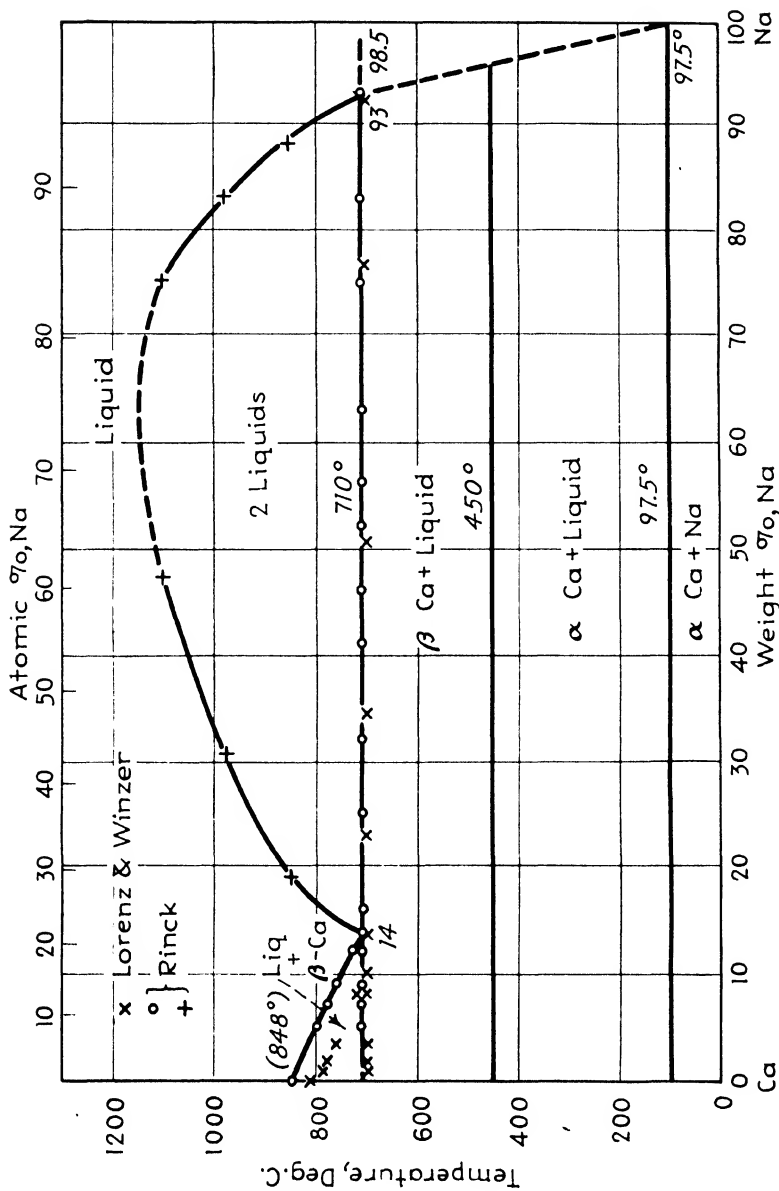


Figure 31. Constitution diagram of sodium-calcium alloys.

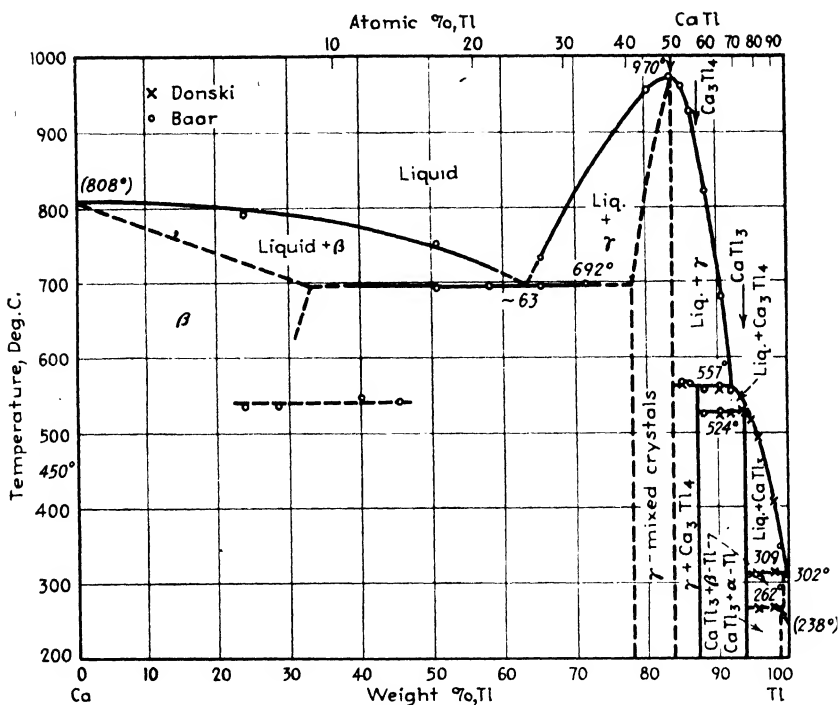


Figure 32. Constitution diagram of thallium-calcium alloys.

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Chapter XVI

Preparation of Chromium, Thorium, Uranium and Zirconium Metal Powders by the Use of Calcium

Metallic chromium powder¹ as well as metallic thorium and uranium may be produced either by electrolytic methods or by the reduction of the corresponding oxides by the use of calcium metal in the presence of calcium chloride as a flux. The oxide, calcium chloride, and finely cut calcium are mixed together and introduced into a bomb, which is sealed with a tapered stopper and heated to red heat or to a temperature of approximately 900°. The calcium serves as a reducing agent, being itself converted to the oxide. After the reaction is completed, the bomb is allowed to cool, the charge removed, disintegrated in cold water, washed in dilute alcohol, and the metallic powder separated. The chromium, thorium, or uranium metal is then sintered into ingots and made into mechanically worked forms and shapes.

The reduction of vanadium pentoxide with calcium in a mixture of fused calcium chloride and barium chloride yields a semicolloidal powder which cannot be converted into a workable form by pressure and heat.² If the powder be mixed with more calcium and the mixture heated with calcium chloride and barium chloride, the resulting metallic powder can readily be pressed into slugs which, after sintering *in vacuo* in an induction furnace, can be cold-forged and rolled. Workable thorium can be prepared in a similar way. Both vanadium and thorium sheets are embrittled by heating in barium chloride, but can be annealed in borax. Reduction of uranic oxide (pitchblende) with calcium under fused chlorides gives a powder part of which is colloidal and pyrophoric; but the heavier particles can be pressed and sintered into a workable form.

On cold working, this metal tends to crack and oxidize in the cracks.

Zirconium metal may be produced by inter-reaction of $ZrCl_4$ with sodium metal. The chloride may be made by chlorination of ZrO_2 . A preferable method involves the reduction of zirconia (ZrO_2) with calcium metal. Marden and Rich³ described the processing of zirconium ores for the production of zirconia. According to Cooper,⁴ the melting point of zirconium is close to that of tantalum and is of the order of 2800°.

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Chapter XVII

Calcium in the Petroleum Industry

The possibility of application of the alkali or alkaline-earth metals as aids in petroleum refining has aroused a large amount of interest. As a sulfur-removing agent, calcium is more effective quantitatively than either potassium or sodium and qualitatively more effective than magnesium. Methods of treatment involve the contacting of the hot oil with the metal in either a solid form such as granules, chips, or flakes, or in a liquid form at temperatures above the melting point of the metal.¹ In this connection, sodium with its low melting point of 97° is applicable as a solid metal only over a very limited temperature range, and ordinarily has to be used in liquid form. The treatment of petroleum oils with calcium or related metals desulfurizes the oil and improves its color and odor. The method gives qualities of final product equal to those made by sulfuric acid refining but involving much smaller losses.

The effect of calcium treatment on the sulfur content and odor of crude benzine has been studied by the authors, using powdered copper, nickel, and iron with and without calcium metal; copper oxide, calcium oxide, and anthracene, as well as calcium metal alone. The sulfur content of the crude benzine was 0.243 per cent, as determined by the standard A.S.T.M. method for sulfur determination in petroleum products. It had a decided odor and was blackish yellow in color.

The experiments showed that temperature is an important factor in the reduction of sulfur, and that the heavier or higher-boiling constituents in the benzine contain the greater portion of the sulfur. Refluxing at temperatures in the range of 100° with calcium alone, copper alone, or calcium and copper mixtures, or with calcium, copper, and anthracene mixtures, does

not give appreciable removal of sulfur. At these temperatures, mixtures of calcium and nickel, and calcium and iron, the nickel and iron being employed as metallic powders, were more effective than calcium alone or calcium and copper. Mixtures of calcium and lime refluxed at a point near the initial boiling point of the benzene, 100° , are about as effective as calcium and nickel powders, while calcium and copper oxide mixtures are more effective than calcium and copper, a little less effective than calcium and iron, but more so than calcium and nickel.

When the crude benzene was distilled over metallic calcium turnings heated to about 400° , sulfur removals greater than 50 per cent were obtained. An original sulfur content of 0.243 per cent was reduced to 0.11 per cent after calcium treatment. In other experiments reductions of the sulfur content were such that the final product ran 0.09 per cent sulfur. It is felt that further experimental work would result in still greater reductions or eliminations of the sulfur in similar petroleum fractions.

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Name Index

A

Alexander, P. P., 59
American Smelting & Refining Co.,
90
Andrieux, J. L., 136
Antropoff, A., 12
Arndt, K., 23

B

Baar, N., 47, 66, 95, 134
Badger, W. L., 23
Bagley, G. D., 27
Bakken, H. E., 20
Bartels, W., 64
Basil, J. L., 53
Bastien, P., 13
Bergeret, L., 116
Betterton, J. O., 86, 88, 91, 92
Bouton, G. M., 69, 70, 73
Brace, P. H., 20, 24, 25
Brandenberg, 49
Bridgman, P. W., 13
Bulian, W., 98
Bullier, 86
Bungardt, W., 42
Bunsen, R. W., 23

C

Caldwell, W. E., 63
Calloy Ltd., 42, 94
Cambi, 131
Caron, 21, 66, 84, 85
Carter, F. E., 134
Cath, P. G., 14
Clarke, B. L., 93
Cooper, 138
Cowan, W. A., 93
Cross, R., 140

D

Daunt, J. G., 105
Davy, H., 11, 22
Dean, R. S., 71
de Campi, 94

Degard, C., 119
Dempster, A. J., 19
Derge, G., 123
Doan, G., 46
Dodero, M., 113
Dollins, 70
Donski, L., 35, 36, 66, 120, 124, 129,
134, 136
Drucker, C., 20
Du Bellay, 100
Durand, J. F., 62

E

Eckel, J. F., 47
Edwards, J., 15, 37
Eilert, A., 131
Einerl, O., 36, 98
Electro Metallurgical Co., 21, 30
Ellis, W. C., 47
Emmert, 119

F

Falk, E., 12
Feussner, 136
Franck, H. H., 116
Frary, F., 15, 23, 42, 45
Fuchs, W., 61

G

Gatti, U., 63
Gessler, 23
Gillis, R., 93
Goodwin, J. G., 14, 24, 25
Goralczyk, R., 46, 124
Graf, L., 13, 16
Greenall, C. H., 71
Grogan, J. D., 46
Guertler, W., 12, 49

H

Haase, C., 53
Hardy, C., 56
Haring, H. E., 93
Hartmann, H., 12
Haughton, J. L., 100

Hayasi, S., 98
 Heil, O. H., 40
 Herschman, H. K., 53
 Hesel, 119
 Heycock Neville, 123
 Hiers, G. O., 93
 Horseman, A., 105
 Houghton, S., 62
 Hull, A. W., 12
 Hume-Rothery, W., 123
 Hunter, M. A., 106
 Hurst, J. E., 110

I

Israilovich, 116

J

Jeffries, Z., 15
 Jensen, 129
 Johnson, W. C., 59

K

Kassner, 59
 Kats, G. A., 62
 Kelley, K. K., 14
 Kinzel, A. B., 30, 116
 Kirsebom, G. N., 46, 81
 Klaiber, H., 119
 Kleiman, 69
 Khokhlova, A. V., 62
 Koto, H., 46
 Kramarov, A., 116
 Krauskopf, F. C., 63
 Kremann, 69, 95, 117
 Kroll, W., 12, 13, 22, 37, 54, 84, 86,
 87, 88, 107, 129, 138
 Kurzyniec, E., 90

L

Lohr, J. M., 106
 Lorenz, R., 84, 135
 Louis, V., 116
 Luft, F., 20

M

Mantell, C. L., 56, 94
 Marden, J. W., 138
 Markus, H., 123
 Masing, G., 47
 Matsuyama, K., 36

Matthiessen, 23
 McDonald, J. C., 100
 Meehan, A. F., 56
 Meerson, G. A., 62
 Meissner, K. L., 37
 Mendelssohn, K., 105
 Metal Hydrides, Inc., 61
 Metallgesellschaft, 21, 43, 78
 Meyer, J., 46, 124
 Mohrheim, A., 46, 99
 Moissan, H., 86, 120
 Moore, 70
 Moore, D. P., 108

N

Negovski, 116
 Neumayr, S., 68
 Neurath, F., 36, 94, 98
 Norddeutsche Affinerie, 88
 Nowotny, H., 44, 99

O

Obinata, I., 98
 Osborg, H., 20, 129
 Overberg, H. S., 16

P

Paris, R., 98, 100, 101, 124
 Parkes, 90
 Partington, J. R., 19
 Pechukas, A., 59
 Pemetzrieder, G., 53
 Petersen, 108
 Petot, H. F., 124
 Pfeil, L. B., 108
 Phillips, A., 69
 Pilling, N. B., 16
 Pirani, M., 12
 Plato, 23
 Porlezza, C., 63
 Pratt, 47
 Pring, T., 86
 Prytherch, W. E., 44

Q

Quasebart, 54

R

Rathenau, 23
 Raub, E., 119

Rich, M. N., 138
 Richards, T. W., 13
 Rinck, 135
 Rosenbaum, C. K., 63
 Roters, H., 119
 Rudberg, E., 20
 Ruff, 23
 Ryjord, J. E., 71

S

Schliephake, 115
 Schneider, R., 12
 Schöpfer, 69, 95, 117
 Schulze, A., 16
 Schumacher, E. E., 47, 69, 70, 73
 Schwarz, C., 116
 Scott, D. M., 56
 Show, L. I., 93
 Sidwell, A. E., 59
 Siegens, J., 87
 Simpkins, L. D., 93
 Sivil, C. S., 134
 Slavinski, 69
 Société d'Electrochimie et d'Electrometallurgie d'Ugine, 26, 30, 94, 116
 Speroni, 131
 Stempel, 59
 Stockem, 95
 Stroup, P. T., 46
 Stubbs, M. F., 59

T

Tamaru, 115
 Tarugi, 86
 Taylor, C. S., 37
 Thomas, U. B., 93
 Townsend, J. R., 71
 Tullis, D. R., 40

U

Ufford, C. W., 69
 Union Carbide Co., 28
 United Lead Co., 79

V

Valdman, G., 136
 Varzanov, 114
 Vines, R. F., 131
 von Kugelchen, 86
 von Steenis, O. L., 14
 Vosskühler, H., 105

W

Walton, J. H., 63
 Watts, J., 54
 Weibke, F., 64
 Weiner, R., 116
 Westby, T. H., 93
 Wettstein, T., 94
 Whitterton, C. H., 93
 Wiens, 49
 Wiggs, 119
 Willard, F. W., 93
 Willner, 23
 Winzer, R., 94, 135
 Wise, E. M., 131
 Wöhler, F., 24, 115
 Wood, R. T., 40
 Wooster, I. A., 93
 Wormnes, E., 46, 99
 Worrall, 94
 Wostall, 69, 95, 117
 Wyman, L., 47, 50

Z

Zieckrick, L., 47, 49, 93
 Zieler, 56
 Zintl, E., 68
 Zuncker, P., 94

Subject Index

A

- Age-hardening alloys, 74
- Allotropes, 13
- Aluminum alloys, 35
 - composition of, 39-41
 - constitution diagram, 35
 - elimination of hot shortness by, 45
 - manufacture, 36
 - modification of, 38
- American practice, 28
- Antimony alloys, 126
- Application, 9
- Atomic weight, 12

B

- Battery grids, 77
- Beryllium alloys, 127
- Bismuth alloys, 127
 - constitution diagram, 128
- Boiling point, 12
- Boron alloys, 127

C

- Cable sheaths, 69
- Cadmium alloys, 129
 - constitution diagram, 130
- Can, 81
- Carbide process for lead alloys, 86
- Carrot, 29
- Casting, 31
- Cell types, 25
- Chemical properties, 17
- Chemistry of, 10
- Chlorides,
 - melting point of, 22
 - specific conductivity of, 23
- Chromium powder, 137
- Color, 11
- Commercial forms, 31, 34
- Comparison with barium and strontium, 17
- Comparison with sodium, 18
- Compounds, 11
- Compressibility, 13

Constitution diagram,

- of aluminum, 35
 - of bismuth, 128
 - of cadmium, 130
 - of copper, 48
 - of gold, 65
 - of lead, 67
 - of magnesium, 96
 - of mercury, 132
 - of nitrogen, 133
 - of silicon, 115
 - of silver, 117
 - of sodium, 135
 - of thallium, 136
 - of tin, 121
 - of zinc, 125
- Contact electrode, 23
 - Copper alloys, 47
 - conductivity of, 49
 - constitution diagram, 48
 - history of, 47
 - master alloys of, 52
 - Copper, effect of calcium on conductivity of, 49
 - Creep, 15
 - Crystal form, 12
 - Crystals, 31

D

- Debismuthizing of lead, 88
- Density, 13
- Dimensions of, 34
- Distillation, 31
- Ductility, 15

E

- Electrical resistance, 14
- Electrochemical equivalent, 14
- Electrolytic separation, 22
- Entropy, 14
- Extrusion, 16

F

- Ferrous metallurgy, calcium in, 54
- Freezing point, 12

G

- Gas concrete, 98
- Getters, 18
- Gold alloys, 64
 - constitution diagram, 65

H

- Hardness, 15
- Heat of vaporization, 16
- High resistance alloys, 107
- Hydride, 57
 - reductant for oxides, 59

I

- Improvement in, 32

L

- Lead alloys, 66
 - ageing of, 74
 - chemical methods for, 81
 - composition of, 82
 - conductivity, 73
 - constitution diagram, 67
 - deformation pressure, 72
 - hardening of, 73
- Lead barium alloys, 79
 - manufacture, 80
- Lithium alloys, 129
- Lurgi metal, 78

M

- Magnesium alloys, 95
 - composition, 102
 - constitution diagram, 96
- Magnetic susceptibility, 16
- Magnewin, 97
- Mercury alloys, 131
 - constitution diagram, 132
- Modulus of elasticity, 15

N

- Nickel alloys, 106
- Nitride, 18
- Nitrogen system, 131
 - constitution diagram, 133

O

- Operating details, 24
- Oxidation, 17
- Oxide, solubility of, 22

P

- Plastic deformation, 16
- Platinum system, 131
- Power consumption, 25
- Production, 21
- Properties, 9
- Protection by calcium chloride, 27

R

- Reaction with rare gases, 18
- Reaction with water, 17

S

- Sateo metal, 81
- Silicon alloys, 110
 - constitution diagram, 115
 - manufacture of, 113
- Silver alloys, 117
 - constitution diagram, 117
- Sodium alloys, 134
 - constitution diagram, 135
- Solubility of, in magnesium, 101
- Specific heat, 14

T

- Tensile strength, 15
- Thallium alloys, 134
 - constitution diagram, 136
- Thermal conductivity, 14
- Thermal expansion, 13
- Thorium powder, 137
- Tin alloys, 120
 - constitution diagram, 121
- Transformation points, 16

U

- Ulco, 78
- Union metal, 81
- Uranium powder, 137
- Uranium, production of, 61
- Use in petroleum, 139

V

- Valence, 14
- Vapor pressure, 16

Z

- Zinc alloys, 124
 - constitution diagram, 125
- Zirconium powder, 137

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