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*GENERAL METALLOGRAPHY*



# GENERAL METALLOGRAPHY

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## PREFACE

This book is intended for beginning students in metallography or physical metallurgy for engineers as an introductory work to the many specialized books and the vast amount of technical information being published in the field. An attempt has been made to include sufficient material for a one-year course and at the same time to make it concise enough for shorter courses.

The order in which various subjects are presented is such that laboratory work can be arranged to follow along with the course. Many years of classroom experience with metallurgical, aeronautical, mechanical, and chemical engineering students have convinced the authors that this arrangement enables these men to grasp the fundamental principles readily.

The authors wish to acknowledge indebtedness to the many books and other technical publications. We have tried to give due credit to other authors for any material used. By far the most of this material is from the *Metals Handbook of the American Society for Metals* for 1939 and we appreciate permission to use it. The micrographs are from our own collection prepared in the metallographic laboratory of the University of Minnesota, with the exception of a few which are credited to others.

Rather definite information about important commercial alloys has been included because it was felt that the engineer needs something more than a theoretical treatment of the subject. After all, he has to work with the alloys available on the market and is definitely interested in their characteristics. Some of the tables of physical and mechanical properties were included to make this volume more useful as an elementary reference book on metals and alloys.

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*Minneapolis, Minnesota*  
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# CHAPTER I

## INTRODUCTION

### **Metallography**

Metallography is the study of the structure of metals and alloys as related to their properties.

Metals and alloys are the most useful of engineering materials, but their full usefulness can be realized only if the proper alloy is selected for a given application. To this end a general knowledge of metallography is essential, and it can also help the engineer to understand the behavior of alloys during processing and heat treatment.

### **Elements**

Elements are the unit substances of which all matter is composed. Each of the 92 chemical elements has a definite atomic number and definite properties summarized in Table 1. Most of them are solids at room temperature although some are gases or liquids.

### **Metals**

Over two-thirds of the elements are classed as metals. These are characterized by a metallic "luster" or high reflectivity of light, high electrical and thermal conductivities, and in most cases a capacity for being shaped or deformed plastically without rupture. Several elements, including carbon, boron, and silicon, resemble metals in some respects and nonmetals in others and are called *metalloids*. A chemical distinction between metals and nonmetals can be made generally on the basis of the basic or acidic nature of their oxides, the oxides of metals being usually base forming.

In the periodic arrangement of the elements, as given in Table 2, they are grouped according to similarities in properties. The elements whose symbols appear in bold-faced type may be classed as metals.

### **Alloys**

An alloy is a metallic substance containing more than one element. It should be pointed out that although most of the alloy-forming elements are metals, the metalloids, some nonmetals, and even several

TABLE 1. PHYSICAL

Element	Symbol	Atomic Number	Atomic Weight (1933)	Density, g/cm <sup>3</sup> at 20°C (68°F)	Density lb/cm in. at 68°F (20°C)	Atomic Volume, cu cm/g atom	Melting Point, °F	Boiling of (760 mm pressure)	Specific Heat cal/g/°C at room temperature = Btu/lb/°F at room temperature	Latent Heat of Fusion, cal/g	Latent Heat of Fusion, Btu/lb
Actinium	Ac	89	227				3272 <sup>d</sup>	> 3092 <sup>d</sup>			
Aluminum	Al	13	26.97	2.70	0.0975	9.99	1214.6	3733	0.2259	93	167.4
Antimony	Sb	51	121.76	6.62	0.2391	18.39	1166.9	2624	0.0493	38.26	68.87
Argon	A	18	39.944	1.6626 × 10 <sup>-3</sup>	6.008 × 10 <sup>-3</sup>		-306.2	-302.4	0.1252	6.71	12.08
Arsenic	As	33	74.91	5.73	0.2070	13.07	1497 <sup>d</sup>	1139 <sup>d</sup>	0.0822		
Barium	Ba	56	137.36	3.5	0.1265	39.25	1562	2980	0.0690		
Beryllium	Be	4	9.02	1.85	0.0658	4.96	2345	5036	0.425	345.5	621.9
Bismuth	Bi	83	209.00	9.80	0.3541	21.33	519.8	2642	0.0290	12.46	22.43
Boron	B	5	10.82	2.3	0.0831	4.70	4172	4622	0.3091		
Bromine	Br	35	79.916	3.2	0.1127	25.62	19.04	137.79	0.0703	16.15	29.07
Cadmium	Cd	48	112.41	8.65	0.3125	12.99	609.6	1412.6	0.0547	13.17	23.71
Calcium	Ca	20	40.08	1.55	0.0560	25.86	1564	2709	0.157		
Carbon (graphite)	C	6	12.01	2.22	0.0802	5.41		8721	0.165		
Cerium	Ce	58	140.13	6.9	0.2493	20.3	1427	2552	0.05		
Cesium	Cs	55	132.91	1.9	0.0686	69.95	78.8	1238	0.0521	3.76	6.77
Chlorine	Cl	17	35.457				-150.88	-30.28	0.226	22.97	41.35
Chromium	Cr	24	52.01	7.14	0.2579	7.29	3488	4500	0.12	31.75	57.15
Cobalt	Co	27	58.94	8.9	0.3216	6.6	2714	5252	0.0989	58.38	105.08
Columbium	Cb	41	92.91	8.57	0.3096	10.8	3542	> 5972			
Copper	Cu	29	63.57	8.94	0.323	7.11	1981.4	4703	0.0918	50.6	91
Dysprosium	Dy	66	162.46								
Erbium	Er	68	167.2								
Europium	Eu	63	152.0								
Fluorine	F	9	19.00				-369.4	304.6		10.06	18.1
Gadolinium	Gd	64	156.9								
Gallium	Ga	31	69.72	5.91	0.2135	11.8	85.6	3760	0.0788	19.16	34.5
Germanium	Ge	32	72.60	5.36	0.1937	13.54	1757.3	4892	0.0733		
Gold	Au	79	197.2	19.3	0.6973	10.22	1945.4	5371	0.0308	16.11	28.99
Hafnium	Hf	72	178.6	11.4	0.4118	15.66	3092	9740			
Hassium	Hs	2	4.003	0.1064 × 10 <sup>-3</sup>	0.6008 × 10 <sup>-3</sup>		< -458.0	-452.0	1.25		
Holmium	Ho	67	163.5								
Hydrogen	H	1	1.008	0.06375 × 10 <sup>-3</sup>	0.3026 × 10 <sup>-3</sup>		-434.4	-422.957	3.415	15.0	27.0
Illinium	Il	61									
Indium	In	49	114.76	7.275	0.264	15.7	322	> 2642	0.0568		
Iodine	I	53	126.92	4.93	0.178	25.7	236.3	363.8	0.0523	15.76	28.40
Iridium	Ir	77	193.1	22.4	0.809	8.6	4368	8852	0.0322		
Iron	Fe	26	55.85	7.87	0.284	7.1	2795	5430	0.1075	65	117
Krypton	Kr	36	83.7	3.488 × 10 <sup>-3</sup>	3.502 × 10 <sup>-3</sup>		-275.22	-250.6			
Lanthanum	La	57	138.92	6.15	0.222	22.6	1518.8	3272	0.0446		
Lead	Pb	82	207.21	11.34	0.409	18.3	621.2	3171	0.030	6.26	11.27
Lithium	Li	3	6.940	0.53	0.0193	13.1	366.8	2502	0.79	32.81	59.02
Lutecium	Lu	71	175.0								
Magnesium	Mg	12	24.32	1.74	0.0628	14.0	1204	2025	0.249	70.0	126
Manganese	Mn	25	54.93	7.44	0.268	7.4	2268	3904	0.107	64.8	116.64
Masurium	Ma	43									
Mercury	Hg	80	200.61	13.55	0.489	14.8	-38.0	674.4	0.0332	2.66	4.78
Molybdenum	Mo	42	95.95	10.2	0.368	9.4	4748	8679	0.0647		
Neodymium	Nd	60	144.27	7.05	0.255	20.5	1544		0.0447		
Neon	Ne	10	20.183	0.8387 × 10 <sup>-3</sup>	3.030 × 10 <sup>-3</sup>		-415.498	-411.34			
Nickel	Ni	28	58.69	8.9	0.322	6.64	2646	5252	0.112	73.8	132.8
Nitrogen	N	7	14.006	1.1649 × 10 <sup>-3</sup>	4.209 × 10 <sup>-3</sup>		-345.87	-320.40	0.247	6.15	11.07
Osmium	Os	76	190.2	22.5	0.812	8.45	4892	9620	0.031		
Oxygen	O	8	16.0000	1.3318 × 10 <sup>-3</sup>	4.8122 × 10 <sup>-3</sup>		-361.12	-297.334	0.2184	3.32	5.98
Palladium	Pd	46	106.7	12.0	0.433	8.9	2831	7196	0.0587	34.2	61.8
Phosphorus (Yellow)	P	15	30.98	1.82	0.0657	17.0	111.4	536	0.177	5.04	9.07

<sup>d</sup>Sublimes

<sup>d</sup>This table was compiled by the Subcommittee on Physical Constants. The membership of the subcommittee was as follows: R. L. Kozony, Chairman; J. B. Johnson, H. W. Russell, and C. S. Barrett. The subcommittee solicited

CONSTANTS OF ELEMENTS\*

Symbol	Physical Constants of Elements							Closest Approach of Atoms, Å		
	Linear Coefficient of Thermal Expansion, /°C at room temperature	Linear Coefficient of Thermal Expansion, /°F at room temperature	Thermal Conductivity, cal/cm <sup>2</sup> /°C/sec at room temperature	Electrical Resistivity, microhm/cm <sup>2</sup>	Modulus of Elasticity (Tension), psi	Type of crystal lattice	Lattice constant (A = 10 <sup>-8</sup> cm) 20°C (68°F)			
							a <sub>0</sub>		b <sub>0</sub>	c <sub>0</sub>
	×10 <sup>-4</sup>	×10 <sup>-4</sup>			×10 <sup>8</sup>					
Ac	24	13.3	0.52	2.655	10	Face-centered cubic	4.0413		2.858	
Al	11.29	6.27	0.0444	39	11.3	Rhombohedral hexagonal	4.4974		2.878	
Sb			0.406 × 10 <sup>-4</sup>			Face-centered cubic		57°6'		
A	3.86	2.14		35		Rhombohedral hexagonal	4.135	54°75'	2.50	
As						Body-centered cubic†	5.015		4.34	
Ba	12.3	6.8	0.3847	18.5	42.7	Hexagonal close packed†	2.281	8.577	2.22	
Be	13.45	7.47	0.0200	115	4.6	Rhombohedral hexagonal	4.736	67°14'	3.104	
B	2	1.1		1.8 × 10 <sup>12</sup>		Hexagonal (?)†				
Br										
Cd	29.8	16.6	0.217	7.59		Hexagonal close packed	2.0727	5.6061	2.972	
Ca	25	13.89		4.6		Face-centered cubic†	5.560		3.93	
C	1.2	0.67	0.057	1000	0.7	Hexagonal†	2.46	6.69	1.42	
Ce				78		Face-centered cubic†	5.143		3.64	
Cl	97	54		20		Body-centered cubic	6.2		5.3	
Co	11.44	6.36	0.172 × 10 <sup>-4</sup>	10 × 10 <sup>15</sup>		Body-centered cubic†	2.878		2.492	
Cr	8.1	4.5	0.165	13.1		Hexagonal close packed†	2.507	4.072	2.50	
CCb	12.08	6.71	0.165	9.7		Body-centered cubic	3.2941		2.852	
CCo	7.2	4		20		Face-centered cubic	3.6080		2.551	
Cu	16.42	9.1	0.923	1.682	16	Hexagonal close packed†	3.74	6.09	3.74	
Dy										
Er										
Eu										
Fa										
Gd	18.3	10.2		57.1		One-faced-centered orthorhombic	4.506	4.506	7.642	
Ge				89 × 10 <sup>9</sup>		Cubic (diamond)	5.647		2.447	
Au	14.4	8.0	0.7072	2.42	11.3	Face-centered cubic	4.0700		2.44	
Hf						Hexagonal close packed†	3.200	5.077	2.878	
He			3.32 × 10 <sup>-4</sup>						3.14	
Ho										
Er			4.06 × 10 <sup>-4</sup>							
Ir										
I	30	16.6	0.057	9		Face-centered tetragonal	4.585	4.941	3.42	
93	93	51.7	10.4 × 10 <sup>-4</sup>	1.3 × 10 <sup>15</sup>		One-faced-centered orthorhombic	4.791	7.248	9.771	
Ir	6.41	3.5	0.141	8.08	74.7	Face-centered cubic	3.8312		2.70	
Fe	11.9	6.6	0.19	9.8	30	Body-centered cubic†	2.8610		2.709	
Kr			0.212 × 10 <sup>-4</sup>						2.478	
Lr				59		Hexagonal close packed†	3.75	6.06	3.7	
Pb	29.5	16.4	0.083	20.65	2.56	Face-centered cubic	4.9389		3.492	
Li	56	31	0.17	8.5		Body-centered cubic	3.51		3.0	
Lu										
Mg	25.7	14.3	0.37	4.46	6.25	Hexagonal close packed	3.2022	5.1991	3.190	
Mn	23	12.8				Cubic (complex)†	8.894		1.065	
Ma										
Hg			0.0200	95.8		Body-centered cubic	3.1403		2.720	
Mo	5.49	3.05	0.350	4.77	50.2	Hexagonal close packed†	3.657	5.880	3.62	
Nd				79						
Ne			1.092 × 10 <sup>-4</sup>							
Ni	13.7	7.6	0.140	6.9	30	Face-centered cubic†	3.517		2.486	
N			0.600 × 10 <sup>-4</sup>							
O	5.70	3.2		9		Hexagonal close packed	2.7304	4.3099	2.670	
Pd	11.60	6.4	0.589 × 10 <sup>-4</sup>	10	17	Face-centered cubic	3.8817		2.744	
P	125	69	0.161	10 <sup>17</sup>						

† Ordinary form at 20°C; other modifications known or probable at other temperatures.

additional data and corrections for future revisions of this table. Communications should be directed to J. E. Donnellan, Secretary of the Committee, 7016 Euclid Ave., Cleveland.

TABLE 1

Element	Symbol	Atomic Number	Atomic Weight (1935)	Density, g/cu cm at 20°C (68°F)	Density lb/cu in. at 68°F (20°C)	Atomic Volume, cu cm/g atom	Melting Point, °F	Boiling Point, °F (760 mm pressure)	Specific Heat, cal/g°C at room temperature = Btu/lb°F at room temperature	Latent Heat of Fusion, cal/g	Latent Heat of Fusion, Btu/lb
Platinum	Pt	78	195.23	21.45	0.0774	9.1	3224	7033	0.0310	27.1	48.78
Polonium	Po	84	210								
Potassium	K	19	39.096	0.86	0.031	45.5	144.1	1425	0.177	14.5	26.1
Praseodymium	Pr	59	140.92	6.63	0.239	21.3	1724		0.458		
Protactinium	Pa	91	231								
Radium	Ra	86	226.05	5.0	0.1808	45.2	1760	2084			
Radon	Rn	86	222	4.40 <sup>a</sup>	0.159	50.45	-95.8	-79.2			
Rhenium	Re	75	186.31	20	0.723	8.9	5432	10,600	0.0346		
Rhodium	Rh	45	102.91	12.44	0.449	8.23	3571	8132	0.0598		
Rubidium	Rb	37	85.43	1.53	0.0553	55.87	101	1292	0.0802	6.095	10.75
Ruthenium	Ru	44	101.7	12.2	0.441	8.33	4442	8852	0.061		
Samarium	Sm	62	150.43	7.7	0.28	19.4	>2400				
Scandium	Sc	21	45.10	2.5	0.09	18.0	2200	4400			
Selenium	Se	34	78.96	4.81	0.174	16.4	428	1270	0.084		
Silicon	Si	14	28.06	2.4	0.087	11.7	2600	4149	0.1762		
Silver	Ag	47	107.880	10.5	0.38	10.27	1761	3634	0.0558	24.3	43.8
Sodium	Na	11	22.997	0.97	0.035	23.7	207.5	1638	0.295	27.53	49.6
Strontium	Sr	38	87.63	2.6	0.094	33.7	1420	2523		25	45
Sulfur	S	16	32.06	2.07	0.075	15.46	235.4	832.3	0.175	9.3	16.7
Tantalum	Ta	73	180.88	16.6	0.60	10.9	5162	11,000	0.0356		
Tellurium	Te	52	127.61	6.24	0.224	20.45	846	1989	0.0468	7.305	13.15
Terbium	Tb	65	159.2				590				
Thallium	Tl	81	204.39	11.85	0.428	17.24	578	2655	0.0311	7.185	12.94
Thorium	Th	90	232.12	11.5	0.416	20.2	3353	9392	0.0276		
Thulium	Tm	69	169.4								
Tin	Sn	50	118.70	7.30	0.264	16.23	449.6	4118	0.054	14.4	25.9
Titanium	Ti	22	47.90	4.5	0.163	10.6	3272	9212	0.142		
Tungsten	W	74	183.92	19.3	0.698	9.53	6098	10,700	0.034	44	79
Uranium	U	92	238.07	18.7	0.676	12.73	3074	6332	0.0276		
Vanadium	V	23	50.95	5.68	0.205	8.97	3110	5432	0.1153		
Xenon	Xe	54	131.3	5.495 × 10 <sup>-3</sup>	5.517 × 10 <sup>-3</sup>		-169.6	-160.78			
Ytterbium	Yb	70	173.04								
Yttrium	Y	39	88.92	5.51	0.199	16.13	2700	8312			
Zinc	Zn	30	65.38	7.14	0.258	9.16	787	1665	0.09	24.09	43.36
Zirconium	Zr	40	91.22	6.4	0.23	14.3	3092	9122	0.066		

<sup>a</sup>Liquid at -62°C.

(Continued)

Symbol	Physical Constants of Elements				Modulus of Elasticity (Tension), psi	Type of crystal lattice	Lattice constant (A = 10 <sup>-8</sup> cm) 20°C (68°F)			Closest Approach of Atoms, A		
	Linear Coefficient of Thermal Expansion/°C at room temperature	Linear Coefficient of Thermal Expansion/°F at room temperature	Thermal Conductivity, cal/cm <sup>2</sup> /°C/sec at room temperature	Electrical Resistivity, microhm-cm			×10 <sup>9</sup>	Type of crystal lattice	Lattice constant (A = 10 <sup>-8</sup> cm) 20°C (68°F)			
									a <sub>0</sub>		b <sub>0</sub>	c <sub>0</sub>
Pt	8.8	4.3	0.166	9.83	21.4	Face-centered cubic	3.9158			2.768		
Po						Monoclinic; β = 92°	7.42	4.29	14.10	2.81		
K	83	46	0.237	7.0		Body-centered cubic	5.333			4.62		
Pr				88		Hexagonal close packed†	3.657		5.924	3.6		
Pa												
Ra												
Rn												
Re				21		Hexagonal close packed	2.755		4.449	2.734		
Rh	a	b	0.213	21	42.5	Face-centered cubic†	3.7957			2.684		
Ru	8.9	4.5		4.93		Body-centered cubic	5.7			4.9		
Rb	90.0	50.0		12.5		Hexagonal close packed†	2.698		4.274	2.644		
Ru	8.5	4.7		10								
Sr												
Sm												
Se	37.0	20.6		12		Hexagonal†	4.337		4.944	2.32		
Si	2.8-7.3	1.6-4.1	0.20	85×10 <sup>9</sup>	16	Cubic (diamond)	5.4173			2.340		
Ag	18.9	10.5	0.974	1.62	10.3	Face-centered cubic	4.0774			2.882		
Na	71	39.5	0.3225	4.6		Body-centered cubic	4.30			3.72		
Sr				22.76		Face-centered cubic†	6.075			4.30		
S	67.48	37.49	0.00063	1.9×10 <sup>17</sup>		Face-centered orthorhombic†	10.48	12.92	24.55	2.12		
Ta	6.5	3.6	0.130	15.5	27.0	Body-centered cubic	3.2959			2.854		
Te	16.8	9.3	0.01433	5.8-33×10 <sup>9</sup>		Hexagonal	4.445		5.912	2.86		
Tb												
Tl	28.0	15.6	0.09315	18.1		Hexagonal close packed†	3.450		5.520	3.40		
Th	12.3	6.84		18		Face-centered cubic†	5.077			3.59		
Tm												
Sn	e	k	0.157	11.5	5.9-7.8	Body-centered tetragonal†	5.819		3.175	3.016		
Ti	8.5	3.96				Hexagonal close packed†	2.963		4.729	2.90		
W	4.0	2.2	0.476	5.48	60	Body-centered cubic†	3.1585			2.734		
U				60		Orthorhombic†	2.852	5.865	4.945	2.76		
V				26		Body-centered cubic	3.033			2.627		
Xe			1.24×10 <sup>-4</sup>									
Yb												
Y						Hexagonal	3.663		5.814	3.59		
Zn	f	g	0.268	h		Hexagonal close packed	2.659		4.936	2.658		
Zr	6.3	3.5		41	10.7	Hexagonal close packed†	3.223		5.123	3.16		

† Ordinary form at 20°C; other modifications known or probable at other temperatures.

\*20-1917°C, 12.5 || crystal axis.

4.7 ⊥ crystal axis.

‡20-1917°C, 6.94 || crystal axis.

2.61 ⊥ crystal axis.

§Liquid at -62°C.

¶Single crystal, 22.4 || crystal axis.

46.4 ⊥ crystal axis.

‡32.5 pure, hot-rolled zinc with grain.

23.0 pure, hot-rolled zinc across rolling.

¶18.0 pure, hot-rolled zinc with grain.

12.8 pure, hot-rolled zinc across rolling.

‡Single crystal, 6.2 || crystal axis.

5.8 ⊥ crystal axis.

‡Single crystal, 12.4 || crystal axis.

25.8 ⊥ crystal axis.

TABLE 2. PERIODIC ARRANGEMENT OF THE ELEMENTS—MENDELEEFF'S\*

Series	Period	Zero Group	Group I		Group II		Group III		Group IV		Group V		Group VI		Group VII		Group VIII		
			___	___	___	___	___	___	___	___	___	___	___	___	___	___	___	___	___
0																			
1																			
2	1	Helium He = 4.002 No. 2	Hydrogen H = 1.0080 No. 1	Lithium Li = 6.940 No. 3	Beryllium Be = 9.02 No. 4	Boron B = 10.82 No. 5	Carbon C = 12.00 No. 6	Nitrogen N = 14.008 No. 7	Oxygen O = 16.000 No. 8	Fluorine F = 19.00 No. 9	Chlorine Cl = 35.457 No. 17								
3	2	Neon Ne = 20.183 No. 10	Sodium Na = 22.997 No. 11	Magnesium Mg = 24.32 No. 12	Aluminum Al = 26.97 No. 13	Silicon Si = 28.06 No. 14	Phosphorus P = 31.02 No. 15	Sulfur S = 30.98 No. 16	Manganese Mn = 54.93 No. 25	Iron Fe = 55.85 No. 26									
4	3	Argon Ar = 39.944 No. 18	Potassium K = 39.10 No. 19	Calcium Ca = 40.08 No. 20	Scandium Sc = 45.10 No. 21	Titanium Ti = 47.90 No. 22	Vanadium V = 50.95 No. 23	Chromium Cr = 52.01 No. 24	Selenium Se = 78.96 No. 34	Ruthenium Ru = 101.7 No. 44	Cobalt Co = 58.94 No. 27								
5	4	Krypton Kr = 83.9 No. 36	Copper Cu = 63.57 No. 29	Zinc Zn = 65.38 No. 30	Gallium Ga = 69.72 No. 31	Germanium Ge = 72.60 No. 32	Arsenic As = 74.93 No. 33	Antimony Sb = 121.76 No. 51	Tellurium Te = 127.5 No. 52	Iodine I = 126.932 No. 53									
6	5	Xenon Xe = 130.2 No. 54	Silver Ag = 107.880 No. 47	Cadmium Cd = 112.41 No. 48	Indium In = 114.8 No. 49	Tin Sn = 118.70 No. 50	Lead Pb = 207.22 No. 82	Bismuth Bi = 209.00 No. 83	Thallium Tl = 204.39 No. 81										
7	6	Radon Rn = 222 No. 86	Barium Ba = 137.36 No. 56	Strontium Sr = 87.63 No. 38	Yttrium Y = 88.92 No. 39	Zirconium Zr = 91.22 No. 40	Niobium Nb = 92.92 No. 41	Molybdenum Mo = 96.0 No. 42	Rhenium Re = 186.31 No. 75	Osmium Os = 190.8 No. 76									
8	7		Mercury Hg = 200.61 No. 80	Radium Ra = 225.97 No. 88	Thallium Tl = 204.39 No. 81	Thorium Th = 232.12 No. 90	Protactinium Pa = 231.04 No. 91	Uranium U = 238.14 No. 92											
9	8																		
10	9																		
11	10																		
12	11																		

\* Bold-faced type indicates metals.

Elements not classified in the table above:  
 Francium  
Fr = 140.92  
No. 59  
 Radium  
Ra = 225.97  
No. 88  
 Actinium  
Ac = 144.27  
No. 60  
 Thorium  
Th = 232.12  
No. 90  
 Protactinium  
Pa = 231.04  
No. 91  
 Uranium  
U = 238.14  
No. 92  
 Neptunium  
Np = 237.04  
No. 93  
 Plutonium  
Pu = 244  
No. 94  
 Americium  
Am = 243  
No. 95  
 Curium  
Cm = 247  
No. 96  
 Berkelium  
Bk = 247  
No. 97  
 Californium  
Cf = 251  
No. 98  
 Einsteinium  
Es = 252  
No. 99  
 Fermium  
Fm = 257  
No. 100  
 Mendeleevium  
Md = 258  
No. 101  
 Nobelium  
No = 259  
No. 102  
 Lawrencium  
Lr = 262  
No. 103  
 Rutherfordium  
Rf = 263  
No. 104  
 Dubnium  
Db = 264  
No. 105  
 Seaborgium  
Sg = 266  
No. 106  
 Bohrium  
Bh = 264  
No. 107  
 Oganesson  
Og = 289  
No. 118  
 Ytterbium  
Yb = 173.5  
No. 70  
 Lutetium  
Lu = 175.0  
No. 71  
 Erbium  
Er = 167.64  
No. 68  
 Holmium  
Ho = 163.5  
No. 67  
 Samarium  
Sm = 150.43  
No. 62  
 Dysprosium  
Dy = 162.46  
No. 66  
 Europium  
Eu = 152.0  
No. 63  
 Terbium  
Tb = 158.93  
No. 64  
 Gadolinium  
Gd = 157.3  
No. 65  
 Terbium  
Tb = 159.2  
No. 65  
 Dysprosium  
Dy = 162.46  
No. 66  
 Europium  
Eu = 152.0  
No. 63  
 Samarium  
Sm = 150.43  
No. 62  
 Gadolinium  
Gd = 157.3  
No. 65  
 Terbium  
Tb = 158.93  
No. 64  
 Ytterbium  
Yb = 173.5  
No. 70  
 Lutetium  
Lu = 175.0  
No. 71  
 Erbium  
Er = 167.64  
No. 68  
 Holmium  
Ho = 163.5  
No. 67  
 Gadolinium  
Gd = 157.3  
No. 65  
 Europium  
Eu = 152.0  
No. 63  
 Samarium  
Sm = 150.43  
No. 62  
 Dysprosium  
Dy = 162.46  
No. 66  
 Terbium  
Tb = 159.2  
No. 65  
 Holmium  
Ho = 163.5  
No. 67  
 Thulium  
Tm = 168.93  
No. 69  
 Erbium  
Er = 167.64  
No. 68  
 Ytterbium  
Yb = 173.5  
No. 70  
 Lutetium  
Lu = 175.0  
No. 71

gaseous elements can combine with metals to form alloys. Ordinary steel is an alloy of iron with the metalloid carbon and also contains the metal manganese, the metalloid silicon, and the nonmetals phosphorus and sulfur.

### **Metallic Atoms**

The atom is the smallest particle of an element and is the fundamental unit from which the grain structure of a metal is built. Although metallography is concerned more with the crystal or grain structure of metals, a clear picture of the nature of atoms will help the student to understand some of the characteristics of metals. An atom is not a rigid body but is built up of a small but heavy nucleus about which light, negatively charged particles travel in orbits that have been likened to those of the planets about the sun. The comparison is not very accurate but it serves to illustrate the relatively large size of the nucleus (sun) and the small size of the negative particles or electrons (planets), the total volume of the atom being analogous to the whole solar system. The atom, however, is an extremely small particle, the average volume being on the order of  $1 \times 10^{-23}$  cubic centimeters. The mass of one atom is about  $1.65 \times 10^{-24}$  grams multiplied by the atomic weight of the element as given in Table 1. The smallest particle of matter that can be resolved with the best metallurgical microscope contains many millions of atoms.

At temperatures above its boiling point, a metal is a monatomic gas. The individual atoms are not in continuous contact with each other but are in a constant state of motion. The boiling point of a metal varies with pressure and the values given in Table 1 are for atmospheric pressure.

In the liquid state, between the boiling and freezing points, the atoms also have considerable mobility but are in much closer contact with each other. In general, there is no permanent bond between neighboring atoms but at any temperature there is an equilibrium between the attractive forces and repelling forces among the atoms. As the molten metal approaches the freezing temperature, the attractive forces become relatively stronger and there is some tendency for the atoms to become temporarily associated in small groups. These groups are unstable above the freezing point and are continually breaking up and reforming. Only after the metal has cooled to the freezing point does the condition of the equilibrium between attractive and repelling forces reach a stage where these groups are stable.



## CHAPTER II

### CRYSTALLIZATION AND CRYSTAL STRUCTURE

#### Crystallization

Below the freezing point all metals are crystalline; that is, their atoms are arranged in a definite geometric pattern called the *space lattice*. The transition from the liquid to the solid state occurs in two stages which are usually designated, respectively, as *nuclei formation* and *crystal growth*. During the first stage stable groups of atoms are formed which are called nuclei. Within one of these groups the atoms are arranged in a definite space lattice.



FIG. 1. Dendrite of copper mineral ( $\text{Cu}_2\text{S}$ ) showing crystal growth along crystal axes. Actual size.

During the second stage of crystallization these nuclei grow by attracting other atoms from the liquid phase into their space lattice. Crystal growth continues in three dimensions, usually along the axes of the crystal, to give a crystallite of a characteristic form called a *dendrite*. Fig. 1 illustrates the characteristic pine-tree shape of a dendrite. Frost figures on window panes and the spangling of zinc on ordinary galvanized iron are examples of the same phenomenon.

As freezing progresses the growth of the dendrite continues until it is halted by contact with neighboring dendrites. The shape of the resultant crystal unit or *grain* is therefore determined by chance meeting with adjacent grains during the final stage of solidification.

Fig. 2 shows the polyhedral grain structure of a commercial grade of cast copper which has been polished and etched with acid to bring out the grain boundaries. Each grain is a separate crystal unit with its own orientation of crystal axes.

The average size of the grains in a cast metal depends to a large extent on how rapidly the metal in the mold freezes. When the cooling

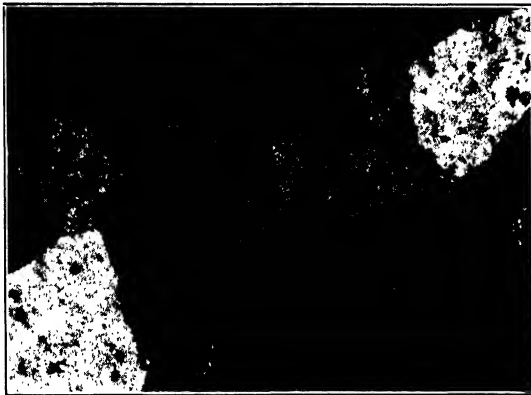


Fig. 2. Copper as cast. Polyhedral grain structure of a commercial grade of cast copper. Etched with copper ammonium chloride.  $\times 50$ .

rate is rapid, freezing begins at a large number of points throughout the metal, resulting in a large total number of grains and a small average grain size. Conversely, a slow freezing rate usually causes a coarse-grained structure.

The shape of the individual grains usually tends to be *equiaxed* or approximately the same size in three directions. In some cast metals, however, the grains are columnar in shape, being longer in the direction perpendicular to the walls of the mold. This columnar structure is due to the fact that freezing begins at the walls of the mold where the heat losses occur and progresses toward the center. Fig. 3 illustrates the columnar structure in a square ingot and also shows how two sets of grains growing in different directions meet along the diagonals of a square casting to give planes of weakness. This defect is usually accentuated by a concentration of impurities along these planes and may cause internal rupture during forging or rolling operations.

The crystalline nature of metals can be demonstrated by several methods. Deeply etched surfaces often show exposed crystal faces in



FIG. 3. Zinc of commercial grade. Treatment — cast into chilled iron mold. Shows columnar crystallization at right angles to the walls of the mold. Reduced one-half.

the form of etching pits or etch figures as illustrated in Fig. 4. Frequently, dendrites on the upper surface of a cast metal become exposed during freezing as a result of solidification shrinkage and appear in relief

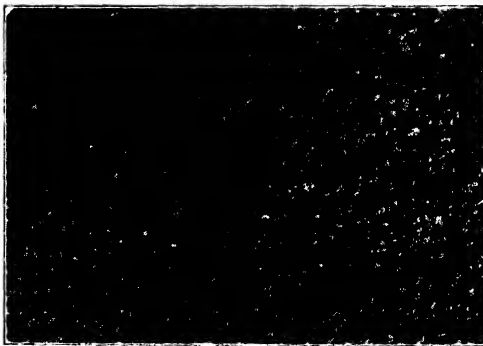


FIG. 4. Ingot iron deeply etched with concentrated  $\text{HNO}_3$  to show etching pits within one particular grain of the wrought metal.  $\times 900$ .

on the surface of the casting. The most complete information about the crystalline nature of metals is obtained by x-ray diffraction studies.

## Crystal Structure

In the solid state each metal has a characteristic arrangement of atoms and the smallest unit of this pattern is called a unit cell of the space lattice. Fig. 5 shows models of unit cells of the three types of space lattice most common among metals. The individual atoms are not held rigidly in fixed positions in the lattice but actually oscillate about the average positions indicated by the model.

A very large number of different types of space lattices is possible and these can be classified, according to their symmetry, into seven crystal systems: cubic, tetragonal, hexagonal, rhombohedral, ortho-

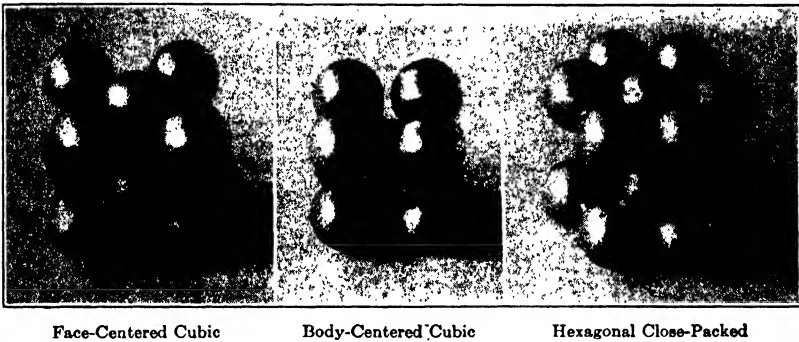


FIG. 5. Three common types of crystal structure with the spheres representing atoms.

rhombic, monoclinic, and triclinic. The cubic system has the highest degree of symmetry; it is the simplest and it can be studied most easily.

Most of the metallic elements crystallize in either the face-centered cubic or the body-centered cubic space lattice. Several others have the hexagonal close-packed lattice. These are the three types illustrated in Fig. 5. Several elements can exist in two or more forms, each having a different type of space lattice; these are called *allotropic* or *polymorphic*. In general, metals whose lattices possess a high degree of symmetry have the highest capacity for plastic deformation.

The layers of atoms or the planes along which atoms are arranged within the crystal are known as atomic or crystallographic planes. Various planes intersect the axes of the crystal at different angles, and there can be a large number of these if the symmetry of the lattice is high. But the important planes are those along which the atoms are spaced close together. Plastic deformation in metals occurs by slippage along certain planes called *slip* planes. In cold or hot working,

this slippage generally occurs along the planes that have the highest atomic concentration and that are spaced the farthest apart.

Various crystallographic planes are usually designated in terms of Miller indices, determined by the manner in which the planes intersect

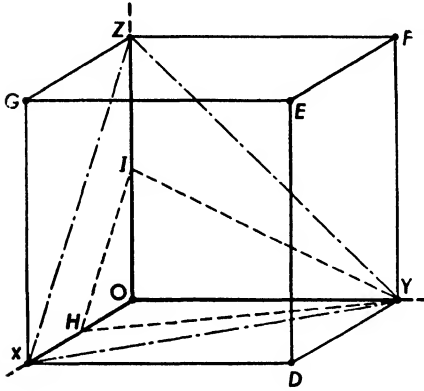


FIG. 6. Crystallographic planes.

the axes of the crystal. In Fig. 6 the principal axes are  $OX$ ,  $OY$ , and  $OZ$ . Only one unit cube is shown, but these axes are continuous and along them the atoms are spaced at regular intervals. Some of the crystallographic planes are indicated in the figure. The plane  $XYZ$  intersects each of the axes at unit distance from the origin,  $O$ , and it can be said that the intercepts of the plane with the  $X$ ,  $Y$ , and  $Z$  axes are 1, 1, and 1 respectively. The Miller indices, in this case 111, are the

reciprocals of these intercepts, with fractions cleared. The plane  $HYI$  has the intercepts  $\frac{1}{2}$ , 1,  $\frac{1}{2}$  and Miller indices 212. Other planes are indicated in Fig. 6.

By using a model containing more than one unit cell of the space lattice, as in Fig. 7,<sup>1</sup> it can be shown that there are sets of uniformly spaced parallel planes which can be designated in terms of the Miller indices of the plane to which they are parallel, as (110), (100), etc.

### X-Ray Diffraction

The parallel sets of planes in a crystal can be used as diffraction gratings with x-rays in much the same manner as fine parallel lines ruled uniformly on a surface are used to diffract ordinary light. The x-ray diffraction pattern obtained with a given crystal can be used to determine the type of space lattice, the arrangement and spacing of atoms within the lattice, and other important information about the crystal. The interpretation of x-ray diffraction patterns is not simple and is beyond the scope of a beginning course in metallography. The following pages give only a brief outline of the subject.

X-rays are transverse waves similar to light waves but their wave length is very much shorter, being on the same order of magnitude as the spacing of atomic planes of crystals. When a beam of x-rays falls

<sup>1</sup> G. L. Clark, *Applied X-Rays*, McGraw-Hill Book Co., 1932, Fig. 72, p. 173.

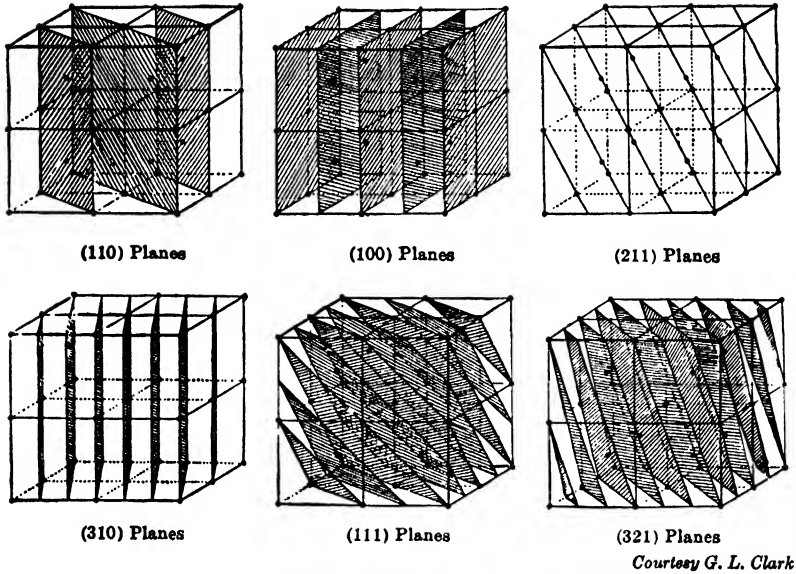


FIG. 7. Typical sets of parallel planes in a cubic lattice.

on a metal crystal a portion of the rays passes through the crystal, another portion is absorbed, and a third portion is reflected by successive layers of atoms or atomic planes. The amount reflected by any one plane is very small, but under certain conditions the reflected beams from several successive parallel planes can reinforce each other to produce a beam of relatively high intensity. The angle at which a beam of x-rays must strike a set of parallel planes to give such a diffraction beam is given by Bragg's law:

$$n\lambda = 2d \sin \theta$$

where  $\lambda$  = wave length of the x-rays

$d$  = distance between successive parallel planes

$\theta$  = angle of incidence and reflection

$n$  = an integer (1, 2, 3, etc.).

In Fig. 8 the horizontal lines represent a series of parallel atomic planes.  $AB, A'B'$ , etc., represent a beam of parallel x-rays of a definite wave length,  $\lambda$ , which are partially reflected by each successive atomic plane in the direction  $BC, B'C'$ , etc. These reflected beams will reinforce each other only if they are exactly in phase with each other. In other words, the additional distance traveled by the ray  $A'B'C'$  as compared with the ray  $ABC$  must be exactly one wave length or its

multiple,  $n\lambda$ . This distance is equal to  $2d \sin \theta$  since  $\lambda/d = \sin \theta$  or  $x = d \sin \theta$  and the distance  $2\lambda = 2x = 2d \sin \theta$ .

By the use of x-rays of known wave length it is possible to measure the spacing of atomic planes in crystals. The diffracted beam is usually recorded on a photographic film on which the angle  $\theta$  can be measured and the interplanar spacing calculated by the use of Bragg's law. Each set of crystallographic planes will give diffracted beams at several angles corresponding to different values of the integer  $n$ . For the first order reflections  $n = 1$ ; second order,  $n = 2$ , etc.

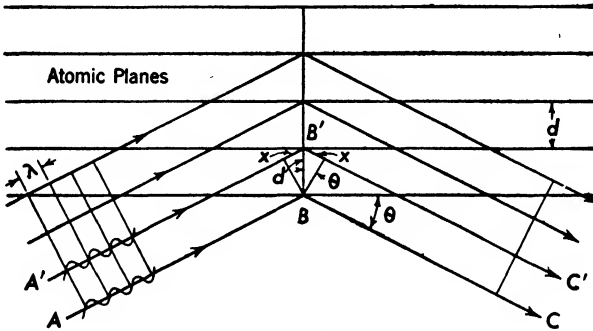


FIG. 8. Reflection of x-rays from atomic planes.

In some crystals several sets of planes have the same spacing and are equivalent as, for example, the (100), (010), and (001) planes in a cubic crystal. All these planes will give reflections at the same angle. Other sets of planes in the same crystal have different spacing and will give reflections at other angles. By rotating a crystal in all directions, all the different planes can be brought into the proper position to give a reflection. The complete series of reflections is called a *diffraction pattern*. Instead of rotating a single crystal one can use a finely powdered specimen in which each particle is a crystal unit with its own orientation.

Each type of space lattice gives a characteristic spacing of lines in the diffraction pattern which depends upon the spacing of various sets of planes in the crystal. For instance, the spacing of various sets of planes in the body-centered cubic lattice is in the ratio  $\frac{1}{\sqrt{2}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{6}} :$

$\frac{1}{\sqrt{8}} : \frac{1}{\sqrt{10}} : \frac{1}{\sqrt{12}}$ , etc., whereas for the face-centered lattice this ratio is

$\frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{8}} : \frac{1}{\sqrt{11}} : \frac{1}{\sqrt{12}} : \frac{1}{\sqrt{16}}$ , etc.

The identification and measurement of the simple lattices found in most metals is not particularly difficult and several short cuts can be taken in making the calculations. By standardizing on the use of one wave length of x-rays and one size of film holder or *cassette*, it is possible to read the spacing of the lines of the diffraction pattern with a scale calibrated to read directly in terms of the spacing of planes in Angstrom units ( $\text{cm} \times 10^{-8}$ ).

In a cubic space lattice of unity (lattice parameter  $a = 1$ ) the distance between planes,  $d$ , is equal to  $a$  divided by the square root of the sums of the squares of their Miller indices.

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

This makes a simple calculation and all families of planes then give the same value of  $a$ , the edge of the unit cube.

A check on the lattice parameter can be made by the density formula,

$$\text{density} = \frac{\text{mass}}{\text{unit volume}}$$

and the experimental density determined from lattice parameters must equal actual density.

*Example.* For body-centered cubic lattice of iron,

number of atoms in unit cell = 2

density = mass of atom of unit atomic weight in grams  $\times$  molecular weight  $\times$  number of atoms divided by the cube of its lattice parameter in centimeters.

$$\text{density} = \frac{(1.649 \times 10^{-24}) (55.84) (2)}{(2.86 \times 10^{-8})^3} = 7.69 \text{ g/cu cm}$$

The face-centered cube of iron would have 4 atoms in the unit cell and a lattice parameter of  $3.60 \times 10^{-8}$  cm and a theoretical density of about 7.91.

A few of the metals and many intermetallic compounds in alloys have complex space lattices whose solution is much more difficult, usually requiring the use of a single crystal specimen and often several different types of equipment. However, a complex space lattice can often be identified simply by comparison with that of a crystal whose space lattice is known.

A more complete discussion of equipment and methods can be found in *A Study of Crystal Structure and Its Application*.<sup>2</sup>

<sup>2</sup> W. P. Davey, McGraw-Hill Book Co., 1934.



The following summary of the applications of x-ray diffraction methods in metallography has been condensed from the *A.S.M. Metals Handbook*, 1939 (page 195).

- Determination of crystal structure.
- Measurement of lattice dimensions.
- Identification of phases in alloys.
- Determination of limits of solid solubility.
- Orientation of individual grains.
- Preferred orientation of grains.
- Estimation of grain size.
- Study of cold work and recrystallization.
- Internal stresses and recovery.

Another important application of x-rays in the metal industries is in the detection of flaws, particularly of internal defects, by radiographic methods.

## CHAPTER III

### ALLOY SYSTEMS AND CONSTITUTION DIAGRAMS

#### Alloy Systems

An alloy system is made up of all the alloys that can be formed by several elements combined in all possible proportions. A binary system contains two elements, a ternary system three, and so on. If only 40 of the most common metals are considered (by the combination formula) and any two are taken at a time, there are 780 binary systems. Any three at a time gives 9880 ternary systems, and any four at a time gives 91,390 quaternary systems, and so on. The number of individual alloys possible is much larger. Considering only the alloys that differ from each other by 10 per cent, there are over eight million alloys. The number of possible alloy combinations containing more than four elements is almost unlimited. Commercial alloys often contain a large number of alloying elements.

#### Classification of Alloys

Because of the extremely large number of alloys that is possible, any study of alloys must be based on some system of classification. A broad classification can be made in terms of the structures of the alloys, and entire alloy systems can be classified according to the type of their constitution diagram.

In their structure, alloys can be either homogeneous or they can be built up of several different phases. A phase is a homogeneous, physically distinct portion of an alloy or of a group of substances which are in equilibrium with each other.

In the one-component system,  $H_2O$ , under certain conditions of temperature and pressure, it is possible to have three phases coexist in stable equilibrium (solid-liquid-gas). A phase, however, is not necessarily a state of matter (solid, liquid, or gas), and in many systems there are several solid phases such as solid solutions, pure metals, and compounds. Some systems may have several liquid phases. The physical characteristics of different phases are, therefore, quite distinct.

Alloys may be classified according to their structure, depending on the type and number of phases present. There are three possibilities: compounds, solid solutions, and mixtures.

**Compounds.** Compounds (intermetallic compounds or intermediate phases) have a strong physical bonding of unlike metal atoms and form phases, usually hard and brittle, having a *definite* composition which can be expressed in terms of a chemical formula such as:  $\text{Fe}_3\text{C}$ ,  $\text{FeAl}_3$ ,  $\text{Fe}_3\text{P}$ ,  $\text{Cu}_3\text{P}$ ,  $\text{CuAl}_2$ ,  $\text{Mg}_2\text{Si}$ ,  $\text{Fe}_3\text{Zn}_{10}$ ,  $\text{PbMg}_2$ ,  $\text{Cu}_2\text{Zn}_3$ , etc. Their crystal lattice is usually different from that of either of the component pure metals and often much more complex. Phases of this type can be identified in a matrix of another phase by microscopic examination; when formed from a melt they frequently occur as crystallites in relief. Compounds are usually designated by the general formula  $A_mB_n$ , where  $m$  is the number of atoms of metal  $A$  and  $n$  is the number of atoms of metal  $B$ .

The characteristics of various intermediate phases may differ in several respects. One important dissimilarity is the degree of variability of composition. Many of them occur as single-phase alloys only when the composition corresponds exactly to the chemical formula; others may vary in composition through a more or less restricted range. The application of the term "compound" is now generally restricted to those phases which have a narrow composition range and which are hard and brittle. A few of the intermediate phases have a rather wide composition range and in several respects they resemble the solid solution type of phase which will be described later. These are sometimes called *intermediate solid solutions*.

The ordinary rules of valence which apply to a simple compound between a metal and a nonmetal hold true for only a few of the intermediate phases. The combining ratio is therefore usually determined by other factors, not all of which are known. In some instances the relative sizes of the atoms involved appear to be an important consideration. Another significant relation has been found by Hume-Rothery.

Among intermediate phases there are several types of crystal structure which occur rather frequently. It has been demonstrated<sup>1</sup> that intermediate phases which have the same type of lattice often have the same *valence-electron concentration*, or ratio of the number of valence electrons to the total number of atoms in the chemical formula. For instance, the phases  $\text{AgCd}$  and  $\text{Cu}_3\text{Al}$  both have the body-centered cubic or  $\beta$  structure and the ratio of valence electrons to total number of atoms is 3 : 2 for both. Silver has a valence of 1 and therefore has one valence electron per atom; cadmium has a valence of 2. In  $\text{AgCd}$  there is a total of three valence electrons for two atoms, giving the ratio 3 : 2. In  $\text{Cu}_3\text{Al}$  three atoms of copper with one valence electron each

<sup>1</sup> W. Hume-Rothery, *Structure of Metals and Alloys*, Chemical Publishing Co., 1936.

are combined with one aluminum atom with three valence electrons, giving a total of six valence electrons for four atoms with a ratio of 3 : 2. Other examples are given in Table 3.

TABLE 3. INTERMEDIATE ALLOY PHASES (HUME-ROTHERY).

Electron Concentration  
or  
Ratio of Number of Electrons to Number of Atoms

3 : 2		21 : 13			7 : 4	
Body-Centered Cubic $\beta$ Structure	Complex Cubic $\beta$ Manganese Structure	Cubic $\gamma$ Structure			Close-Packed Hexagonal Structure	
AgCd	Cu <sub>3</sub> Al	Ag <sub>5</sub> Cd <sub>8</sub>	Cu <sub>5</sub> Zn <sub>8</sub>	Co <sub>5</sub> Zn <sub>21</sub>	AgCd <sub>3</sub>	Au <sub>5</sub> Al <sub>2</sub>
AgMg	Cu <sub>3</sub> Ga	Ag <sub>5</sub> Hg <sub>8</sub>	Cu <sub>9</sub> Al <sub>4</sub>	Fe <sub>5</sub> Zn <sub>21</sub>	Ag <sub>3</sub> Sn	CuCd <sub>2</sub>
AgZn	Cu <sub>5</sub> Sn	Ag <sub>5</sub> Zn <sub>8</sub>	Cu <sub>9</sub> Ga <sub>4</sub>	Ni <sub>5</sub> Zn <sub>21</sub>	Ag <sub>5</sub> Al <sub>3</sub>	CuZn <sub>2</sub>
AuCd	CoAl	Au <sub>5</sub> Cd <sub>8</sub>	Cu <sub>9</sub> In <sub>4</sub>	Pd <sub>5</sub> Zn <sub>21</sub>	AuCd <sub>3</sub>	Cu <sub>3</sub> Ge
AuZn	FeAl	Au <sub>5</sub> Zn <sub>8</sub>	Cu <sub>31</sub> Si <sub>8</sub>	Rh <sub>5</sub> Zn <sub>21</sub>	AuZn <sub>3</sub>	Cu <sub>3</sub> Si
CuBe	NiAl	Cu <sub>5</sub> Cd <sub>8</sub>	Cu <sub>31</sub> Sn <sub>8</sub>	Pt <sub>5</sub> Zn <sub>21</sub>	Au <sub>3</sub> Sn	Cu <sub>3</sub> Sn
CuZn		Cu <sub>5</sub> Hg <sub>8</sub>	Na <sub>31</sub> Pb <sub>8</sub>	Ni <sub>5</sub> Cd <sub>21</sub>		
Possibly MgTl, CaTl, and SrTl						

*Note:* Transition elements Co, Fe, Ni, Pd, Pt, and Rh must be considered as having zero valence electrons in these calculations.

**Solid Solutions.** A solid solution is a phase which contains two or more different kinds of atoms in one type of space lattice, and in which the various kinds of atoms are not combined in a definite proportion. When atoms of metal *B* dissolve in solid metal *A* they usually replace *A* atoms in the space lattice. In other respects the lattice remains similar to that of pure metal *A*. This is the so-called *substitutional* type of solid solution and is the most common.

The degree of solubility is not the same in different alloy systems. Copper and nickel can dissolve in each other in all proportions, since both have the same type of space lattice and their atoms are nearly the same size. On the other hand, copper can dissolve in silver up to a maximum of about 9 per cent. The alloy 90 Ag-10 Cu contains more copper than can be dissolved in the silver-rich solid solution and the excess copper is present in the form of a second phase, a copper-rich solid solution. This type of limited solubility often occurs when two metals have unlike types of space lattice or if the size of the two kinds of atoms is substantially different.

Occasionally two elements with widely different atomic sizes form

another kind of solid solution known as the *interstitial type*. Carbon, hydrogen, and nitrogen, all with very small atomic size, often dissolve in solid metals to form this type of solution. The space lattice of the solution is like that of the pure metal and the C, H, or N atoms occupy the vacant spaces or interstices between the metal atoms. Austenite, the  $\gamma$  solid solution in iron-carbon alloys, is an example of the interstitial type of solid solution.

It has been stated that in most solid solutions the different kinds of atoms occupy random positions within the space lattice. Some of these random solutions undergo atomic rearrangement if they are cooled slowly through a critical temperature below which each type of atom assumes a definite position within the space lattice, the random arrangement being lost.

An alloy of 25% Au and 75% Cu (atomic per cent) may be quenched from above a red heat and the Cu and Au atoms will occupy random or disordered positions in the face-centered cubic lattice. If slowly cooled, however, the Au atoms assume corner positions of the lattice and the Cu atoms move to the face-centered positions. This results in an appreciable increase in hardness and, consequently, strength, because of the ordered arrangement. This type of structure is known as an *ordered solid solution* or *superlattice*.

Examples of such ordered solid solution phases are CuAu, CuPd, CuBe, CuZn ( $\beta$  brass), AgMg, AgZn, AgCd, AuNi, NiAl, FeCo, AuCu<sub>3</sub>, PtCu<sub>3</sub>, PdCu<sub>3</sub>, FeNi<sub>3</sub>, and MnNi<sub>3</sub>. Their composition can be expressed in terms of a chemical formula; in this respect, they resemble compounds. Their mechanical properties are usually intermediate between those of solid solutions and compounds. But the ordered solid solutions cannot be distinguished microscopically from the random solid solutions; neither can they be coagulated by diffusion so as to appear as separate phases. They are frequently designated as  $\alpha'$ ,  $\beta'$ ,  $\gamma'$ , etc.

**Mixtures.** Alloys of this type are composed of mechanical mixtures of two or more different phases. These phases can be pure metals, solid solutions, or compounds. Alloys of copper and lead contain nearly pure copper with practically pure lead distributed as spheroids. Most copper-silver alloys are made up of two solid solutions, one rich in copper and the other rich in silver. Annealed steels contain two phases: ferrite, almost pure iron, and iron carbide, a compound of iron and carbon, Fe<sub>3</sub>C.

### The Freezing of Alloys and Thermal Analysis

Whereas pure metals always freeze at a constant temperature, most alloys solidify gradually through a range of temperatures. For each

alloy composition there is a definite temperature at which freezing begins on cooling and this is also the temperature at which fusion is completed on heating. The temperature at which freezing is completed on cooling is also the temperature at which fusion begins on heating. These two limits of the freezing range of an alloy have sometimes been called the *freezing point* and the *melting point* respectively.

**Thermal Analysis.** The freezing range of alloys is usually found by *thermal analysis*. The various alloy compositions are melted in crucibles, a pyrometer is inserted, and the alloy is cooled at a fairly even rate. It is customary to plot temperature-time cooling curves. When pure metals freeze the temperature remains constant for considerable time as the metal gives up its latent heat of solidification. Fig. 9 shows *temperature-time cooling curves*.

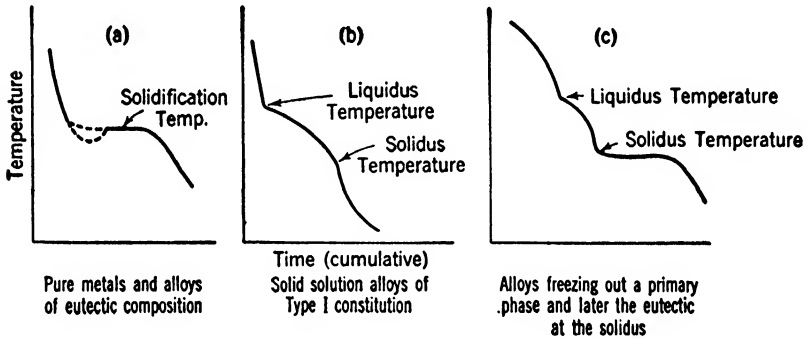


FIG. 9. Temperature-time cooling curves.

The dotted dip in Fig. 9a, typical of the freezing curve of tin, is called undercooling, subcooling, or supercooling. It can be eliminated by cooling more slowly, by inoculation with small particles of solids, and by agitation or vibration of the pyrometer tube. Temperature-time curves are by far the most important of the cooling or heating curves and are equally suitable for studying transformations in the solid state.

Another type of cooling curve frequently used by investigators, though having less merit, is called the *inverse rate curve*. Here temperature is plotted as the ordinate and the difference in time required either to heat or cool through equal intervals of temperature as the abscissa. Small intervals of temperature should be used. Theoretically it should have the advantage of a sharper break or change in direction for a given change in cooling rate. Actually this advantage is likely to be more than

nullified by its susceptibility to misinterpretation, particularly if the reading of data is not performed with a very high degree of accuracy.

A few investigators have used the *direct rate curve*, plotting the temperature drop for a definite interval of time (cooling rate) as the abscissa and temperature as the ordinate.

An important curve seldom used is the *differential curve*, where the abscissa scale is the difference in temperature between the specimen having a transformation point and a neutral body having none, and the ordinate is temperature. The laboratory set-up involves considerable experimental difficulty and the method is not well adapted to fast rates of cooling or heating.

It is highly desirable in thermal analysis to obtain uniform rates of heating or cooling, and in order to eliminate somewhat the lag at transformation points it is well to use a small amount of metal and thin crucibles or containers and have thin protection tubes for thermocouples. The ideal furnace is designed with little thermal insulation and little heat capacity.<sup>2</sup>

Automatic machines have been made to plot curves, one of which has been described in considerable detail.<sup>3</sup> A recording pyrometer can be coupled with a controlling pyrometer operated by a synchronous motor to change the setting continuously so that temperature-time curves can easily be obtained at a definite cooling rate.

### Constitution Diagrams

A constitution diagram (equilibrium or phase diagram) is a graphical representation of a system. It shows the melting and freezing temperatures of various alloys which make up the system and also the phases in equilibrium with each other under various conditions of temperature, concentration of components, and pressure. Slight changes in pressure, such as variations in atmospheric pressure, have a negligible effect on equilibria in solid or liquid metals and alloys, and therefore can be excluded from consideration. The important factors which control equilibrium in alloys are temperature and concentration of components (composition). These are the two variables plotted on a constitution diagram.

Fig. 10 is the copper-nickel constitution diagram. Temperatures are plotted in the vertical direction and composition along the horizontal scale in weight per cent. The two ends of the horizontal scale

<sup>2</sup> W. Rosenhain, *J. Inst. Metals*, Vol. 13, p. 160 (1915); H. Scott and J. R. Freeman, National Bureau of Standards, Scientific Paper No. 348, 1919.

<sup>3</sup> H. J. French, A Recording Chronograph for Inverse Rate Method of Thermal Analysis, *Trans. Am. Soc. Steel Treating*, Vol. 3, 640-648 (1923).

represent pure copper and pure nickel respectively; intermediate compositions are plotted along this scale in terms of per cent nickel. Each individual alloy is represented by a vertical line on the diagram (composition vertical), the alloy 25% Ni, 75% Cu being represented by a dotted line in Fig. 10. On cooling from the liquid condition this alloy begins to freeze at the temperature indicated by the letter *a* in Fig. 10 and is completely solidified at the temperature *b*. The solid

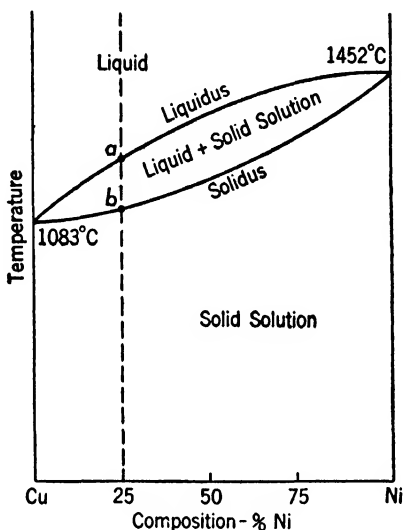


FIG. 10. Copper-nickel constitution diagram.

line drawn through the point *a* is known as the *liquidus* or *liquidus curve* and represents the temperatures at which various alloys begin to solidify on cooling from the liquid state. These are also the temperatures at which melting is completed when the solid alloys are heated. The *solidus curve*, drawn through point *b*, represents the temperature at which solidification is completed on cooling and at which melting begins on heating. The vertical distance between the liquidus and solidus then represents the temperature range of melting or solidification for each of these alloys.

Some alloys undergo transformations in the solid state and the temperatures at which these occur are also represented by additional lines on the constitution diagram. The various fields on a constitution diagram are labeled to indicate the number and kind of phases present in any alloy at each temperature.



# CHAPTER IV

## CLASSIFICATION OF CONSTITUTION DIAGRAMS

### Binary Constitution Diagrams

Because of the large number of systems represented by constitution diagrams, many of which are modifications of others, it is desirable to consider them as various types, classified primarily according to solubility in the liquid and solid states and the formation of intermediate phases.<sup>1</sup>

#### Type I System

*The two metals are soluble in each other in all proportions in the liquid and solid states. This type may be divided into two sub-groups: I-a,*

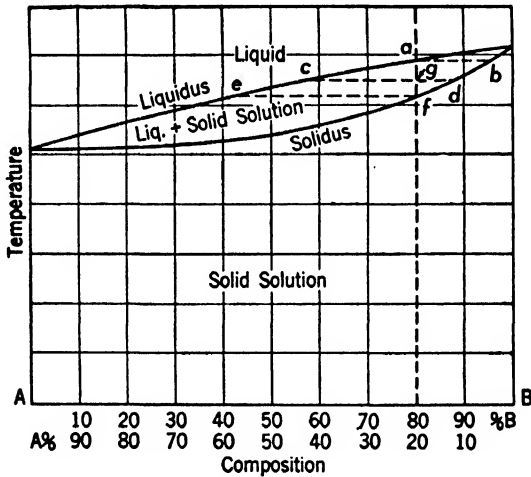


FIG. 11. Type I-a. Constitution diagram of metals A and B. Completely soluble in the liquid and solid states. Examples: Cu-Ni, Ag-Pt, Au-Ag, Ag-Pd, Pt-Rh.

where the melting point varies continuously between the metals A and B (components), and I-b, where the liquidus and solidus lines pass through a minimum called a pseudo-eutectic point.

The dotted line in Fig. 11 represents an alloy of 80% B and 20% A.

<sup>1</sup> Gustav Tammann, *Lehrbuch der Metallographie*, Verlag von Leopold Voss, 1914; S. L. Hoyt, *Principles of Metallography*, McGraw-Hill Book Co., 1920.

When this alloy is cooled in the liquid state to a temperature of  $a$ , a dendrite begins to form, the composition of whose core is shown at  $b$  to be 95%  $B$  + 5%  $A$ . At any selected temperature  $ab$  all alloys having compositions between  $a$  and  $b$  will have a composition of the liquid phase of  $a$  and a composition of the solid phase of  $b$ . Liquid of composition  $a$  and solid of composition  $b$  are in equilibrium and will remain so until the temperature either rises or falls. Continued cooling below temperature  $a$  results in the building up of the dendrites and the core

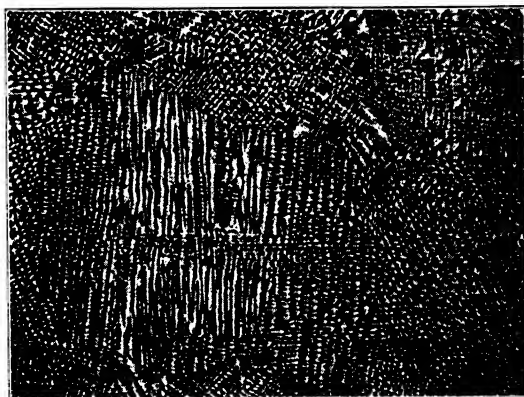


FIG. 12. Cast solid solution alloy of 60% gold, 40% silver, showing manner in which it solidifies as dendrites which grow together to make up the various grains. Light-colored dendrites are rich in gold.  $\times 100$ .

increases in concentration of metal  $A$  until it has a final composition,  $f$ , 80%  $B$  + 20%  $A$ , and there will be some diffusion of more  $A$  atoms into the core of the dendrites. At the equilibrium temperature,  $ef$ , the composition of the last liquid to freeze around the dendrites is  $e$ ,<sup>2</sup> 44%  $B$  + 56%  $A$ , but there is only a trace of it present. If the gap between the liquidus point  $a$  and the solidus point  $f$  had been larger there would have been even more segregation or difference in composition between the core of the dendrite and the filling matter or ground mass. Fig. 12 illustrates the microstructure of a cast solid solution alloy. If this alloy is held at a temperature just below  $f$  for a long time the segregation will tend to be eliminated by diffusion and the alloy

<sup>2</sup> This is true only under conditions of complete equilibrium, never fully attained in practice. Even with the slowest cooling rate the diffusion of  $A$  atoms into the core of the dendrite is not complete and the average composition of the dendrite is richer in  $B$  than the equilibrium composition 80%  $B$  + 20%  $A$ . It therefore follows that the last liquid to freeze must be somewhat richer in  $A$  than the equilibrium composition of 44%  $B$  + 56%  $A$ .

will be a homogeneous solid solution with its microstructure resembling that of a high-purity metal. During freezing of alloy 80% *B* + 20% *A* the composition of the liquid varies from composition *a* to *e* and the solid from *b* to *f*.

A rule may now be stated which will give the composition of the phases present at any chosen temperature on any chosen field of a binary constitution diagram where two phases are in equilibrium with each other.

**1. Composition of Phases — Rule I.** The actual chemical composition of the phases of an alloy in equilibrium at any temperature is found by extending the horizontal line representing temperature on both sides of the vertical line representing the alloy until it intersects the two lines (conjugate lines) bounding the heterogeneous field. These points of intersection with the lines bounding the heterogeneous field may be dropped to the base line and the composition of each phase read directly. The composition scale of constitution diagrams is given in per cent by weight unless otherwise stated.

*Example.* With alloy 80% *B* + 20% *A* at the temperature *cgd* the composition of the liquid phase is 59% *B* + 41% *A* and the composition of the solid phase in equilibrium with it is 88% *B* + 12% *A*.

Another rule may now be stated which also holds for all constitution diagrams at any chosen temperature and under equilibrium conditions.

**2. Proportion of Phases — Rule II.** The relative amounts of phases in a given alloy at a definite temperature within a heterogeneous field are found by drawing a horizontal line at that temperature from one side of the field to the other and also a vertical line to designate the composition of the alloy. The composition vertical divides the temperature horizontal into two parts whose lengths are inversely proportional to the amounts of the two phases present.

*Example.* Given alloy of 80% *B* + 20% *A* at the temperature *cgd*. To find the proportion of phases (liquid and solid solution in this case) the per cent of liquid will be  $(gd/cd) \times 100$ ; the per cent of solid solution will be  $(cg/cd) \times 100$ . To obtain the exact ratio we have

$$\text{per cent liquid} = \frac{88 - 80}{88 - 58} \times 100 = 26.6\%$$

$$\text{per cent solid} = \frac{80 - 58}{88 - 58} \times 100 = 73.3\%$$

These rules can be used also for equilibria in the solid state at any selected temperature if two phases are present.

In the Type I-*b* diagram (Fig. 13) the alloy of composition *O* would melt and freeze at a constant temperature similar to a pure metal. The point *O* is called a pseudo-eutectic point because it is the alloy of the series having the lowest freezing point and somewhat resembles eutectic systems of the Type II class. It is also possible to have a diagram such that the point *O* is elevated above the melting points of the components. There are some nonmetallic systems but no metallic system of this modification.

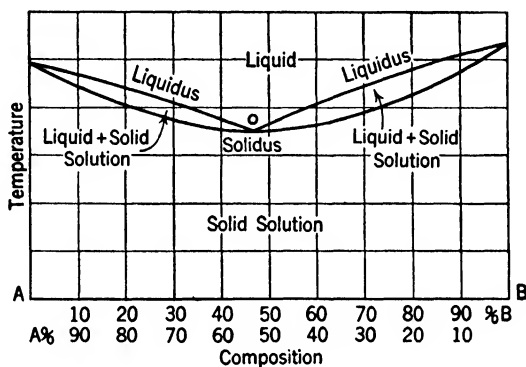


FIG. 13. Type I-*b*. Constitution diagram of metals *A* and *B* as above except two branches of the liquidus and solidus meet at a pseudo-eutectic point. Examples: Cu-Au, Ni-Pd.

Ordinarily metals forming Type I alloys are those where the components have

1. Similar atomic volumes.
2. Similar crystal structures.
3. Melting points not too widely different.

The only true isomorphous solid solution is, of course, where both components have the same type of crystal lattice. In this type the most common components are face-centered cubic metals.

## Type II System

*The two metals are soluble in all proportions in the liquid state and incompletely soluble in the solid state, the curves of primary solidification intersecting at a minimum (the eutectic point).*

**Type II-*a* System.** *The two metals are insoluble in the solid state (Fig. 14). Alloys of this type usually crystallize in different crystal forms and the like atoms have slightly more affinity for each other than the unlike ones. In the eutectic alloy (40% B + 60% A) both pure A*

and pure  $B$  are present as an intimate mixture in the solid alloy and can be resolved by a microscope. The two metals in this alloy, however, do not freeze at their customary temperatures but each inhibits the freezing of the other until the temperature  $aob$  is reached, where they freeze simultaneously at constant temperature like a pure metal. The word *eutectic* is from the Greek and means minimum.

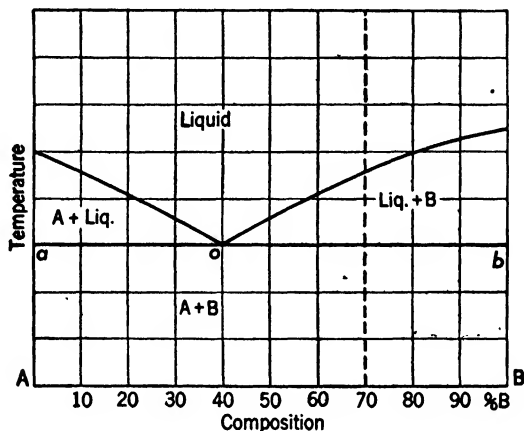


FIG. 14. Type II-a. Constitution diagram of eutectiferous system representing metals soluble in the liquid state and insoluble in the solid state. Examples: Sn-Zn, Bi-Cd, Be-Si.

If alloy of 70%  $B$  + 30%  $A$  is cooled to just below the liquidus line it will be in the heterogeneous field of liquid +  $B$  and the composition of the first solid formed is pure  $B$ . Pure  $B$  continues separating as dendrites until temperature  $aob$  is reached. At the same time the composition of the remaining liquid varies along the liquidus line until at this temperature it reaches the eutectic composition (40%  $B$  + 60%  $A$ ), and the two solid phases, pure  $A$  and pure  $B$ , freeze out simultaneously at constant temperature to give the eutectic structure. On cooling below temperature  $aob$  nothing further happens structurally. Alloys with compositions between  $a$  and  $o$  have only pure  $A$  freezing out between the liquidus and solidus temperatures.

*Phase Rule.* One of the important contributions to physical chemistry was the phase law by J. Willard Gibbs.<sup>3</sup> This rule is of importance in checking equilibrium conditions for various systems and may be stated as follows:

A system possesses only three independently variable factors —

<sup>3</sup> Alexander Findlay and A. N. Campbell, *The Phase Rule and Its Applications*, Longmans, Green and Co., 1938.

temperature, pressure and concentration — of the components of the system. The phase rule defines the conditions of equilibrium as the relationship between the number of phases and components of the system. Expressed in mathematical form it is

$$F = C + 2 - P$$

where

$F$  = the degrees of freedom or independently variable factors

$C$  = the number of components in the system

2 is a constant

$P$  = the number of phases present in the system.

Since metallographic investigations are generally carried on at atmospheric pressure, it is customary to eliminate pressure as a variable or degree of freedom. Therefore, when we remove one of the degrees of freedom, it is necessary to subtract one (1) from the other side of the equation, and the above equation when applied to metallography becomes

$$F = C + 1 - P$$

A few illustrations will help to make this rule and its applications understood.

A pure metal in the molten condition has one component and one phase:  $F = 1 + 1 - 1 = 1$ . Composition is fixed but temperature can vary as long as there is only one phase present. At the freezing point a second phase, solid metal, appears:  $F = 1 + 1 - 2 = 0$ . This means that there is no freedom, or that it must stay at a constant temperature until one of the phases disappears. This is another way of stating that pure metals freeze or melt at a constant temperature.

Consider an alloy of Type I-a. Above the liquidus there are two components and only one phase:  $F = 2 + 1 - 1 = 2$ . This means there are two degrees of freedom, and temperature or concentration may be varied as long as we have only one phase. As soon as freezing begins a solid phase appears and we have  $F = 2 + 1 - 2 = 1$ . This means that there is only one degree of freedom and as soon as either temperature or concentration is chosen the other is fixed as long as two phases are present. Below the solidus there is only one phase and there are again two degrees of freedom.

The eutectic must freeze at a constant temperature because of this relation. There are present three phases, namely, liquid and the two solid phases which are freezing out. Thus we have  $F = 2 + 1 - 3 = 0$ ; that is, the system is invariant. This means that it must stay at a constant temperature until one or more phases disappear.

Systems which have zero degrees of freedom are invariant; those with one degree of freedom are univariant; and those with two degrees of freedom are bivariant, etc.

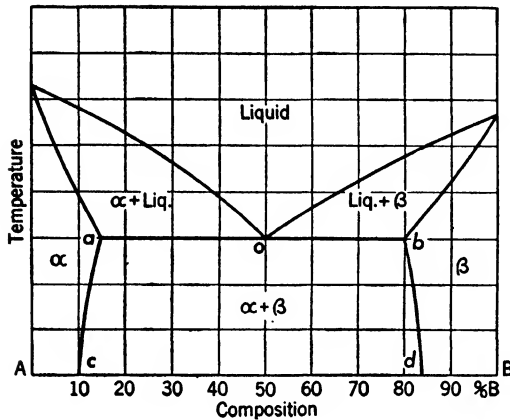


FIG. 15. Type II-b. Constitution diagram of eutectiferous system representing metals soluble in the liquid state and partly soluble in the solid state. Examples: Pb-Sn, Pb-Sb, Cu-Ag, Cd-Zn.

Actually there are probably no systems of exactly this type (II-a), as it is likely that one metal is always slightly soluble in the other, especially at elevated temperatures.

A modification of this type is shown by Hoyt<sup>4</sup> where the eutectic point is moved toward one of the pure metals and the pure metal is the eutectic limit of the series. Theoretically this is possible but practically

there are no systems where the eutectic comes closer to the pure metal than about 0.2 per cent, copper-bismuth having a eutectic point at about 99.8% bismuth.

#### Type II-b System.

The metals are partly soluble in the solid state (Fig. 15). In this type the letters  $\alpha$  and  $\beta$  represent two different solid solutions of limited solubility, where  $\alpha$  is a solid solution of B atoms in the solvent A lattice and  $\beta$  is a solid solution of A atoms in the solvent B lattice. The solidus is the line *aob* together with the extension on each end to the melting points of the pure metals. The maximum solubility of B in

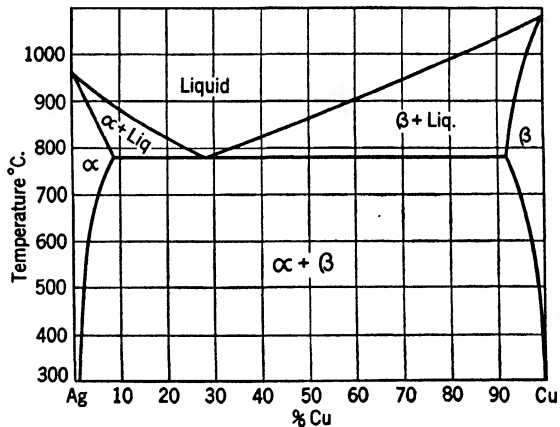
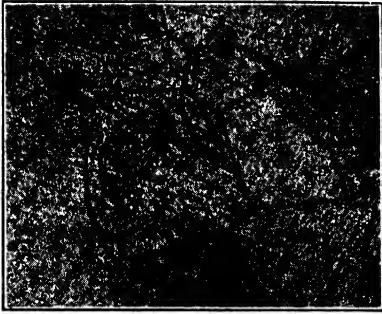
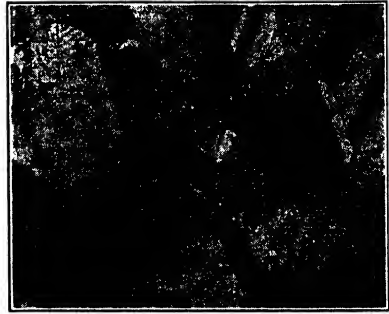


FIG. 16. Silver-copper constitution diagram.

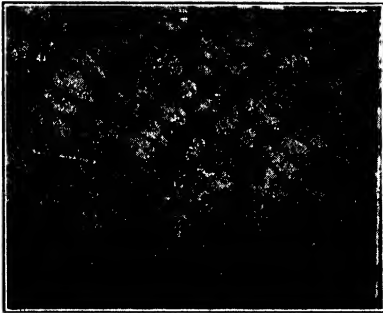
<sup>4</sup> S. L. Hoyt, *Principles of Metallography*, McGraw-Hill Book Co., 1920.



(a)



(b)



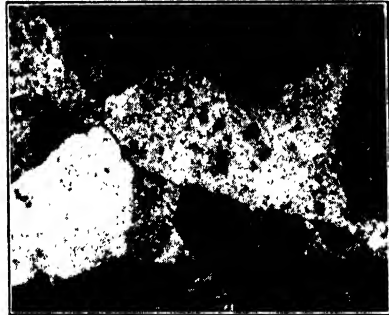
(c)



(d)



(e)



(f)

FIG. 17. Silver-copper system.

(a) Silver. Etchant: chromic acid + sulfuric acid.  $\times 100$ . (b) 97.5% Ag-2.5% Cu. Etchant: chromic acid +  $H_2SO_4$ .  $\times 100$ . (c) 83% Ag-17% Cu. Etchant: ammonium persulfate + KCN.  $\times 100$ . (d) 71.5% Ag-28.5% Cu. Etchant: ammonium persulfate + KCN.  $\times 150$ . (e) 35% Ag-65% Cu. Etchant: copper ammonium chloride.  $\times 100$ . (f) Copper, cast. Etchant: copper ammonium chloride.  $\times 100$ .



$A$  is at  $a$  (15%  $B$  + 85%  $A$ ) whereas the maximum solubility of  $A$  in  $B$  is at  $b$  (20%  $A$  + 80%  $B$ ). The lines  $ac$  and  $bd$  are called solid solubility lines and recently have also been called *solvus lines*.

At the low temperature  $cd$  the solubility of these systems is usually considerably less than at the eutectic temperature  $ab$ . Alloys having compositions between  $a$  and  $b$  at the temperature  $ab$  will have zero degrees of freedom and consequently must remain at constant temperature while both solid solution phases,  $\alpha$  and  $\beta$ , and the liquid phase are in equilibrium.

There are many systems of this type, e.g., silver-copper (Fig. 16) and cadmium-zinc (Fig. 18). In these systems it should be noted that dendrites (primary) of either  $\alpha$  or  $\beta$  always separate between the liquidus and solidus, depending on which side of the eutectic point the alloy happens to be. In passing through the eutectic temperature, the temperature remains constant and the two phases  $\alpha$  and  $\beta$  separate simultaneously and envelop the primary phase in a *matrix* having the eutectic composition.

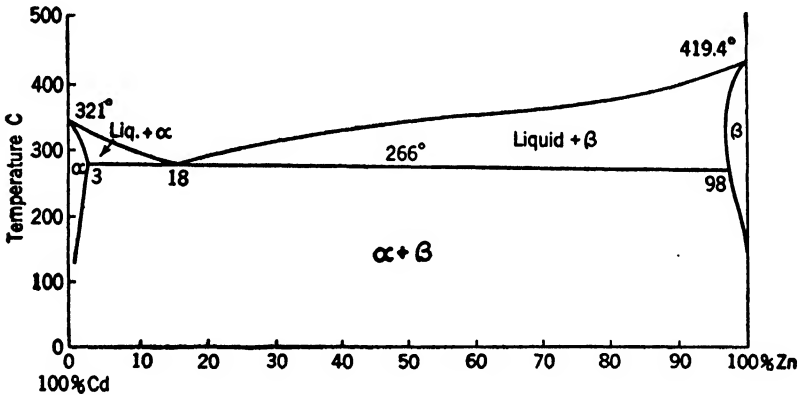


FIG. 18. Cadmium-zinc constitution diagram.

If an alloy of 50% cadmium and 50% zinc is cooled from the liquid state, solid  $\beta$  will start freezing when the liquidus temperature is reached (320°C). The composition of the first  $\beta$  to form will be about 97% Zn and 3% Cd (Fig. 18, Rule I). As cooling progresses more  $\beta$  freezes and the composition of the remaining liquid will increase in cadmium until the eutectic temperature (266°C) is reached. Here the liquid of 18% Zn and 82% Cd freezes to form a eutectic mixture of the  $\alpha$  and  $\beta$  phases surrounding the primary  $\beta$  (Fig. 19d).

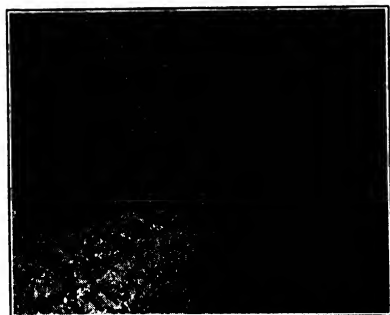
The phases in equilibrium at a temperature just above 266°C (solidus) are liquid and solid  $\beta$ . Rule II gives the relative proportions in per



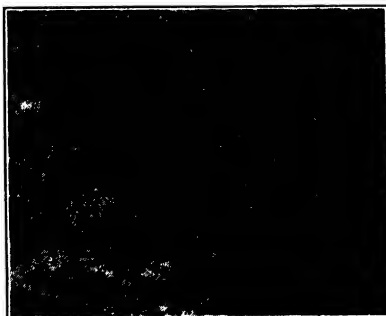
(a)



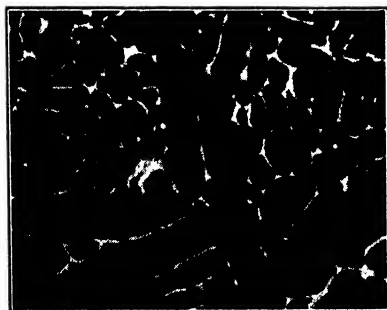
(b)



(c)



(d)



(e)



(f)

FIG. 19. Cadmium-zinc system.

(a) Cadmium. Etchant: picric acid in alcohol.  $\times 100$ . (b) Cd 90%-Zn 10%. Etchant: concentrated nitric acid.  $\times 100$ . (c) Cd 82%-Zn 18%. Etchant: concentrated nitric acid.  $\times 100$ . (d) Cd 50%-Zn 50%. Etchant: 10% nitric acid in water.  $\times 100$ . (e) Cd 10%-Zn 90%. Etchant: 10% nitric acid in water.  $\times 100$ . (f) Zinc. Etchant: concentrated nitric acid, etched lightly to show twinning.  $\times 100$ .

cent by weight of each in the alloy 50% Cd-50% Zn:

$$\text{per cent liquid} = \frac{98 - 50}{98 - 18} \times 100 = \frac{48}{80} \times 100 = 60\%$$

$$\text{per cent } \beta = \frac{50 - 18}{98 - 18} \times 100 = \frac{32}{80} \times 100 = 40\%$$

The per cent of eutectic ( $\alpha + \beta$ ) in the solid alloy below 266°C is the same as the per cent of liquid just above this temperature, namely, 60 per cent. If the calculation is made just below the eutectic temperature the total per cent of  $\beta$  (primary  $\beta$  + eutectic  $\beta$ ) can be determined.

$$\text{per cent } \beta = \frac{50 - 3}{98 - 3} \times 100 = \frac{47}{95} \times 100 = 49.5\%$$

$$\text{per cent } \alpha = \frac{98 - 50}{98 - 3} \times 100 = \frac{48}{95} \times 100 = 50.5\%$$

At 0°C  $\alpha$  and  $\beta$  are 50 per cent each, because the relative solubilities of cadmium in zinc and of zinc in cadmium become zero.

Rules I and II are of considerable aid to a metallographer in determining the approximate compositions of alloys from the microstructure when the equilibrium diagram is known. The rules are useful also in the working out of a constitution diagram with a limited number of alloys.

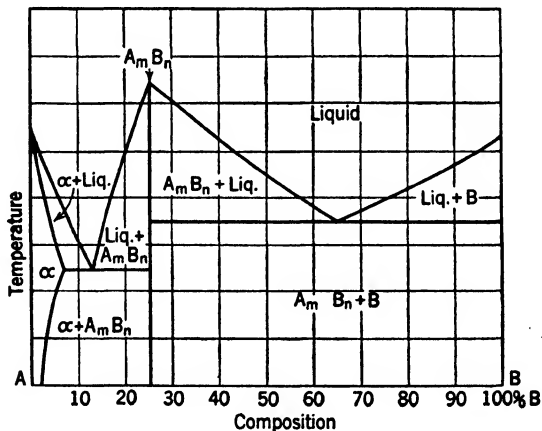


FIG. 20. Type II-c. Constitution diagram of eutectiferous system where the metals are soluble in the liquid state and partly soluble in the solid state. The metals also form a compound  $A_m B_n$  and two eutectics. Examples: Mg-Sn, Mg-Sb, Mg-Pb.

**Type II-c System.** *The metals form compounds and two or more*

*eutectiferous series.* This type, as shown in Fig. 20, can be considered as two separate systems — Type II-b on the left side and Type II-a on the right side, the components being  $A + A_mB_n$  and  $A_mB_n + B$  respectively. The significant fact here is the presence of compounds or intermediate phases.

In working out a constitution diagram of two metals it is very desirable to plot the composition in atomic per cent instead of the customary weight per cent in order to aid the investigator in locating possible compounds. If the composition scale of Fig. 20 is expressed in atomic per cent instead of weight per cent, the compound  $A_mB_n$  will contain 75 atomic per cent of  $A$  and 25 atomic per cent of  $B$ .

*Atomic Composition.* To convert a binary alloy composition from weight per cent to atomic per cent the following formula is useful.

$$\begin{aligned} \text{Let} \quad & P = \text{weight per cent of metal } A \\ & 100 - P = \text{weight per cent of metal } B \\ & a = \text{atomic weight of metal } A \\ & b = \text{atomic weight of metal } B \\ & X = \text{atomic per cent of metal } A \\ & 100 - X = \text{atomic per cent of metal } B \end{aligned}$$

$$X = \frac{100P}{P + \frac{a}{b}(100 - P)} = \text{atomic per cent of } A \text{ (number of atoms of } A \text{ in 100 atoms of } A + B)$$

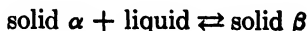
To convert atomic per cent to weight per cent:

$$P = \frac{100X}{X + \frac{b}{a}(100 - X)} = \text{weight per cent of } A$$

### Type III System

*The two metals are soluble in the liquid state, partly soluble in the solid state, and the curves of primary solidification intersect at a peritectic temperature horizontal.*

**Type III-a.** *The product of the peritectic reaction is a solid solution.* The point  $o$  is the peritectic or transition point. If an alloy of composition  $o$  (52%  $B$  + 48%  $A$ ) is cooled from the liquid state,  $\alpha$  dendrites form and grow between the liquidus and the peritectic temperature  $aob$ . At this temperature  $\alpha$  (composition 20%  $B$  + 80%  $A$ ) and liquid (composition 78%  $B$  + 22%  $A$ ) react to form a new solid solution  $\beta$  (composition 52%  $B$  + 48%  $A$ ). This reaction can be expressed by the equation



In cast alloys of this type the peritectic reaction is usually incomplete. The product of the reaction forms on the surface of the primary dendrites and prevents contact between the reacting phases. Since further progress of the reaction depends on the relatively slow process of diffusion in the solid state, a longer time is required for the completion of the reaction than is ordinarily available during the freezing of a cast alloy.

The microstructure of a cast alloy of the composition 52% *B* in Fig. 21 would then consist of unstable primary dendrites of the  $\alpha$  solid solution surrounded by a rim of the reaction product  $\beta$ . The equilib-

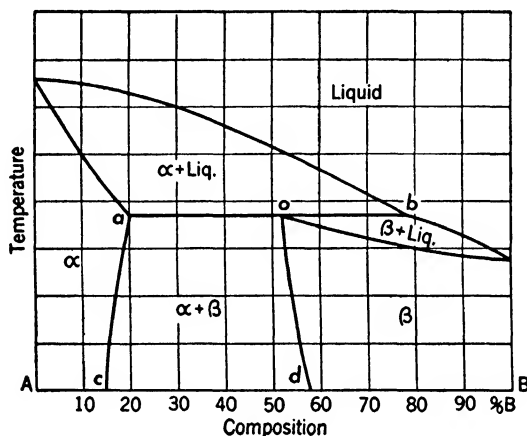


Fig. 21. Type III-a. Constitution diagram of peritectic series where the peritectic reaction results in a solid solution. Examples: Cd-Hg, Ag-Pt.

rium structure of 100%  $\beta$  could be obtained in this casting only by prolonged annealing at a temperature just below *aob* which would permit the necessary diffusion of *B* atoms into the primary  $\alpha$  dendrites.

Other alloys of compositions falling between the points *a* and *o* likewise begin to freeze as the  $\alpha$  solid solution and the peritectic reaction takes place at the temperature *aob*, until all the remaining liquid is used up and the alloy is completely solidified. Both the  $\alpha$  and  $\beta$  phases are stable in these alloys below the solidus. Alloys whose compositions fall in the range between *o* and *b* form primary  $\alpha$  during the first stage of solidification, but under equilibrium conditions all of this would be transformed into  $\beta$  during the peritectic reaction, leaving  $\beta$  + liquid just below the temperature *aob*. The remaining liquid would then freeze gradually between this temperature and the solidus to give more  $\beta$ .

**Type III-b.** *The product of the peritectic reaction is a compound* (Fig. 22). In this type the compound (intermediate phase) is formed by the reaction  $\alpha + \text{liquid} \rightleftharpoons A_mB_n$ , and its composition is represented as a straight, vertical line at 30% B + 70% A. Since this compound does not form as a primary phase it is frequently referred to as having a "concealed maximum" which distinguishes it from a Type II system or the "open maximum." Fig. 22 shows  $A_mB_n$  as a compound having but one composition and not capable of dissolving more A or more B in solid solution.

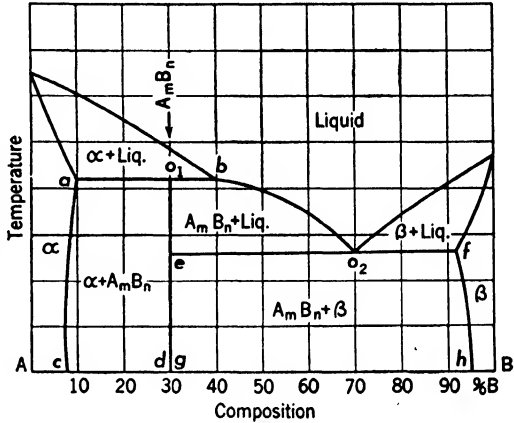


FIG. 22. Type III-b. Constitution diagram of peritectic series where the peritectic reaction results in a compound. Examples: Sn-Sb, Ag-Hg, Ag-Sn.

In some alloy systems the product of the peritectic reaction is an intermediate phase extending over a considerable range in composition.

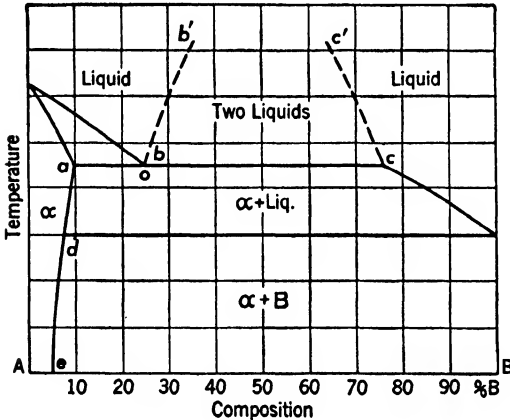


FIG. 23. Type IV-a. Constitution diagram showing partial solubility in both liquid and solid states. Examples: Cu-Pb, Ag-Cr.

**Type IV System**

The two metals are not completely soluble in both liquid and solid states.

**Type IV-a.** The metals are partly soluble in both liquid and solid states.

Fig. 23 shows a diagram of this type. If we choose alloys having compositions between  $b$  and  $c$  at a temperature just above  $abc$  there are two liquid solutions having compositions  $b$  and  $c$  respectively. The

dotted lines  $bb'$  and  $cc'$  show the compositions of the respective liquid phases at higher temperatures. These approach each other as

the temperature is raised and might become completely miscible at higher temperatures. Experimental difficulties usually prevent accurate determination of these two lines and they are shown as dotted lines to indicate that their position is not definitely determined.

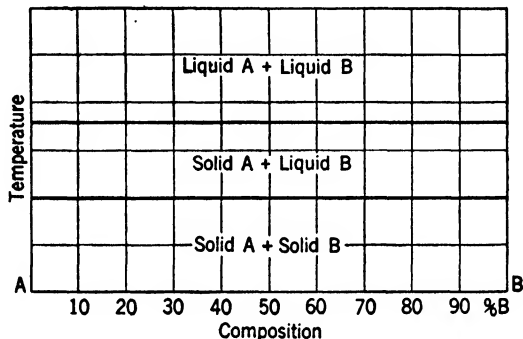


FIG. 24. Type IV-b. Constitution diagram showing total insolubility in both liquid and solid states. Examples: Fe-Ag, Si-Tl.

**Type IV-b.** *The metals are insoluble in the liquid and solid states* (Fig. 24). The metals in this system do not form true alloys but theoretically they should be considered in our classification. If iron and silver are melted together, liquid silver will be on the bottom, because of its higher density, and liquid iron on the top. On solidification they also form two distinct layers with a sharp line of contact and practically no diffusion.

The four types of systems discussed previously can be combined in various ways to make up actual cases. The prime reason for classifying them according to solubility in the liquid and solid states is to acquaint the reader with the important equilibrium relations so that actual constitution diagrams will not appear so complicated.

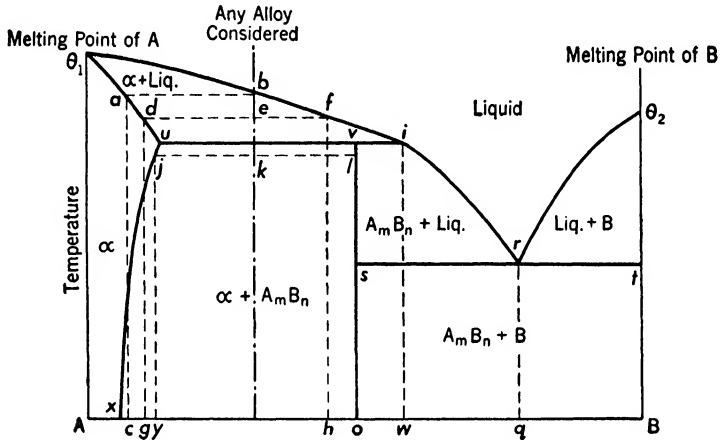
A summary of the nomenclature of lines on a constitution diagram and methods of determining the compositions and relative amounts of phases are given in Fig. 25.

### Transformations in the Solid State

There are many equilibrium changes which take place wholly in the solid state; these are called polymorphic or allotropic transformations.

**Allotropy or Polymorphism.** Some substances change from one crystal form to another when heated through a definite transformation temperature. Substances which can exist in more than one form are called allotropic or polymorphic.

The various forms and transformation temperatures of several allotropic metals are listed in Table 4. The transformation reaction is usually reversible, each form being stable through a definite range of temperature. Under equilibrium conditions two forms of a metal can exist together only at the transformation temperature.



*Analysis or Composition of Phases*

- c* is composition of first solid to freeze, or of  $\alpha$  at temperature *ab*.
- g* is composition of  $\alpha$  at temperature *def*.
- h* is composition of liquid at temperature *def* } phases in equilibrium.
- w* is composition of last liquid to freeze
- y* is composition of  $\alpha$  at temperature *jkl*.
- o* is composition of compound  $A_mB_n$  at temperature *jkl* and below *v*.

*Relative Proportion of Phases*

At temperature *def*:  $\% \alpha = ef/df \times 100$ ;  $\% \text{Liq.} = de/df \times 100$ .  
The sum of these must be 100.

At temperature *jkl*:  $\% \alpha = kl/jl \times 100$ ;  $\% A_mB_n = jk/jl \times 100$ .

Line *ux* is called solid solubility line of *B* in  $\alpha$ .

Point *u* represents maximum solubility of *B* in *A* to form the  $\alpha$  solid solution.

*q* is composition of eutectic alloy. It freezes at constant temperature at point *r*. The reaction is  $\text{Liq.} = B + A_mB_n$ .

Line *st* is the eutectic temperature.

Liquidus line is  $\theta_1bfir\theta_2$ .

Solidus line is  $\theta_1uvst$ .

Peritectic reaction at temperature *uvi* on cooling alloy of composition *o* is  $\alpha + \text{Liq.} = A_mB_n$ .

FIG. 25. Summary of methods of determining compositions and relative amounts of phases.

**Transformations in Solid Alloys.** Various types of structural changes occur in solid alloys on heating and cooling which are somewhat similar to the allotropic transformations in pure metals. Several of these are illustrated in Fig. 26.



TABLE 4. SEVERAL ALLOTROPIC METALS AND THEIR TRANSFORMATION POINTS

Substance	Forms	Transformation Temperatures
Iron	Alpha Body-centered cubic	910°C (1670°F) 1400°C (2552°F)
Tin	Gamma Face-centered cubic  Beta (ordinary tin) White, double body-centered tetragonal	Sluggish 18°C (65°F)
Manganese	Alpha Body-centered cubic 58 atoms to unit cell  Beta Cubic 20 atoms to unit cell  Gamma Face-centered tetragonal 4 atoms to unit cell	742°C (1368°F) 1191°C (2176°F)
Cobalt	Alpha Close-packed hexagonal  Beta Face-centered cubic	477°C (892°F)

(The disintegration of tin at low temperatures has been referred to as "tin plague.")

In diagram *a*, metal *A* is allotropic, the transformation temperature being designated by the letter *c*. The  $\alpha$  solid solution has the same type of space lattice as the low-temperature form of *A*, whereas the  $\beta$  solid solution resembles both pure *B* and the high-temperature form of *A*.

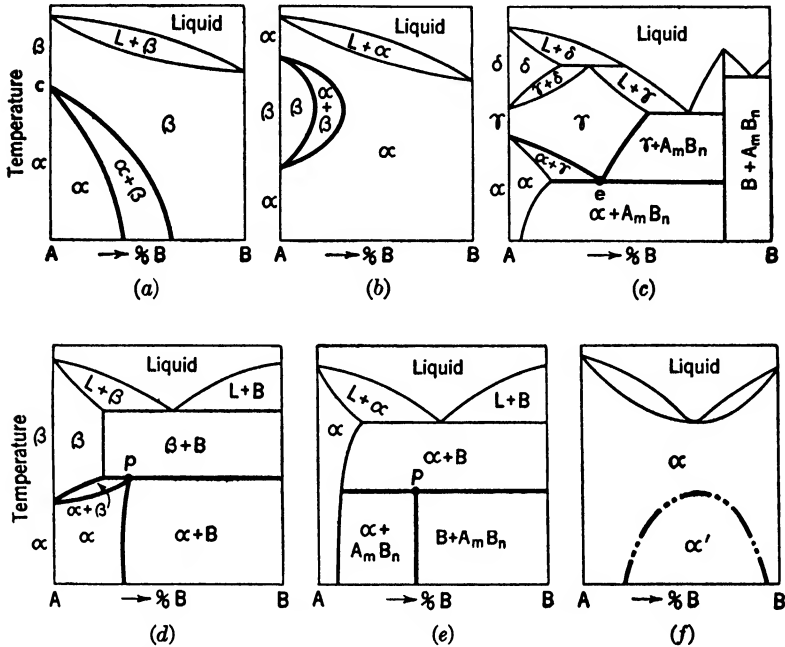


FIG. 26. Constitution diagrams showing various types of transformation in the solid state.

(a) Metal *A* has one allotropic transformation. (b) Metal *A* has two allotropic transformations. (c) Metal *A* has two allotropic transformations and the gamma solid solution undergoes a eutectoid inversion. (d) Peritectoid transformation forming a solid solution. (e) Peritectoid transformation forming a compound. (f) Transformation of a solid solution to an "ordered" solid solution or "superlattice."

Alloys rich in metal *A* undergo the transformation from one structure to the other gradually through a range of temperatures as indicated on the diagram by the two dark lines bounding the field marked  $\alpha + \beta$ . It might be said that when metal *B* dissolves in metal *A* it lowers the transformation temperature. Examples of this type of transformation are found in the systems iron-nickel and iron-manganese.

Fig. 26*b* illustrates a similar transformation from one type of solid solution to another but the  $\beta$  solid solution field is "looped" in this example. Pure metal *A* and alloys rich in *A* undergo two transforma-

tions on heating and the structure is the same at room temperature as above the upper transformation. Alloys rich in metal *B* do not undergo transformation in the solid state. Examples of looped solid solution fields are found in the systems iron-silicon, iron-aluminum, iron-molybdenum, iron-tungsten, iron-vanadium, iron-phosphorus, and iron-chromium.

In Fig. 26c pure metal *A* and alloys rich in metal *A* also undergo two transformations, but here the temperature of the upper transformation is raised when metal *B* dissolves in metal *A*. The iron-carbon diagram is of this type.

The *eutectoid* transformation, sometimes called the *eutectoid inversion*, is a common type of change in the solid state. It is similar to the freezing of a eutectic but in this case a solid solution transforms on cooling into two new solid phases. The mechanism of the two reactions is the same and the microstructures formed are very similar. In Fig. 26c the eutectoid point is designated with the letter *e* and the products of this reaction are a solid solution and a compound. The eutectoid structure in annealed steel, pearlite, illustrates this type of reaction ( $\gamma$  solid solution =  $\alpha$ Fe + Fe<sub>3</sub>C).

A much less common type of reaction in the solid state, called the *peritectoid*, is illustrated in Figs. 26d and 26e at the points marked *P*. Here two solid phases react to form a new phase on cooling. The reaction is similar to the peritectic. In Fig. 26d the  $\beta$  solid solution reacts with the metal *B* to form  $\alpha$  solid solution, whereas in Fig. 26e the  $\alpha$  solid solution reacts with *B* to form the compound  $A_mB_n$ . Reactions of this type occur in the systems iron-tungsten, iron-gold, silver-aluminum, nickel-tin, and iron-zirconium.

Fig. 26f illustrates the formation of an "ordered" solid solution which has been discussed previously. Since these "superlattices" tend to occur at a composition which can be expressed in terms of a chemical formula and since the change in mechanical properties is in the direction of greater hardness and lower ductility, this reaction has in the past been considered as a case of compound formation. Recent investigations indicate, however, that the mechanism of the transformation does not follow the phase rule, as do ordinary phase changes, and the older method of representing it on the constitution diagram with two solid lines separated by a two-phase field is not justified. The broken line in Fig. 26f therefore represents the critical temperature at which an abrupt change occurs from almost complete disorder to the partially ordered condition.

**Suppressed Transformations.** It has been pointed out that complete equilibrium between phases is not always attained during the

freezing and cooling of alloys. The dendritic segregation in cast solid solution alloys and the reaction rims formed during peritectic reactions are good examples of incomplete equilibrium. Transformations in the solid state are in most cases sluggish since the mobility of atoms and their ability to diffuse in the solid state are reduced to a marked degree at low temperatures. Consequently the degree of equilibrium actually attained during such a reaction depends to a large extent on the rate of cooling through the transformation temperature range. Rapid cooling may suppress the transformation altogether and permit the retention of an unstable high temperature phase at room temperature in some alloys. The structure and properties of many alloys can be varied at will through the choice of a proper heat treatment. The hardening of steel by quenching and the age hardening of duralumin-type alloys by controlled precipitation of a second phase in the solid state will be discussed later. The hardening of dental gold alloys, based on the formation of a superlattice, has been mentioned under the discussion of solid solutions.

### Ternary Constitution Diagrams

The graphical representation of systems comprising more than two components is not a simple problem, particularly if more than three components are involved. For ternary systems, composition can be plotted most conveniently by means of triangular coordinates, as proposed by Gibbs. In Fig. 27 each of the components is represented by one corner of an equilateral triangle. The sides of the triangle represent the three binary systems,  $A-B$ ,  $A-C$ , and  $B-C$ , and the points lying on these lines represent individual binary alloys. Each ternary alloy is represented by a point within the triangle and its composition is given by the perpendicular distances from the point to the sides of the triangle.

If the altitude of the triangle is divided into 100 units, the perpendicular distances can be measured in these units to give the composition of the alloy in per cent. In Fig. 27 the composition of the alloy represented by the point  $x$  can be obtained in the following manner. The percentage of  $A$  is given by the length of the perpendicular to the *opposite* side of the triangle, namely, 50%; the percentage of  $B$  is 30, of  $C$ , 20. The most convenient arrangement of scales is also shown in Fig. 27 where the percentage of one metal is read on each side of the triangle.

The temperatures are represented at right angles to the plane of the triangle representing compositions. This can be done by the use of a solid model in the form of a triangular prism as shown in Fig. 28. This model represents the system bismuth-tin-lead. Each vertical face of

the prism represents one of the binary systems (Bi-Sn, Bi-Pb, and Sn-Pb), temperatures being plotted vertically. The top of the model

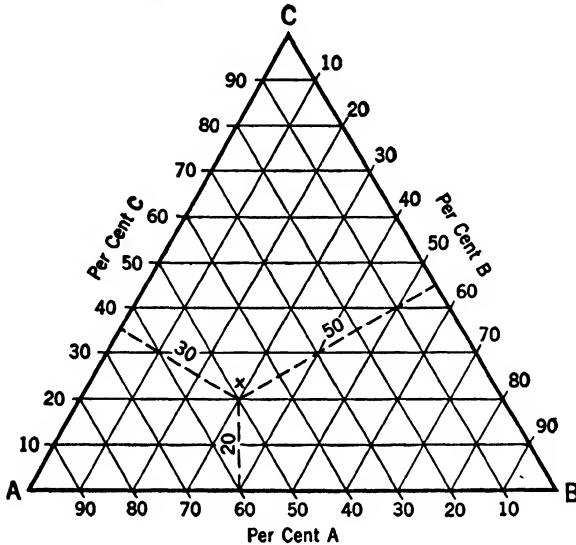


FIG. 27. Method of finding ternary composition of alloy  $x$  which is 50%  $A$ , 30%  $B$ , and 20%  $C$ .

represents the liquidus surfaces which intersect to form valleys. The lowest point in the liquidus surface is at the intersection of the three valleys and represents the ternary eutectic.

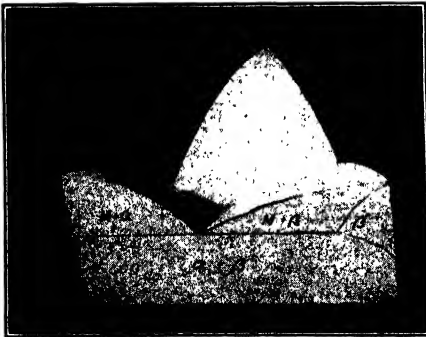


FIG. 28. The ternary system Bi-Sn-Pb represented by a solid model.

Instead of using a solid model, liquidus temperatures can also be represented in the plane of the composition triangle by drawing a series of isothermal lines, each line representing one definite temperature.

Details of a ternary diagram can be projected into a single plane, as shown in Figs. 29 and 30. These represent a system in which the three metals are completely insoluble in each other in the solid state. Fig. 29 illustrates the changes which occur in the composition of the liquid phase during

the freezing of two alloys. The ternary eutectic is designated by the letter  $O$  and points  $O_1$ ,  $O_2$ , and  $O_3$  represent the binary eutectics in the systems  $A$ - $B$ ,  $A$ - $C$ , and  $B$ - $C$  respectively. The lines connecting these four points are the projections of the binary eutectic valleys of the liquidus surface.

When an alloy of composition  $z$  begins to freeze, the first solid to form is pure  $C$ . The same primary constituent would freeze first in any alloy whose composition falls within the area  $CO_2OO_3$ . As the freezing of alloy  $z$  progresses, more primary  $C$  freezes out while the ratio of  $A$  to  $B$  in the remaining liquid is constant. This means that the composition of

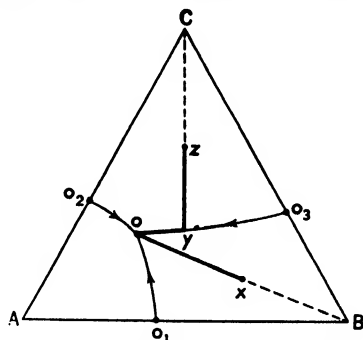


FIG. 29. The freezing of ternary alloys.

the remaining liquid must vary along the continuation of a straight line drawn from  $C$  through  $z$  in the direction of  $y$ . At  $y$  the composition of the remaining liquid reaches the binary eutectic valley and the pseudo-eutectic mixture of  $C$  and  $B$  begins to form. After this the composition of the remaining liquid varies along the binary eutectic valley ( $O_3O$ ) until it finally reaches the composition  $O$ . This point represents the ternary eutectic and here all three phases,  $A$ ,  $B$ , and  $C$ , freeze out simultaneously at a constant temperature as long as any liquid remains. The microstructure of this alloy consists of primary dendrites of  $C$ , a binary eutectic mixture of  $C + B$ , and a ternary eutectic mixture  $A + B + C$ .

During the freezing of a second alloy of the composition  $x$  primary  $B$  freezes first while the composition of the remaining liquid changes directly toward the ternary eutectic. The microstructure of the solidified alloy is made up of primary dendrites of  $B$  surrounded by the ternary eutectic mixture.

The temperatures at which the various constituents begin to freeze in any given alloy can best be shown by drawing vertical sections through the ternary model. Fig. 30 includes a basal projection of a ternary diagram and four vertical sections. All alloys represented in section I-I' contain 10%  $B$ ; in section II-II', 20%  $B$ ; in section III-III', 30%  $B$ ; and section IV-IV' represents all alloys containing equal amounts of  $A$  and  $B$ , the  $C$  content varying from 0 to 100%. In all these sections the uppermost lines indicate the liquidus, the horizontal lines the solidus or ternary eutectic temperature, and the intermediate lines

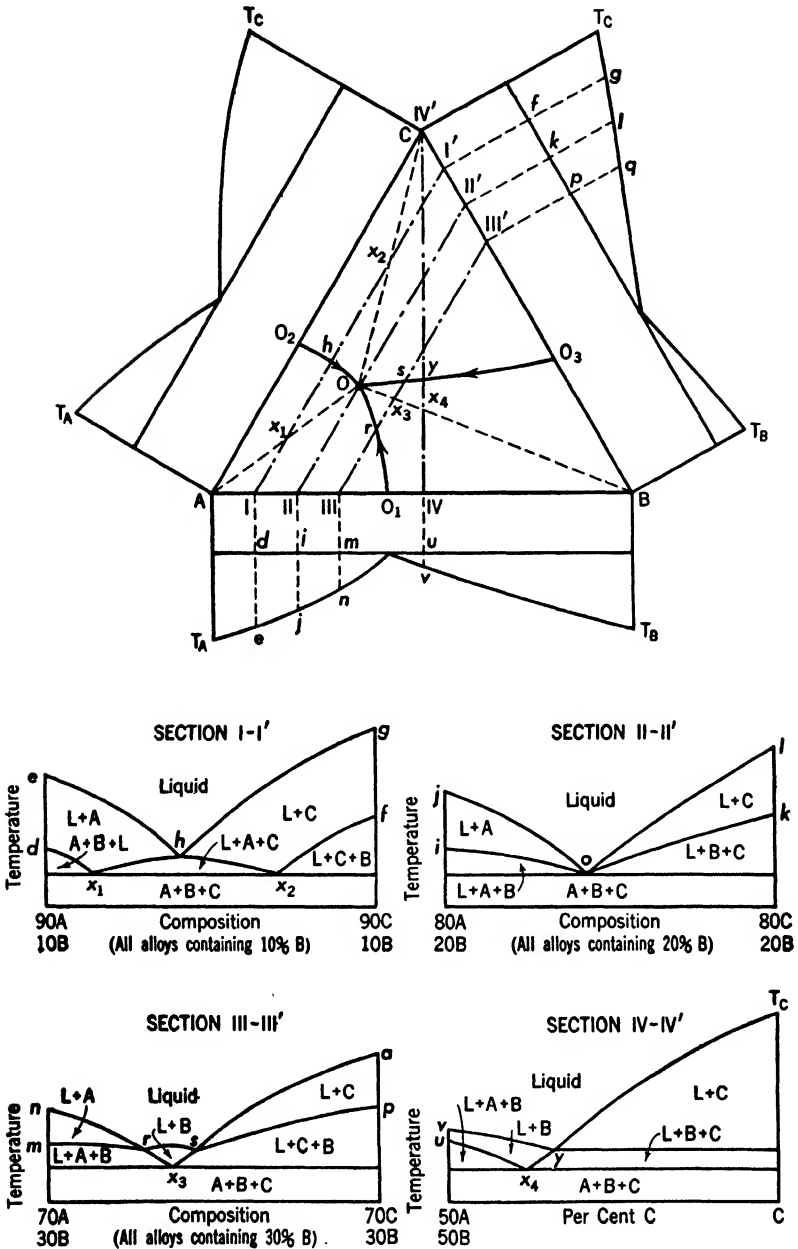


FIG. 30. Ternary system showing metals completely insoluble in the solid state, and vertical sections.

represent the temperatures at which the binary eutectic begins to freeze out. The small letters indicate the relation between points in the basal projection and corresponding points in the vertical sections.

For more complex ternary systems, isothermal sections (horizontal) through the solid model are very useful in showing the phases present in each alloy at room temperature or at some other constant temperature. Fig. 31 gives the phases at room temperature in alloys of three metals which are partially soluble in the solid state.

This very brief treatment of ternary diagrams is intended only as an introduction to the subject. A more thorough discussion can be found in *Principles of Phase Diagrams*.<sup>5</sup>

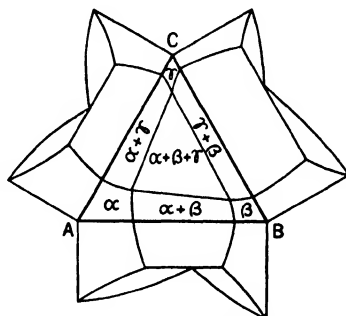


FIG. 31. Ternary system showing metals partially soluble in the solid state, and basal projections of phases present at room temperature. Area  $ABC$  is an isothermal section.

### Laboratory Methods for Working Out Constitution Diagrams

The data required for the construction of constitution diagrams is usually obtained in the laboratory by means of thermal analysis, microscopic examination, and x-ray diffraction methods. Occasionally these are supplemented by a study of changes in various physical properties with changes in temperature or composition. Almost any of the physical properties of alloys might be studied in this manner, but the following list includes the methods which have been found to be the most useful. Several of these will be discussed more fully later.

1. Thermal analysis; cooling and heating curves.
2. Microscopic examination; number and identity of phases.
3. X-ray diffraction studies; crystal structure.
4. Dilatation; changes in volume with temperature.
5. Electrical resistivity and temperature coefficient of resistivity.
6. Hardness; Brinell, Rockwell, etc.
7. Tensile properties: tensile strength, yield point, proportional limit, per cent elongation, reduction of area.
8. Magnetic properties: permeability, coercive force, etc.
9. Thermoelectric force; alloy used as one element of a thermocouple.
10. Electrolytic potential.

<sup>5</sup> J. S. Marsh, McGraw-Hill Book Co., 1935.



## CHAPTER V

### PYROMETRY

#### Measurement of Temperature

**Temperature Scales.** The standard temperature scale used mostly in scientific research is the centigrade scale on which the temperature interval between the freezing and boiling points of water is divided into 100 degrees. The standard fixed points on the International Temperature scale adopted in 1927 are the boiling points of oxygen, water, and sulfur at  $-182.97$ ,  $100.00$ , and  $444.60^{\circ}\text{C}$ , respectively, and the freezing points of water, silver, and gold at  $0.00$ ,  $960.5$ , and  $1063^{\circ}\text{C}$ , all determined at standard atmospheric pressure. The division of the scale between these points is accomplished by means of a standard resistance thermometer below  $660^{\circ}\text{C}$ , the standard platinum thermocouple between  $660$  and  $1063^{\circ}\text{C}$ , and the optical pyrometer above  $1063^{\circ}\text{C}$ .

It is an unfortunate circumstance that in American industrial plants a different temperature scale — the Fahrenheit — is used almost exclusively. The relation between the two scales is expressed by the following equations:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) \frac{5}{9}$$

$$^{\circ}\text{F} = \frac{9}{5} ^{\circ}\text{C} + 32$$

#### Pyrometers

A pyrometer is an instrument used for measuring temperature. In metallographic work the thermocouple pyrometer is the most useful and will be discussed in detail later. Other types of pyrometers will be mentioned briefly.

**Expansion Thermometers.** These are based on the principle of thermal expansion of liquids, solids, or gases and are useful mainly at low temperatures. They are classified as follows.

##### 1. Liquid.

###### a. Common types.

Mercury (range,  $-35^{\circ}\text{C}$  to  $+350^{\circ}\text{C}$ ).

Alcohol (range,  $-114^{\circ}\text{C}$  to  $+78^{\circ}\text{C}$ ).

- b. Gas filled with CO<sub>2</sub> or N<sub>2</sub> under pressure (usually over Hg) (range -35°C to +500°C).
  - 2. Solid.
    - a. Single metal, based on principle of thermal expansion (obsolete).
    - b. Bimetallic, based on principle of differential expansion of two metals of relatively high and low expansions which actuate indicating or controlling mechanism. (Range from room temperature to about 500°C.) Chief use in thermostats.
  - 3. Gas.
    - a. Vapor tension. Ether, sulfur dioxide, methyl or ethyl chloride, used to about 750°C. Rather limited use.
    - b. Gas thermometer. Originally used as basis for the standard temperature scale. Apparatus cumbersome. Not used for industrial temperature measurement.

**Electrical Resistance Thermometers.** These thermometers make use of the variation with temperature in the resistance of an electrical conductor, usually a coil of fine platinum wire. They are very accurate but their industrial application is limited to service at low temperatures.

**Optical and Radiation Pyrometers.** These pyrometers measure the radiant energy from a hot body. They are used in metallurgical work for measuring higher temperatures than can be measured with thermocouples and are not highly accurate. The most common form of optical pyrometer matches the brightness of the hot body with a standard light source like the filament of an electric lamp, whereas the ordinary radiation pyrometer measures the intensity of the radiant heat and light rays from the hot body by focusing them on a thermocouple.<sup>1</sup>

**Pyrometric Cones or Seger Cones.** Made of refractory materials, each has a fairly definite softening temperature, and is used chiefly in the ceramic industry.

### Thermocouple Pyrometer

**Thermocouples.** A thermocouple consists of two dissimilar metals or alloys in the form of wires or rods, joined at one end, preferably by welding. When the welded junction, usually called the *hot junction* or *variable junction*, is heated above or cooled below the temperature of the free ends, an electromotive force is developed which can be measured by some form of measuring instrument. The connections between the free ends and the measuring instrument, or the extension wire leads, are called the *cold junction* or *fixed junction* and are usually maintained at a constant temperature. The magnitude of the electromotive force generated by the couple is a function of, and sometimes directly pro-

<sup>1</sup> A.S.M. *Metals Handbook*, 1939, pp. 285-310.

portional to, the difference in temperature between the fixed and variable junctions.

The measuring instruments may be calibrated in millivolts (1/1000 volt) and a calibration curve or table is required to convert the reading into degrees centigrade or Fahrenheit. In industrial plants, when an instrument is always used with one type of thermocouple, it is often calibrated in degrees Fahrenheit. The instrument may be a galvanometer (millivoltmeter) or a potentiometer. The galvanometer type is simpler in construction and operation but is the less reliable of the two since the potentiometer type gives readings which are independent of changes in the electrical resistance in the external circuit. (See Fig. 32.)

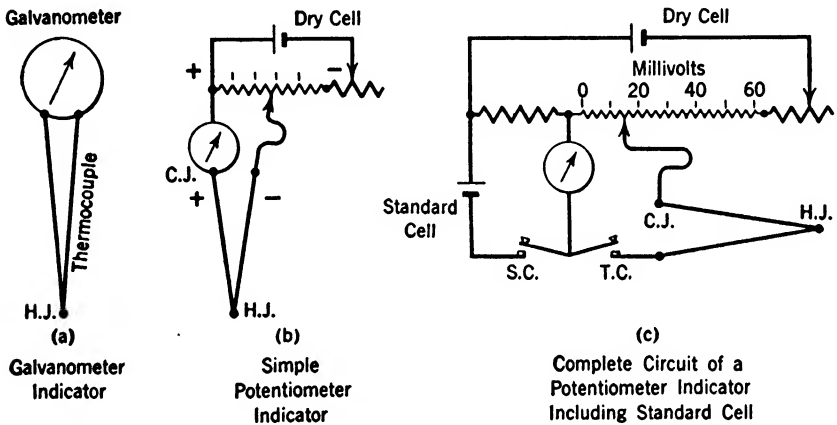


FIG. 32. Wiring diagram of potentiometric measuring instruments.

**Noble Metal Couple.** The standard platinum couple consists of one wire of pure platinum and another of 90% platinum and 10% rhodium. It is frequently used up to 2732°F (1500°C) and lasts indefinitely if protected from reducing gases and general contamination. Below this temperature its calibration remains very constant, but if used between 1500 and 1650°F it must be recalibrated frequently and its useful life is reduced. Its melting point is about 3190°F (1755°C). Platinum couples are usually welded by means of a carbon arc without a flux and they can be annealed simply by passing an electric current through them.

The only other noble metal couple being used to any extent at present is one of platinum and 87% Pt-13% Rh.

**Base Metal Couples.** Base metal couples are numerous but the following combinations are of most importance at present and are given in the order of their service in metallurgical applications.

	APPROXIMATE COMPOSITION
1. Chromel-alumel	(Ni 90, Cr 10) — (Ni 94, Mn 3, Al 2, Si 1)
2. Iron-constantan	(Fe) — (Ni 46, Cu 54)
3. Chromel-X-copel	(Ni 64, Cr 11, Fe 25) — (Ni 45, Cr 55)
4. Copper-constantan	(Cu) — (Ni 46, Cu 54)

The chromel-alumel couple is the most widely used of all couples. It has a fairly straight line calibration curve and good resistance to oxidation. It is frequently used up to 2000°F (1094°C) in continuous service and intermittently up to 2400°F (1315°C).

The iron-constantan couple is not recommended for continuous use under oxidizing conditions at temperatures above 1400°F (760°C), but under reducing conditions it has a longer life and is more satisfactory than chromel-alumel up to 1800°F (981°C).

The copper-constantan couple is not generally used above 600°F (315°C).

Base metal couples are much less expensive than platinum couples but their calibration is more liable to change with use and they cannot be used at as high a temperature.

Table 5 gives the representative emf values for the commercial couples.

**Calibration of Thermocouples.** Thermocouples can be checked against the freezing points of pure metals or by comparison with standard couples of known accuracy. Certified pure metals are obtainable from the National Bureau of Standards for a nominal sum and the metals most commonly used are lead, tin, zinc, and silver.

A furnace similar to that shown in Fig. 33<sup>2</sup> is recommended for basic calibrations. If several couples are to be calibrated the variable junctions can be welded together and the emf values compared at a constant temperature. Control couples for furnaces should be placed near the heat source as shown on the diagram.

The values of the emf generated by the couple at several different temperatures can be used to construct a calibration curve, plotting millivolts against degrees Fahrenheit or centigrade. The curve usually fits the equation

$$E = a + bt + c(t)^2$$

where  $E$  is the emf

$t$  is the temperature

$a$ ,  $b$ , and  $c$  are constants.

<sup>2</sup> W. F. Roeser and H. T. Wensel, "Methods of Testing Thermocouples and Thermocouple Materials," National Bureau of Standards, R.P. 768; *Res. Journ.*, Vol. 14, p. 259 (1935).

TABLE 5. CALIBRATION TABLES FOR COMMERCIAL THERMOCOUPLES\*

(Emf in millivolts. Cold junction 0°F.)

Temperature °F	90 Pt, 10 Rh vs. Platinum	Chromel vs. Alumel	Iron vs. Constantan	Copper vs. Constantan
0	0	0	0	0
100	0.313	2.20	2.88	2.19
200	0.687	4.50	5.84	4.64
300	1.108	6.77	8.87	7.32
400	1.565	8.99	11.94	10.19
500	2.048	11.24	15.01	13.24
600	2.549	13.53	18.08	16.44
700	3.067	15.86	21.15	
800	3.597	18.20	24.23	
900	4.136	20.56	27.33	
1000	4.686	22.93	30.46	
1100	5.247	25.30	33.66	
1200	5.817	27.66	36.96	
1300	6.399	30.01	40.38	
1400	6.990	32.33	43.88	
1500	7.592	34.62	47.40	
1600	8.204	36.88	50.82	
1700	8.826	39.11	54.44	
1800	9.457	41.30	57.96	
1900	10.099	43.45		
2000	10.749	45.57		
2100	11.408	47.65		
2200	12.069	49.69		
2300	12.734	51.68		
2400	13.397	53.63		
2500	14.060	55.53		
2600	14.721			
2700	15.380			
2800	16.035			
2900	16.688			
3000	17.339			

\* Data from Leeds &amp; Northrup Co. Standard Conversion Tables, No. 21031 (1941).

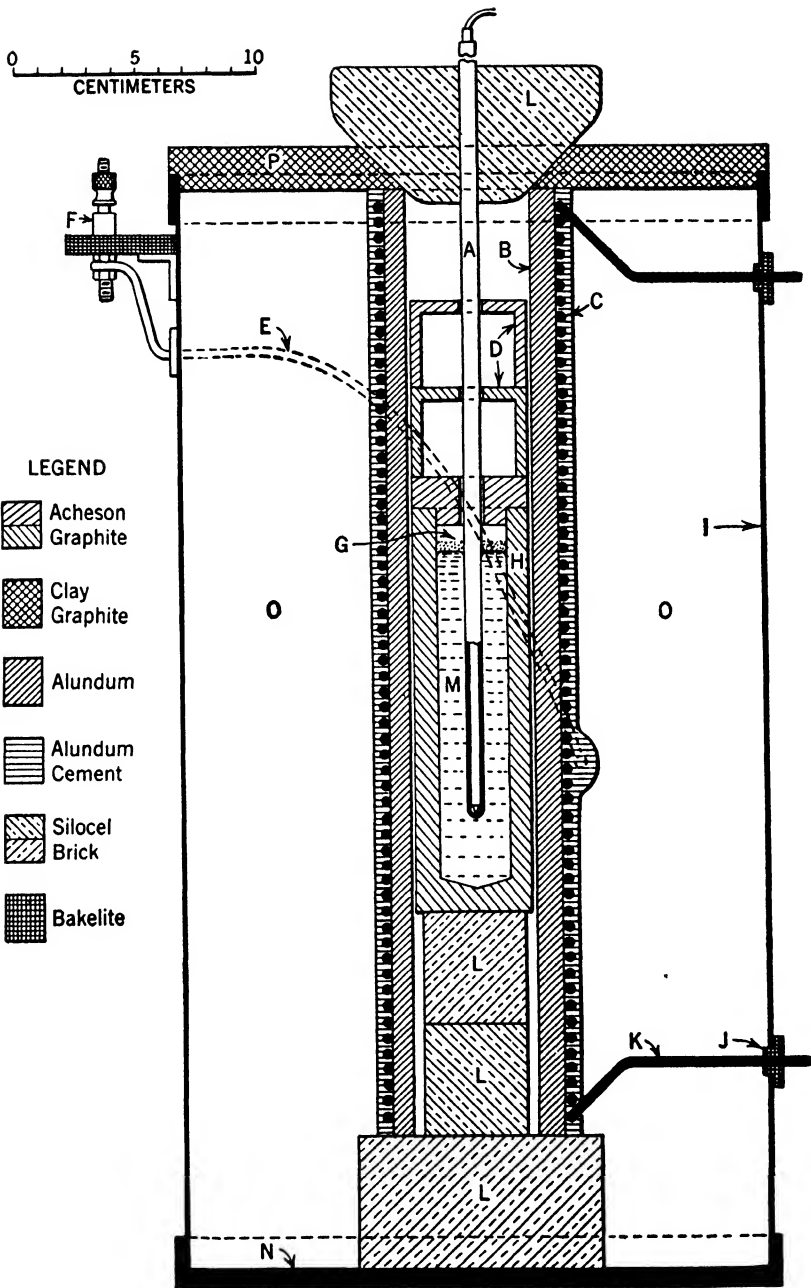


FIG. 33. Furnace for determining freezing points. (After Roeser and Wenzel, National Bureau of Standards.)

If standard calibration tables are available for the type of couple being used, any deviations from the standard tables can be noted. A calibration curve or table is accurate only for one cold junction temperature. When the couple is used at any other cold junction temperature a cold junction correction must be applied:

$$\text{Correct temp} = \text{reading} + (\text{actual C. J. temp} \\ - \text{calibration C. J. temp})K$$

The values for the constant  $K$  are 1 for a chromel-alumel couple, approximately 0.5 for the standard platinum couple, 0.9 for the iron-constantan, and 0.85 for the copper-constantan couple. These values vary slightly with the hot junction temperature. Most indicating and recording instruments are provided with manual or automatic cold junction compensators and the cold junction is usually at room temperature. A special pair of extension leads is available for each common type of couple and the thermoelectric characteristics of the lead wires are similar to those of the thermocouple wires. Their use permits the spacing of the cold junction at a distance from the furnace.

The hot junction of a thermocouple is usually protected against contact with molten metal or corrosive atmospheres by a protecting tube made of impervious and refractory material.

Automatic temperature-controlling or -recording instruments are usually actuated by thermocouples and are available in either the potentiometer or the galvanometer type of instrument. Bare couples are used for measuring ladle temperatures of molten brass, etc., in order to obtain fast readings with little lag.

## CHAPTER VI

### MECHANICAL PROPERTIES

The term *mechanical properties* is usually applied to properties determined by ordinary static and impact tests, particularly the tensile test. Under *physical properties* are usually classed those which are ordinarily determined in a physics laboratory, such as thermal and electrical conductivity, specific heat, boiling point, etc.

#### Stress

When a force or a load is applied to a metal there is an equal and opposite amount of resistance within the metal which is referred to as a *stress*. Stresses are described by their direction and magnitude. They are usually classified according to their direction as: tensile, compressive, and shear. The term stress usually implies a unit stress and is measured as force per unit area, in this country as pounds per square inch (psi) and in Europe as kilograms per square millimeter.

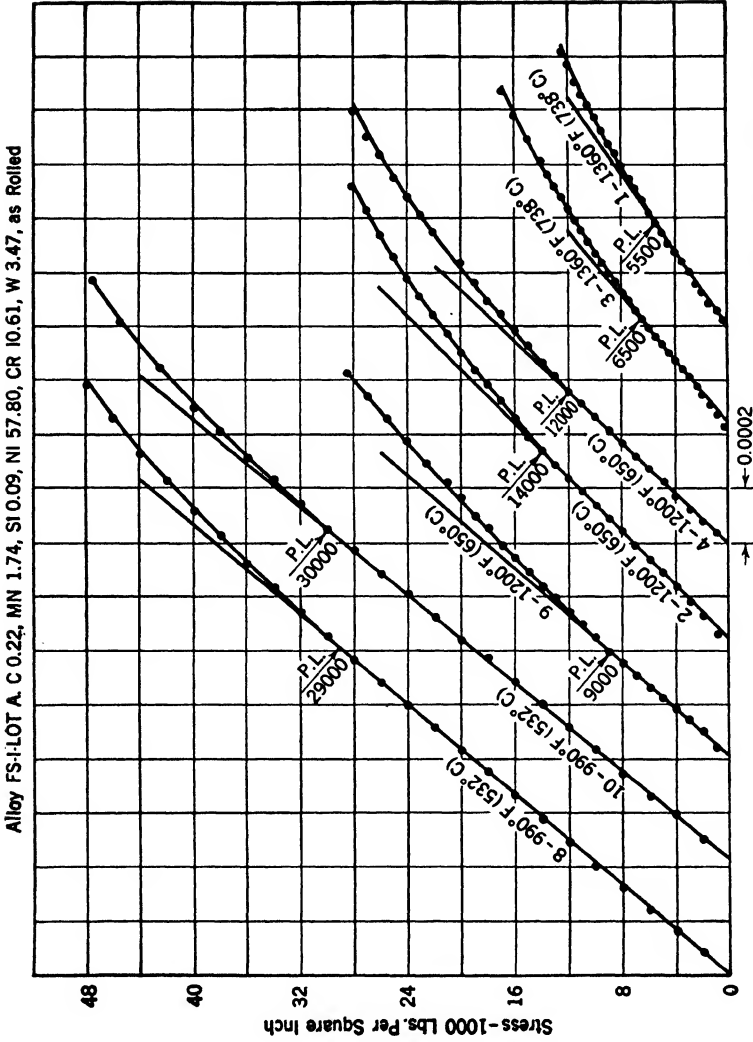
A stress in a body is always accompanied by a deformation called a *strain*. Strain is measured in terms of deformation per unit dimension, and usually as inches per inch. A strain is not a force.

**Proportional Limit (P.L.).** Proportional limit is the stress at which the deformation ceases to be proportional to the load. It is determined by a strainometer (extensometer for tension, compressometer for compression, and deflectometer for transverse tests), values being read from plotted results.<sup>1</sup> Fig. 34 shows that the proportional limit decreases as the testing temperature increases. Within the proportional limit, stress is proportional to strain (Hooke's law) and the stress-strain curve below the proportional limit is a straight line.

**Elastic Limit (E.L.).** Elastic limit is the stress at which the initial permanent deformation (elongation or shortening of the gage length) occurs, as shown by an instrument of high precision (determined from set readings with extensometer or compressometer). In transverse tests, the extreme fiber stress at which the initial appreciable permanent deflection occurs as determined with deflectometer. Tests are rarely made for elastic limit since they involve repeated application and

<sup>1</sup> Nat. Bur. Stand. Circ. 101, "Physical Properties of Materials."





Courtesy National Bureau of Standards

Fig. 34. Stress-strain curves in tension at elevated temperatures to show decrease in both proportional limit and modulus of elasticity at increased testing temperature.

release of load and require considerable time. For practical purposes the elastic limit may be regarded as equal to the proportional limit.

**Yield Point (Y.P.).** The yield point is the stress at which marked increase in deformation of specimen occurs without increase in load, as determined usually by drop of the beam; on hydraulic machines, by change of direction of load indicator, or by dividers. A definite yield point is observed in testing soft steels which have not been cold worked but other metals and alloys do not possess this property. For these it is customary to report a *yield strength*, which is the stress required to produce a definite amount of permanent deformation, usually 0.2 per cent in 2 in.

**Tensile Strength (T.S.).** The tensile strength is the maximum stress applied when a specimen is broken in tension.

*Example.* Given a wire of cross-sectional area of 0.001 sq in. A load of 60 lb is required to break it in tension.

$$\text{T.S.} = \frac{60}{0.001} = 60,000 \text{ psi}$$

Tensile strength is also called ultimate strength, maximum strength, and breaking strength. The cross-sectional area is referred to as the original area before testing and not the final area.

**Elongation (Per Cent).** This is the percentage of elongation or extension of a tensile bar after rupture and is found by dividing its increase in length by the original gage length. Steels usually "neck" at the point of rupture; consequently, the shorter the gage length, the higher the percentage of elongation for such metals. Elongation is an indication of the ductility of the material.

$$\text{per cent elongation} = \frac{\text{final length} - \text{original length}}{\text{original length}} \times 100$$

**Reduction of Area (Per Cent).** This is the percentage of reduction or contraction in area of a tensile bar after rupture and is found as the ratio of the difference between the original and broken area of cross section to the original area.

$$\text{per cent R. A.} = \frac{\text{original area} - \text{final area}}{\text{original area}} \times 100$$

**Poisson's Ratio ( $\lambda$ ).** This is the ratio of lateral contraction per unit of diameter to longitudinal extension per unit of length of a round bar under terminal tension within the proportional limit. If the volume remained constant the value would be 0.5. Actually there is an increase in volume and the ratio for various metals falls between 0.24 and 0.42.

**Modulus of Elasticity in Tension or Compression ( $E$ ).** This is the ratio of stress within the proportional limit to the corresponding strain as determined with a precise strain gage. The more accurate determinations are made with a gage length at least 8 in. Fig. 34 shows the modulus of elasticity to decrease with the testing temperature. When the term modulus of elasticity ( $E$ ) is used it refers either to tension or compression.

**Modulus of Elasticity in Shear ( $E_s$ ).** This is the ratio of stress within the proportional limit to the angular strain (in radians). The following theoretical relation exists between the modulus of elasticity in shear and the ordinary modulus of elasticity.

$$E_s = \frac{E}{2(1 + \lambda)} \quad \lambda = \text{Poisson's ratio}$$

It is usually determined by the torsion of a round bar.

**Modulus of Rupture ( $R$ ).** This is the maximum stress in the extreme outer fiber of a beam tested to rupture, as computed by the empirical application of the flexural formula to stresses above the transverse proportional limit. For a simple rectangular beam with concentrated load at the center

$$R = \frac{1.5 \times \text{load} \times \text{span}}{\text{area} \times \text{depth}}$$

Brittle metals, e.g., tungsten carbide, are tested in this manner. The theoretical value of  $R = Mc/I$  where

$$\begin{aligned} M &= \text{bending moment or } \frac{1}{8} \text{ load} \times \text{length} \\ c &= \text{distance of outer fiber from neutral axis} \\ I &= \text{moment of inertia of section} \end{aligned}$$

**Torsional Strength or Modulus of Rupture in Torsion ( $S$ ).** This is the maximum stress in the extreme fiber of a specimen tested to rupture by empirical application of the torsional formula to stresses above the torsional proportional limit.

$$\text{For round specimens } S = \frac{5.1 \times \text{twisting moment}}{\text{diameter}^3}$$

In ductile materials the stress at rupture is considered uniformly distributed over the area and

$$S = \frac{3.82 \times \text{twisting moment}}{\text{diameter}^3}$$

The theoretical value for round specimens is  $S = (Ppc)/J$  or

$$S = \frac{\text{load acting at a distance } p \text{ from axis of twist} \times \text{radius of bar}}{\text{polar moment of inertia}}$$

**Modulus of Resilience.** This is the amount of energy stored up in a body when one unit volume of the body is stressed to its proportional limit.

$$\text{modulus of resilience} = \frac{(\text{proportional limit})^2}{2(\text{modulus of elasticity})} = \frac{(\text{P.L.})^2}{2E}$$

**Ductility.** Ductile materials are those capable of undergoing considerable permanent (plastic) deformation when tested in tension. A metal which can be drawn easily into wire is ductile. Ductility is dependent on both plasticity and tensile strength. Ductile metals actually fail in shear, grain by grain, along their slip planes.

**Malleability.** Malleable materials are those which can be readily deformed by compression as by hammering, swaging, or rolling. Malleability is dependent on plasticity but more independent of strength than is ductility.

**Toughness.** Tough materials are those which require a large amount of work (force  $\times$  distance) to rupture them. The area under the stress-strain curve, if the specimen is carried to fracture, is proportional to the toughness. Lead is plastic, quite malleable, having low ductility and low toughness because it has a rather low load-carrying ability.

**Brittleness.** Brittle materials usually have high load-carrying ability but little plasticity or slippage; they cleave rather than slip when stressed to rupture. They have exceedingly low ductility and malleability and usually have considerable hardness.

## Hardness

Hardness may be defined as resistance to penetration. One of the early hardness tests used by mineralogists was Mohs' white hardness scale of ten minerals, listed in the order of increasing hardness: talc, gypsum, calcite, fluorite, apatite, orthoclase, quartz, topaz, corundum, and diamond. The hardness of an unknown mineral was determined by scratching with the ten standard minerals. Table 6 shows that there is a large gap in hardness between topaz and diamond.

The most common methods for testing hardness of metals are described as follows.

**Brinell.** In this test the hardness of a metal is determined by the size of an impression produced by a ball penetrator under a definite load. The Brinell Hardness Number is simply the load on the pene-

TABLE 6. HARDNESS OF MOHS MINERALS AND ABRASIVE MATERIALS\*

<i>Samples</i>	<i>I</i> †
Gypsum	32
Calcite	135
Fluorite	163
Apatite    to axis	360
Apatite ⊥ to axis	430
Albite	490
Orthoclase	560
Crystalline quartz    to axis	710
Crystalline quartz ⊥ to axis	790
Topaz	1250
Carbology	1050-1500
Regular alundum No. 1	1635
Regular alundum No. 2	1625
Regular alundum No. 3	1620
98 — alundum No. 1	1670
98 — alundum No. 2	1680
Black silicon carbide No. 1	2150
Black silicon carbide No. 2	2050
Green silicon carbide No. 1	2130
Green silicon carbide No. 2	2140
Molded boron carbide No. 1	2250
Molded boron carbide No. 2	2260
Molded boron carbide No. 3	2250
Diamond	8200-8500

\* C. G. Peters and F. Knoop, "Metals in Thin Layers — Their Microhardness," *Metals and Alloys*, Vol. 12, 297 (September, 1940).

† *I* is indentation hardness nearly identical with Vickers hardness.

trator divided by the spherical area of the impression, in kilograms per square millimeter, and this applies to any size of penetrator and any load.

The standard Brinell test makes use of a steel ball or tungsten carbide penetrator of 10 mm diameter and a load of 3000 kg for steel or 500 kg for brass, bronze, and soft metals in general. The load is usually applied for 30 sec, but a minimum of 10 sec is permitted by A.S.T.M. specifications in iron and steel specimens. Steel ball penetrators can be used safely for hardness values up to 500 Brinell, and tungsten carbide balls are useful for values up to approximately 800 Brinell. The diameter of the impression is measured in millimeters and this value is converted into the Brinell Hardness Numbers (often reported simply as "Brinell") by means of a table or by the formula

$$\text{BHN} = \frac{L}{\pi \frac{D}{2} (D - \sqrt{D^2 - d^2})}$$

where  $L$  = load in kilograms  
 $D$  and  $d$  respectively = the diameters of the ball and of the impression  
in millimeters.

The size of the specimen tested must be large enough so that no visible effect of cold work can be observed on the side next to the anvil. For testing small specimens, lighter loads and smaller penetrators are sometimes used. Such tests meet the A.S.T.M. specifications provided the ratios of the load to the diameter of the penetrator are

$$L = 30D^2 \text{ for iron and steel, or}$$

$$L = 5D^2 \text{ for brass, bronze, and soft metals in general}$$

**Vickers.** The Vickers hardness test is similar to the Brinell test but the penetrator used is a  $136^\circ$  diamond pyramid which can be used on very hard metals. The load is varied from 1 to 120 kg, according to requirements. The operation of the machine is semiautomatic, the load being applied for a predetermined period, usually 10 or 30 sec. A measuring microscope, conveniently mounted for swinging into position over the impression, is used to measure the diagonals of the square impression. The Vickers Hardness Number is calculated by the formula

$$\text{VHN} = \frac{1.854 \times \text{load in kilograms}}{(\text{diagonal of impression in millimeters})^2}$$

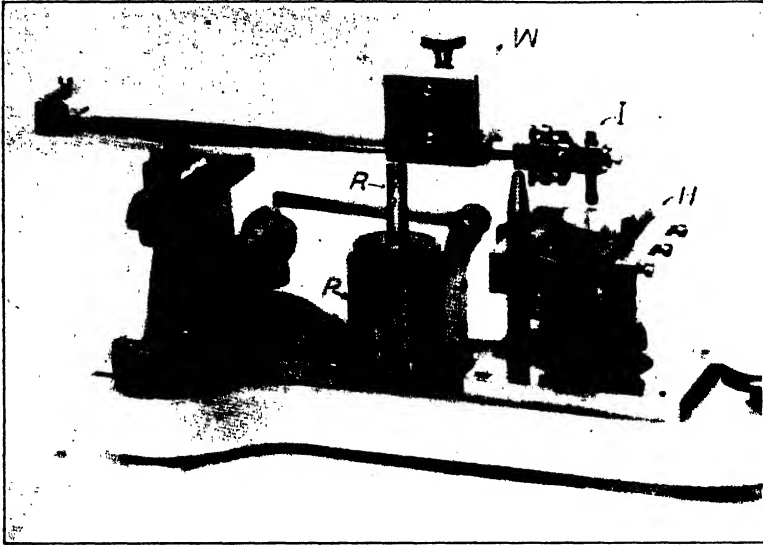
The values for VHN are practically identical with the Brinell up to 300 but are greater for harder specimens.

The diamond penetrator distorts very little even when very hard materials are tested, permitting high accuracy over a wide range of hardness values, from very soft metals like high-purity lead of about 4 Brinell up to as high as 1800 VHN.

**Knoop Indenter.** A micro-Brinell (Fig. 35), recently developed by Peters and Knoop, shows much promise in the testing of either thin or thick material of all hardness ranges. The indenter is a diamond crystal of pyramidal shape with angle of  $172^\circ 30'$  in one direction and  $130^\circ$  at right angles to it. The loads ordinarily vary from 50 g to 2 kg, and the indentation hardness,  $I$ , is the ratio of the load in kilograms to the unrecovered projected area of the impression in square millimeters. The impressions are determined with an ordinary micrometer microscope. The  $I$  values are nearly identical with Vickers numbers, as would be expected.

Table 6 shows the hardness of Mohs minerals, as used by mineralogists

for scratch hardness, and of abrasive materials as tested with the Knoop indenter. One of its important fields of application is in the determination of hardness of various microconstituents.



*Courtesy Metals & Alloys, and National Bureau of Standards*

FIG. 35. Knoop hardness testing machine.

**Rockwell.** The Rockwell test operates on the same principle as the Brinell but the depth of penetration is measured instead of the diameter of the impression. A diamond cone penetrator ( $120^\circ$ ) with a slightly rounded tip (radius 0.2 mm) is loaded with a minor load of 10 kg, primarily to seat the penetrator; a major load (regularly 150 kg for "C" scale) is applied and released after a specific time, usually 10 sec. The hardness is measured by the difference in depth of the major and minor loads so the work must be very rigid. The increment of depth for an increment of load is 0.00008 in. for each point of hardness on the Rockwell scale; e.g., if a die steel is C 60 at one location and C 55 at another the latter impression is deeper than the former by  $5 \times 0.00008$  in. Thus, hardened steels can be easily tested as the depth of penetration is about 0.005 in. With the "Superficial" model the penetration is about 0.002 in. so even thin work can be tested. There are two standard hardness scales usually used with the standard model—the B for softer steels and nonferrous metals and the C for hardened and tempered steels. The various scales in use are shown in Table 7.

As the Rockwell machine is direct reading and fast in operation it

TABLE 7. SCALES USED IN ROCKWELL HARDNESS TESTING

Scale	Penetrator	Load in Kilograms	Reading
B	1/16" steel ball	100	Red numerals
C	Diamond cone	150	Black numerals
<b>Special Scales</b>			
A	Diamond cone	60	Black
D	Diamond cone	100	Black
E	1/8" steel ball	100	Red
F	1/16" steel ball	60	Red
G	1/16" steel ball	150	Red
H	1/8" steel ball	60	Red
K	1/8" steel ball	150	Red

Standard blocks are available for checking purposes.

has found wide application in industry for work which can be properly supported. Both Rockwell and Brinell machines mark the work and for highly finished parts of hardened steels these impressions may not be desirable.

**Shore Scleroscope.** The scleroscope measures the height of rebound of a diamond-tipped hammer, with a well-rounded point, when released from a low height. With hardened surfaces well polished there is little marking of the work. There are two main types, one in which the hammer is pneumatically operated in a glass tube and the operator must watch for the height of rebound, and the other a more precise type having a dial recording the height of rebound indicated by a hand on a dial. The work must be smooth and rigid for this test and the surface must be normal to the fall of the hammer. The instrument is reliable only when in the hands of a skilled operator; it is one which must be checked constantly against standards of the maker. The instrument still has an important place in industry; it is more easily portable and can be taken to large and heavy work.

**Microcharacter.** The microcharacter, developed by Bierbaum, is a hardness testing instrument capable of determining the scratch hardness of various microconstituents when distributed finely in alloys. The hardness of various microconstituents is obtained by scratching with the cube edge of a diamond, accurately ground, with a load of 3 g. Any good microscope, with a filar screw micrometer ocular of 15 or 25 $\times$  and an objective capable of resolving one micron (1 = 0.001 mm) and equipped with a vertical illuminator, will suffice to measure the microhardness numbers (K).

$$K = (\text{width of cut in microns})^{-2}10^4$$



Table 8, which formerly appeared on this page, was erroneously accredited to the *Wilson Mechanical Instrument Company*. It has been replaced by the better and more complete table actually prepared by them.

. (The new table is shown on the facing insert)







Application has been limited mostly to the hardness of microconstituents of bearing metals.

Table 8 shows general conversion values for many of the hardness numerals.

### Fatigue or the Progressive Failure of Metals

Many parts of automobiles and tractors are designed so they seldom fail from static loads. About 90 per cent of the failures of rear axles, front spindles, crankshafts, and gears fail at stresses below their proportional limit and fracture as though brittle, showing no apparent plastic deformation. Static tests on these same parts usually show high ductility as measured by the percentage of elongation.

Frequently, laymen describe these failures as "crystallized" and believe erroneously that the metal crystallizes in service. Actually, no grain growth can occur in steel at ordinary temperature, even under repeated stresses. A careful examination of this type of fracture usually shows that it started at some "stress-raiser" which may have been a nick, scratch, inclusion, or an abrupt change in section without the proper fillet. High concentration of stress at this point caused local overstressing of the metal and a minute crack appeared which progressed very gradually at first with each application of the load. As the crack increased in size, the stresses were intensified at this point and the crack progressed at an accelerated rate until the remaining section could no longer sustain the load and failed at once. The resultant fracture shows two distinct zones: Near its origin the faces of the original crack have rubbed together and the fracture is usually smooth and polished, whereas the last part to fail looks like an ordinary ductile fracture and this area is frequently very small. Fig. 36 illustrates another common characteristic of this type of fracture, namely, zone lines which indicate the progress



FIG. 36. Fatigue fracture of steering arm from passenger automobile. Section was subjected to reversed bending and progressive cracking took place at the top and later also at the bottom position in the figure.  $\times 2$ .

of the fissure at various stages, sometimes referred to as "oyster shell" markings. The micrograph (Fig. 37), shows that the path of the progressive crack is across the grains (transgranular) and along the crystallographic planes.



FIG. 37. Path of progressive fissuring in ingot iron showing transgranular cracking paralleling slip planes.  $\times 1000$ .

This progressive fissuring is called *fatigue*, which is really a misnomer. It is customary for designing engineers to use the so-called "endurance limit" of a material in calculating allowable stresses in highly stressed aircraft and automobile parts, etc. The endurance limit is the maximum stress which can be applied repeatedly for an infinite time without causing failure. It is determined experimentally by the use of various "fatigue testing" machines which usually stress the specimen by reverse bending, but sometimes by plain bending, plain torsion, reverse torsion, axial loading in tension, or in alternate tension and compression. Most of the published values for endurance limits have been obtained with a *rotating beam* type of machine which can be operated at high speeds. A specimen of circular cross section is deflected elastically by a known force (bending) and as it is rotated the stresses at any point in the surface undergo a reversal from 100 per cent tension through 100 per cent compression during each revolution. A number of specimens are broken at various loads and the results plotted on semi-log paper as shown in Fig. 38. The number of reversals or cycles which caused

failure is plotted against the load. If all the test bars are uniform and polished axially there is very little scattering of points. For steels and a few nonferrous alloys, a definite "knee" occurs in this curve at the endurance limit. Ten million reversals are sufficient to determine the endurance limit of steel whereas nonferrous alloys usually are tested

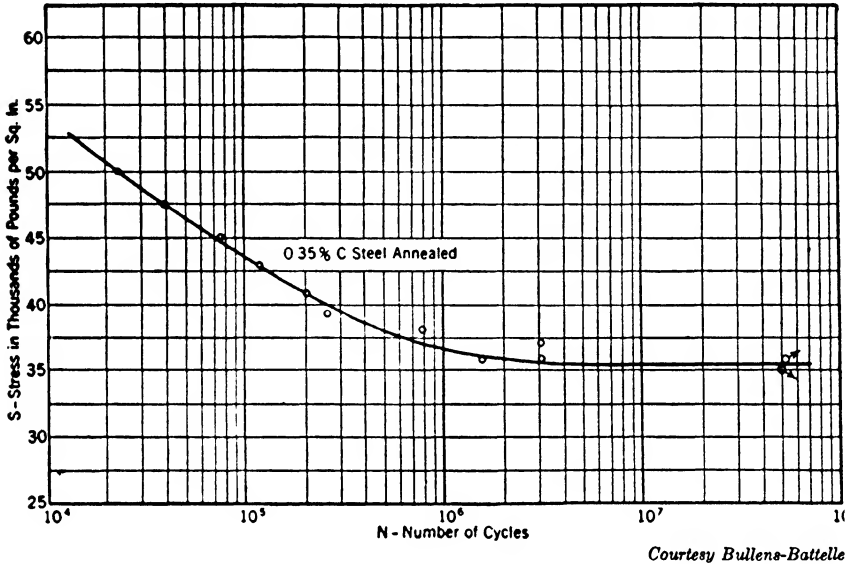
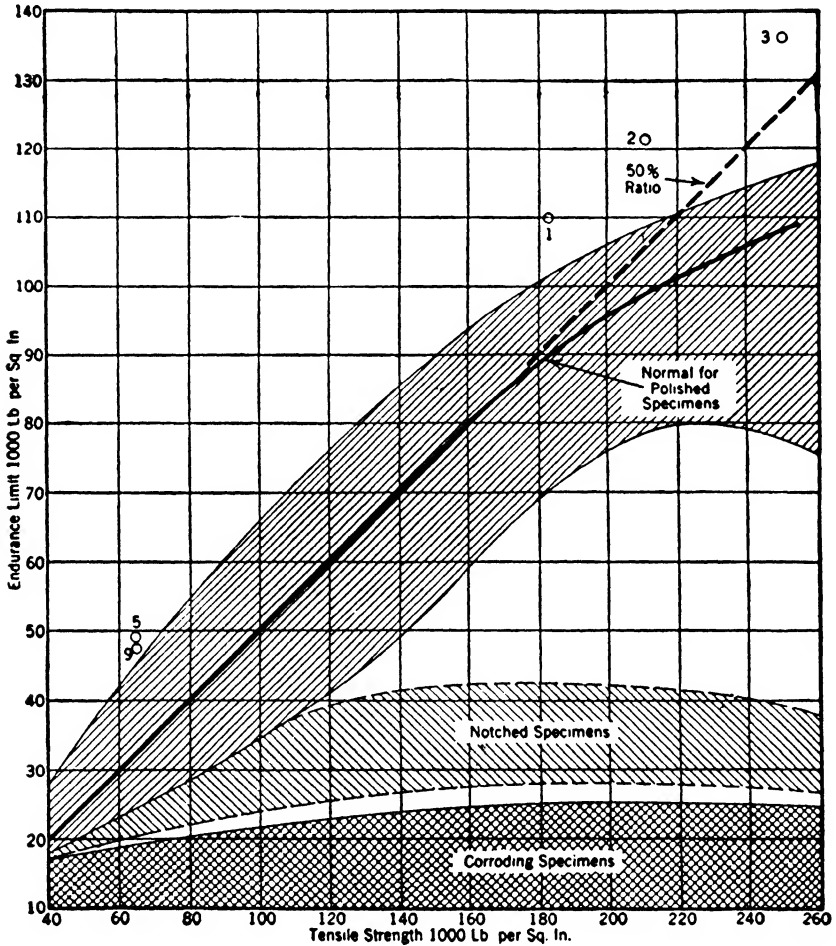


FIG. 38. S-N curve for determination of endurance limit. Note the logarithmic plotting for cycles. This is a semi-log plot. Log-log plots, with stress as well as cycles plotted on logarithmic scales, are also used. The arrows indicate specimens unbroken after 50 million cycles.

for a larger number of cycles, depending upon the expected number of load reversals in service. For these, the curve shows no definite knee and the number of reversals should be stated with the test results. Aluminum and magnesium alloys are usually tested for 500 million cycles.

Tensile strength and Brinell hardness appear to be more closely related to endurance limit than other mechanical properties. For steels, below 180,000 psi tensile, the average ratio between endurance limit and tensile strength is 50 per cent as shown in Fig. 39. The approximate endurance limit can also be calculated by multiplying the Brinell hardness number by 250. Surface hardened steels (carburized, nitrided, etc.) have their endurance limit raised more when tested by repeated bending than by axial loading. For nonferrous alloys the

ratio of endurance limit to tensile strength is less definite, but usually falls within the range of 25 to 50 per cent.

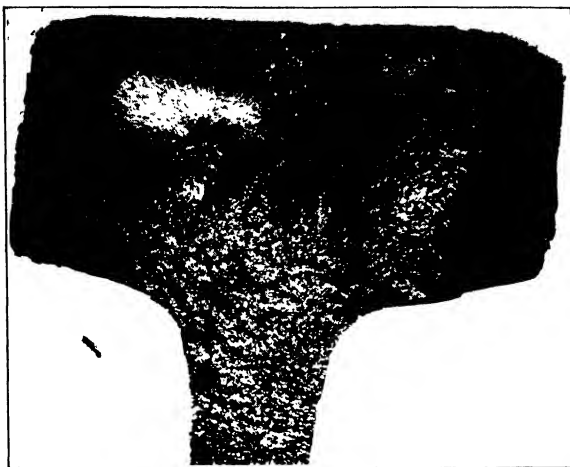


*Courtesy Bullens-Battelle*

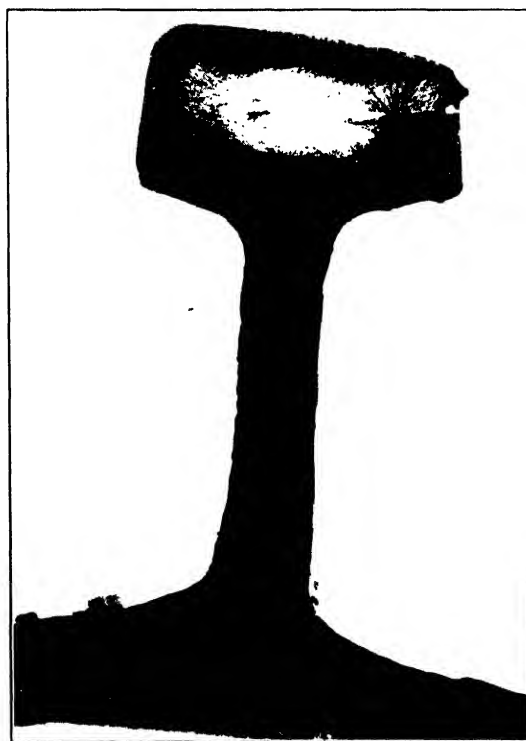
**FIG. 39.** Relation between tensile strength and endurance limit for steels.

**Internal Fissures.** Most fatigue cracks start from a surface imperfection, but internal flaws may also be the cause. Transverse fissures in railroad rails are progressive cracks caused by internal "shatter cracks" which in turn are produced by too rapid cooling of the rails after rolling in the steel mill. Under repeated stresses these transverse cracks often progress until the head of the rail is internally broken almost





(a)



(b)

FIG. 40. Fractured rails showing "interior transverse fissures." (a) Small fissure.  
(b) Large fissure.

all the way across (Fig. 40) without any indication being visible on the surface.

**Corrosion Fatigue.** Under conditions of combined corrosion and repeated stress there is no definite endurance limit and high tensile steels have about the same usefulness as low tensile steels if their resistance to corrosion is about the same, as shown in Fig. 39. If corrosion problems are encountered, as in diamond drill rods and sucker rods, the only solution is to use steels with a high resistance to corrosion.

## CHAPTER VII

### METALLOGRAPHIC CONTROL

#### Inspection and Control

**Visual Examination.** The inspection of ingots, blooms, billets, slabs, bars, and wire is largely visual. The surface is carefully checked by experienced men and surface defects are marked. If not too deep they can be removed by chipping hammers, cutting torch, or grinding. Forging steels and slabs for sheets receive this treatment to prevent the defects from being carried through to the finished piece. Some of the important defects found by visual inspection are pipe (see Chapter IX), blisters, dirt pits, scratches, scale, slivers, seams, scabs, and stringers.

**Upsetting.** Wire rod and bars of metals to be forged or wire to be drawn to smaller sizes are "upset" to detect seams, slivers, etc. The process is carried out at ordinary temperature and is a drastic test for

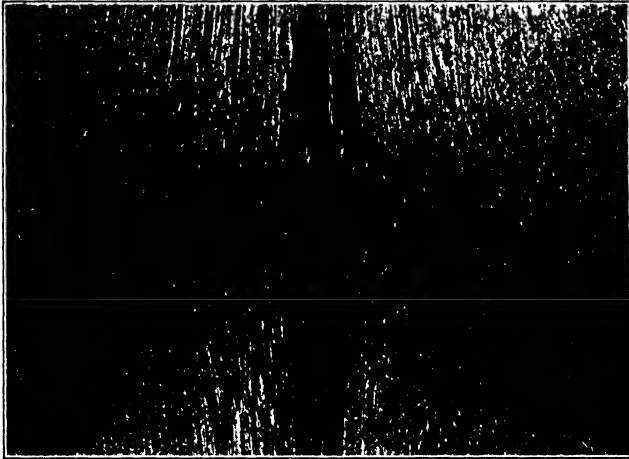


FIG. 41. Cold upsetting test, etched for flow lines. Transverse section through the center after upsetting. Outside bowed surface should be examined for seams and slivers.  $\times 4$ .

its purpose. Fig. 41 is a macrograph (meaning that it was photographed at a magnification of less than ten diameters) of a cylindrical bar which was cold upset by applying pressure at the top and bottom so as to flatten it endwise.

**Twisting.** Strands of wire are frequently twisted together and later untwisted for detection of slivers and seams. This is a good test also for coating brittleness of galvanized steel wire.

**Magnetic Powder.** A nondestructive method of inspection is used extensively for detecting in magnetic materials, small cracks or seams that would ordinarily be missed by visual means. The method consists in magnetizing the bar and covering it with a very fine, dry, magnetic powder (magnetite or  $\text{Fe}_3\text{O}_4$ ) or an emulsion of such powder in a light oil such as kerosene. Semifinished tool steel bars are often 100 per cent inspected in this way to insure a sound finished product. The method is also applied to quenched, ground, and welded parts to guard against defects that would eventually result in failure.

**Fracture and Grain Size.** One of the oldest tests is simply to nick and break off a section for examination of the fracture to show grain size, pipe, segregation, etc. The Swedish or Jernkontoret test for tool steel fractures is similar to the Shepherd test in which the standard consists of a series of ten steels of varying grain sizes. This test is made by comparison with actual standards in a few minutes and checks well with the A.S.T.M. grain size Designation E-19 determined by microscopic examination at 100 diameters. In the Shepherd test, however, there are ten sizes whereas in the A.S.T.M. E-19 there are only eight sizes, varying on the geometric progression as follows.

- No. 1, up to  $1\frac{1}{2}$  grains (per sq in. at  $100\times$ )
- No. 2,  $1\frac{1}{2}$  to 3 grains
- No. 3, 3 to 6 grains
- No. 4, 6 to 12 grains
- No. 5, 12 to 24 grains
- No. 6, 24 to 48 grains
- No. 7, 48 to 96 grains
- No. 8, with 96 and more grains

Carburizing steels are frequently purchased on a grain-size basis called the "McQuaid-Ehn" whereby the steel is carburized about 8 hr at  $1700^\circ\text{F}$  followed by slow cooling and then polished and etched for A.S.T.M. grain size.

The nonferrous standard, A.S.T.M. Designation E-2, lists ten grain sizes which give the average grain diameter in millimeters at 75 magnification as

0.010	0.065
0.015	0.090
0.025	0.120
0.035	0.150
0.045	0.200

Small sections of metals are bent forward and reverse to failure in checking for segregation, seams, pipe, etc. This test reveals also the relative brittleness of bars, strip, and sheet.

**Grinding Cracks.** Many properly fabricated and hardened parts are ruined in the grinding operation. Two factors appear to be the source of most of the trouble. Since all quenched parts not properly

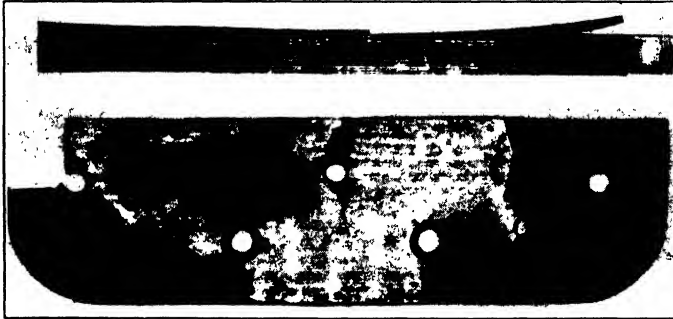


FIG. 42. Shear blade severely cracked by grinding. *Above*, the edge; indicates the depth of metal affected; *below*, the ground surface of the blade.

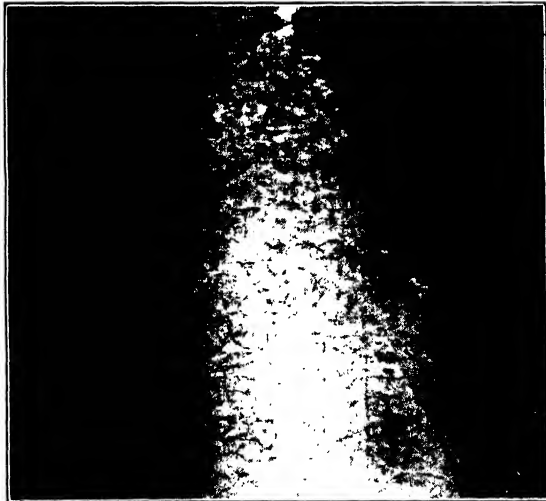


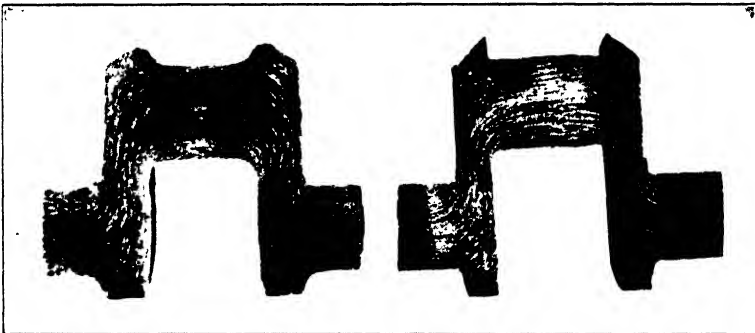
FIG. 43. Grinding cracks on a case-hardened piston pin in untempered state.

tempered are highly stressed, the removal of material from one side will have a tendency to redistribute stresses and cause warpage. The other factor is the removal of excess stock without regard for the proper precautions. The piece becomes overheated by too rapid grinding, "loaded" wheels, or improper cooling, and cracking may result. Cases

of this kind usually show blue spots on the ground surface, indicating rise of temperature due to friction. Fig. 42 shows a shear blade severely cracked by grinding. Fig. 43 is an example of grinding cracks on a piston pin; it shows the typical criss-cross checked pattern of grinding cracks.

**Spark Test.** Steels of different types are frequently identified by noting the shape and color of the spark pattern when held against an ordinary grinding wheel. Most laboratories have a series of iron and steel samples of known composition so the test is easily made by comparison in a few minutes. This test aids considerably in sorting mixed stock.

**Hot Etching.** The customary hot etching solution for steel is 50% concentrated HCl, or muriatic acid, plus 50% water, heated to a temperature of 160–175°F. For carbon steels about 30 min is sufficient to show pipe, porosity, or seams, and distribution of forging lines. Flow and forging lines are shown in Figs. 44 and 45.



*Courtesy Wyman-Gordon Co.*

**FIG. 44.** Flow and forging lines. *Left*, proper design of forging dies and proper shaping of metal; *right*, the result of poor design in the forging dies resulting in improper flow and distribution of metal.

Hardened steels with high internal stress will crack profusely when deep etched whereas tempered steels without appreciable internal stress will not crack.

Many other deep-etching solutions, either hot or cold, will show fiber lines and cracks in wrought metals.

Some of the many tests used in inspecting metal products may be listed as follows.

Chemical analysis

Dimensions, camber, waves, etc.

**Mechanical properties**

Hardness: Brinell, Rockwell, scleroscope, file, etc.

Tensile properties: tensile strength, elastic limit, proportional limit, yield point, elongation, reduction of area

Impact tests: Charpy, Izod, etc.

Torsion tests

Bend tests

Twist test

Shear test

Upsetting, heading

**Surface finish and appearance (visible)**

Blisters, dirt pits, scratches, scale, slivers, seams, scabs, stringers, pipe, stretcher strains, chatter marks, waves, grinding cracks, coatings

**Internal inspection**

Macrostructure: grain size, segregations, deep etching for flow lines, forging lines, or fiber

Microstructure: microconstituents and distribution; inclusions

Magnetic: "Magnaflux," permeability, etc.

X-ray: crystal orientation, radiography for ruptures, cracks, and blow holes

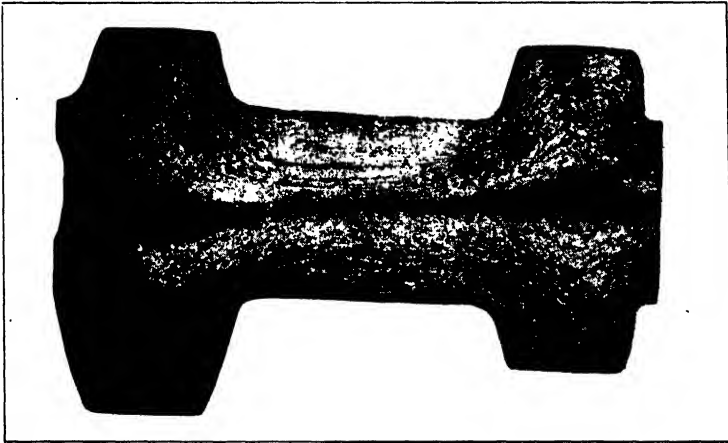


FIG. 45. Section of a camshaft in which the forging lines are satisfactory. Dark line through the center indicates a pipe in the original bar. This results from insufficient cropping of the ingot.

**Microscopic Examination**

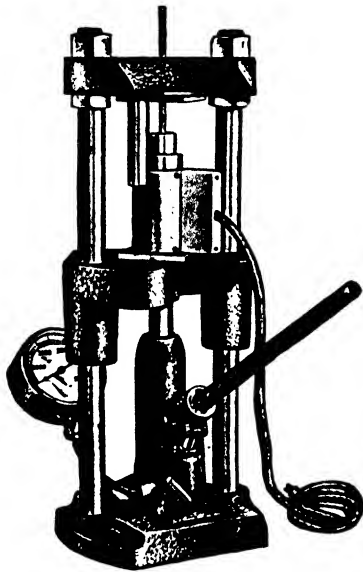
The microscope is by far the most important tool of the metallographer from both the scientific and technical standpoints. The early investigators, around 1885 — Sorby, Martens, Osmond, Wedding, etc. — are responsible for changing the ordinary technique with petrographic

and biological microscopes using transmitted light and thin sections to that of reflected light from the surface of a polished and etched metal. One of the most important points in metallography is, therefore, the preparation of a microsection relatively free from scratches and cold-worked metal (surface flow).

**Sample Preparation.** In general the sample, from wrought or cast metals, is selected by sectioning so it will give the maximum information over the smallest area because the larger the area the longer the time for grinding and polishing. An area about a half-inch square is a very convenient size. With wrought metals it is desirable to have a longitudinal section in the direction of working because any grain distortion from mechanical work, or segregations and inclusions, can be more easily detected. The choice of the proper sample for a microsection is of extreme importance with metals which have failed in service; the

sample is usually taken next to the failure. Small samples, i.e., wire, turnings, and powders, are preferably mounted in a small "plastic press" in a matrix of lucite, bakelite, etc. (Fig. 46).

In order that photomicrographs can be made of extreme edges at high magnifications, it is necessary to prevent the edges from beveling during polishing. This is accomplished by plating on a metal of somewhat similar hardness, as chromium on hardened steel and copper on soft steel, or by inserting a metal of like hardness adjacent to the sample and mounting in plastics or in low-melting materials—sulfur, rosin, sealing wax, plaster of Paris, etc. There is a great advantage in mounting the inserts in plastics because the matrix is quite inert to alcohol and the usual etching solu-



*Courtesy A. I. Buehler*

FIG. 46. Press for mounting specimens.

tions. Also, transparent plastics enable one to note the orientation of the sample with reference to the plane of polishing.

Sawing is the most common way of cutting out samples. With hardened metals, "cutting-off" wheels of silicon carbide bonded with rubber or resins are used and the metal temperature is preferably kept low by water cooling.



**Grinding.** The best grinding is done with bench grinders having relatively soft bonded wheels of alumina (Grade 50-N3L or 50-K4A); they will remain quite flat if the operator tries to keep them so. A silicon carbide wheel is required for hard tungsten carbide samples and other hard materials. An ordinary surface grinder, available in most shops, is a good tool for large samples. Minimum pressure in this and following operations should be used. In all succeeding grinding operations the sample is ground until all scratches from the preceding step are eliminated. There is a considerable advantage in slightly beveling corners and edges if they are not needed for edge examination. Sharp corners may tear polishing cloths and fins may break off and scratch the samples.

The second grinding operation in the University of Minnesota laboratories is done on a silicon carbide paper (No. 320-A Wetordry Tri-m-ite) made by electrostatic bonding with the carbide grains standing on end. This paper is one of the fastest cutting papers of that fineness made.

The next operation follows a sequence of fine polishing papers — 1, 0, 00, and 000 — made by Behr-Manning or Hubert of France.

The best polishing is still done by hand on flat surfaces; the sample is moved forward and backward by hand motion, keeping a minimum of pressure. Soft samples which tend to load are operated on these papers by wetting with kerosene or a little paraffin dissolved in benzol. This washes away the grit as it is loosened, lowers the temperature, and prevents loading of the surface of soft metals such as lead, aluminum, and tin.

The last fine grinding operation (at the University of Minnesota) is done with a paraffin lap composed of No. 600 silicon carbide mixed with liquid paraffin and cast onto a flat disk, slightly roughened, for a thickness of about half an inch. Specimens are held and rotated slowly by hand on vertical disks running at about 600 rpm, and cutting is fast without the customary scratches obtained with 000 paper. Some of the advantages of the paraffin lap are:

1. Fast operation. Alloys of Al, Mg, Cu, and Fe can be polished quickly with less resultant scratches than with dry papers.
2. Abrasive is not worked into the surface of soft metals.
3. It is exceedingly economical in operation.
4. Samples do not *heat as much* and consequently do not flow as much with increased pressure because of the lubricating effect.
5. It is especially good for cast and malleable iron as it keeps graphite from smearing.
6. Cracked samples have the cracks filled with paraffin; this prevents seepage of etchant.

It is generally accepted that the best grinding, fine or coarse, and polishing are done at the slowest speeds, with the minimum pressure, and at the lowest temperature. A wet operation throughout is desired; however, dry grinding if properly done is satisfactory and used mostly in large laboratories because it is more convenient.

Probably the best method of fine grinding is to use lead laps with No. 600 or finer powders, but this method is recommended only when one or two polishing operators are involved who can maintain them. This method is especially desirable for complex mineral samples having soft and brittle minerals together in the sample.

There are several automatic polishing machines available which require the mounting of specimens in special holders. In most cases, however, one good specimen polisher, by hand methods, can produce polishes better than the output from several machines. There are probably no two metallographic laboratories using the same grinding and polishing technique but in general the final results are about the same.

**Final Polishing.** After fine grinding most polishing is accomplished wet on horizontal disks of aluminum alloys, brass, or plastics, covered with broadcloth, billiard felt, or velvet. If the fine grinding has been properly done, a cloth with the minimum nap will be most satisfactory to avoid a pitted or rough surface. A considerable quantity of abrasive is required on smooth polishing cloths to keep samples wet and cool because the abrasive is centrifuged off and polishing is relatively slow but inclusions are not pulled out. If the samples are thoroughly washed or wiped clean of abrasive before polishing there is little chance of obtaining scratches from a clean polishing wheel. A rubberized cotton fabric (with the rubberized side on the wheel) is satisfactory for the best work because these cloths can be scrubbed periodically without taking them off the disks and excess abrasive cannot build up from below the cloth.

Jeweler's rouge or levigated alumina is used for most polishing operations. About two spoonfuls of abrasive are added to a 600-cc suction flask filled with water and corked at the top. If the operator is careful and decants the suspension from the top there will be little difficulty from scratching. In this operation specimens are rotated from time to time and care must be exercised so as not to overpolish.

In conclusion, it appears that the best polishes are produced when the samples are optically flat and shiny and when any inclusions are in place, and these results are best accomplished when the operator uses methods which keep the surface heat of the samples at a minimum.

There is still some art in polishing technique which one can obtain only through experience.

**Microscopic Examination of Polished Specimens.** In most cases it is desirable to examine polished sections with a microscope to detect inclusions consisting of oxides, sulfides, silicates, alumina, and graphite. This is the real test of the polishing operation and if one reports a section of metal as "dirty" one must be able to show that the inclusions are not arrow-shaped holes formerly occupied by the inclusions. In order to develop the structure of metal beneath the polished surface it is nearly always necessary to etch in a suitable etching reagent.

**Etching.** The theory of etching polished surfaces of metals is that different phases will have different solution pressures and consequently will etch at different rates. The more insoluble phases are left in relief whereas others more soluble are dissolved away. Naturally, certain etching reagents will etch certain metals better than others; however, proper technique is of more importance in many cases than the choice of the reagent. Etching may be divided into two main classes, micro and macro.

*Micro-etching*, as the name implies, is etching for microscopic examination at magnifications above about  $10\times$ . *Macro-etching* is, consequently, etching for magnifications below about  $10\times$  and is much deeper than micro-etching.

The proper time for etching a metal is determined only from experience, but in general the procedure for most metals may be stated as follows:

1. Clean the polished specimen of its polishing abrasive in a stream of clean, cold water. If oil and grease are present it may be necessary to clean again with ethyl alcohol.
2. Swab specimen lightly with cotton batting saturated with the etchant. Watch specimen closely and when the polish disappears rinse with cold water.
3. Dry immediately by blotting on a clean, flat towel and examine at magnification desired.

For general nonferrous etching a solution of 10%  $\text{HNO}_3$  in ethyl alcohol (nital) is desirable, and for general structures of iron and steel, cast iron, and malleable cast iron, a saturated solution (about 5%) of picric acid in ethyl alcohol is most desirable.

Tables 9 and 10 give etching reagents for micro- and macro-etching and Table 11 for inclusion identification for steels.

Table 12 gives etching reagents used for nonferrous metals.

TABLE 9. ETCHING REAGENTS FOR MICROSCOPIC EXAMINATION OF STEELS AND IRONS\*  
(Only reagents of higher analytical purity should be used.)

I. General Reagents for Irons and Steels (Carbon, Low and Medium Alloy Steels)			
No. Etching Reagent	Composition	Uses	Remarks
1. Nitric acid (Nital)	White nitric acid s.g. 1.42... 1-5 ml Ethyl or methyl alcohol, 95% or absolute.....100 ml (also amyl alcohol)	In carbon steels (1) to darken pearlite and give contrast between pearlite colonies; (2) to reveal ferrite boundaries; (3) to differentiate ferrite from martensite.	Etching rate is increased, selectivity decreased, with increasing percentages of HNO <sub>3</sub> . Reagent 2 (picric acid) usually superior. 4% in amyl alcohol useful for grain boundary and contrast of low-carbon materials. Etching time, a few seconds to a minute.
2. Picric acid (Pical)	Picric acid..... 4 g Ethyl or methyl alcohol, 95% or absolute.....100 ml (Use absolute alcohol only when acid contains 10% moisture or more.)	For all grades of carbon-steels (1) annealed, (2) normalized, (3) quenched, (4) quenched and tempered, (5) spheroidized, (6) austempered. For all low alloy steels attacked by this reagent.	Superior to reagent No. 1 except for those specific uses listed thereunder. More dilute solutions occasionally useful. Does not reveal ferrite grain boundaries as readily as No. 1. Etching time a few seconds to a minute or more.
3. Hydrochloric and picric acids	Hydrochloric acid..... 5 ml Picric acid..... 1 g Ethyl or methyl alcohol, 45% or absolute.....100 ml	For revealing the austenite grain size in quenched and quenched and tempered steels.	Best results are obtained when the martensite is tempered for 15 min at 400-475°F.
4. Chromic acid	Chromic acid..... 10 g Water.....100 ml	For various structures except grain boundaries of ferrite. Attacks cementite very rapidly, austenite less rapidly, ferrite and iron phosphide very slowly if at all.	Used electrolytically, the specimen as anode, the cathode stainless steel or platinum, $\frac{3}{4}$ -1 in. apart; 6 volts usually used. Time of etching 30-90 sec depending on specimen. M. Baeyer, <i>Trans. A.S.M.</i> , 1937, vol. 25, p. 1185.

\* A.S.M. Metals Handbook, 1939, pp. 722-725.

TABLE 9 (Continued)

No.	Etching Reagent	Composition	Uses	Remarks
5.	Heat tinting	Heat only	Pearlite first to pass through a given color, followed by ferrite; cementite less affected; iron phosphide still less. Especially useful for cast irons.	Clean, dry-polished specimen heated face upon hot plate to 400-700°F. Time and temperature both have decided effects. Bath of sand or molten metal may be used.
<i>II. General Reagents for Alloy Steels (Stainless and High-Speed Steels)</i>				
6.	Ferric chloride and hydrochloric acid	Ferric chloride..... 5 g Hydrochloric acid..... 50 ml Water..... 100 ml	Structure of austenitic nickel steels.	
7.	Aqua regia	Hydrochloric acid..... 75 ml Nitric acid..... 25 ml	Structure of stainless steel.	Mixture should stand 24 hr. before using; used full strength for rapid work, but requires careful handling.
8.	Chrome regia	Hydrochloric acid..... 25 ml Chromic acid 10% solution in water..... 5-50 ml	Heat-treated 18-8 stainless steels.	Activity is controlled by amount of chromic acid.
9.	Ferric chloride and nitric acid	Saturated solution of ferric chloride in hydrochloric acid, to which a little nitric acid is added.	Structure of stainless steel.	Use full strength.
10.	Mixed acids in glycerol	A. Nitric acid..... 10 ml Hydrochloric acid..... 20-30 ml Glycerol..... 30-20 ml	Structure of iron-chromium base alloys, high-speed steels, and austenitic manganese steel. Etches nickel-chromium alloys satisfactorily.	Warm specimen in water before etching. For best results use method of alternate polishing and etching. If given sufficient time, will etch totally austenitic alloys, but better results are obtained by using reagent 10-C.
		B. Nitric acid..... 10 ml Hydrofluoric acid..... 20 ml Glycerol..... 20-40 ml	Structure of high silicon alloys of the Duriron type.	Amount of glycerol may be varied to suit metal.

TABLE 9 (Continued)

No.	Etching Reagent	Composition	Uses	Remarks
		C. Nitric acid..... 10 ml Hydrochloric acid..... 20 ml Glycerol..... 20 ml Hydrogen peroxide..... 10 ml	For etching iron-chromium nickel, iron-chromium manganese, and all other austenitic iron-chromium base alloys.	Amount of hydrochloric acid may be varied if reagent acts too rapidly or too slowly. For best results employ method of alternate polishing and etching.
11.	Oxalic acid	Oxalic acid..... 10 g Water..... 100 ml	For austenitic stainless steels and high-nickel alloys. Carbides and general structure revealed depending on etching time.	Used electrolytically, the specimen as anode, the cathode stainless steel or platinum, about 1 in. apart; 6 volts usually used. Precipitated carbides in stainless steels may be revealed in 10-15 sec, the general structure in about 1 min. For study of carbides, 1.5-3 volts may be used, thus increasing the etching time and improving control of etch. Apply by swabbing.
12.	Mixed acids and cupric chloride	Hydrochloric acid..... 30 ml Nitric acid..... 10 ml Saturate with cupric chloride and let stand 20-30 min before use.	For stainless alloys and others high in nickel or cobalt.	Apply by swabbing.
13.	Nitric and acetic acids	Nitric acid..... 30 ml Acetic acid..... 20 ml	For stainless alloys and others high in nickel or cobalt.	Etch 2-10 min. Snyder and Graf, <i>Metal Progress</i> , 1938, vol. 33, p. 377.
14.	Hydrochloric and nitric acids in alcohol	Hydrochloric acid..... 10 ml Nitric acid..... 3 ml Methyl alcohol..... 100 ml	To distinguish between ferrite and sigma phase in iron-chromium, iron-chromium-nickel, iron-chromium-manganese, and related alloys. Colors sigma phase light blue, ferrite yellow.	Must be fresh. Use boiling. Burgess and Forggeng, <i>A.I.M.E. Tech. Pub.</i> , April 1938.
15.	Ferricyanide solution	Potassium ferricyanide..... 30 g Potassium hydroxide..... 30 g Water..... 60 ml	Structure of stainless steels.	Marble's reagent.
16.	Cupric sulfate	Cupric sulfate..... 4 g Hydrochloric acid..... 20 ml Water..... 20 ml		

TABLE 9 (Continued)

No.	Etching Reagent	Composition	Uses	Remarks
3.	Hydrochloric and picric acids	Hydrochloric acid..... 5 ml Picric acid..... 1 ml Ethyl or methyl alcohol, 95% or absolute..... 100 ml	For etching many steels of the iron-chromium, iron-chromium-nickel, and iron-chromium-manganese types.	
<i>III. Phosphorus Segregation, Phosphides, and Strain Lines</i>				
17.	Cupric chloride	A. Cupric chloride..... 1 g Magnesium chloride... 4 g Hydrochloric acid..... 1 ml Water..... 20 ml Alcohol, absolute..... 100 ml B. Cupric chloride..... 5 g Hydrochloric acid..... 40 ml Water..... 30 ml Ethyl alcohol..... 25 ml	For showing segregation of phosphorus or other elements in solid solution; copper tends to deposit first on areas lowest in phosphorus.  To reveal strain lines and their microstructure, and precipitation-hardening in steel.	Dissolve salts in least possible quantity of hot water. Etch for about 1 min, repeating if necessary. Stead's reagent.  May be used cold. Etching time, about 10 sec. Fry's reagent.
18.	Sodium picrate, (neutral)	Sodium picrate..... 1 g Water..... 100 ml (Wash salt well with alcohol to remove excess acid or alkali.)	Shows difference between phosphides and cementite; iron phosphide attacked, cementite unattacked.	Use boiling. Etching time 20 min.
19.	Chromic acid and heat tinting	Chromic acid..... 8 g Water..... 100 ml Followed by heat tinting.	Distinguishes between iron phosphide and cementite in phosphide eutectic of cast iron; iron phosphide is colored darker.	Etch first in picric acid (No. 2) then for 1 min in chromic acid; heat tint by heating face upon hot plate at about 500°F for 1 min.
<i>IV. Structure and Depth of Case of Nitrided Steels</i>				
20.	Cupric sulfate and cupric chloride	Cupric sulfate..... 1.25 g Cupric chloride..... 2.50 g Magnesium chloride..... 10 g Hydrochloric acid..... 2 ml Water..... 100 ml Dilute above solution to 1000 ml with 95% ethyl alcohol.	For showing total depth, structure, and various zones of nitrided chromium-vanadium steels and Nitralloy.	Proportions must be accurate. Etch by immersion to avoid confusing edge effects.

TABLE 9 (Continued)

No.	Etching Reagent	Composition	Uses	Remarks
21.	Picric and nitric acids	4% picric acid (No. 2) . . . . . 10 parts 4% nitric acid (No. 1) . . . . . 1 part	For depth of case and structure of Ni-tralloy.	Best results are obtained when the specimen is annealed in lead at 1475°F before etching.
1.	Nitric acid (nital)	Nitric acid . . . . . 2 ml Ethyl or methyl alcohol, 95% or absolute . . . . . 100 ml	For structure and depth of case of nitrified steels.	Marble's reagent.
16.	Cupric sulfate	Cupric sulfate . . . . . 4 g Hydrochloric acid . . . . . 20 ml Water . . . . . 20 ml	Total depth of nitrified case.	
<i>V. Carbides, Nitrides, Tungstides, and Their Differentiation</i>				
22.	Sodium picrate, alkaline	Picric acid . . . . . 2 g Sodium hydroxide . . . . . 25 g Water . . . . . 100 ml	Colors cementite, but not carbides high in chromium; in tungsten steels, iron tungstide (Fe <sub>3</sub> W) and iron tungsten carbide (Fe <sub>3</sub> W <sub>2</sub> C) are colored more rapidly than cementite, but tungsten carbide is unaffected; attacks sulfides. De-lineates grain boundaries in hyper-eutectoid steels in slowly cooled condition.	Use boiling, 5-10 min. or, preferably, electrolytically at room temperature; for the latter, specimen is anode, cathode is platinum or stainless steel; with 6 volts, about 40 sec is usually sufficient.
23.	Hydrogen peroxide and sodium hydroxide	Hydrogen peroxide . . . . . 10 ml Sodium hydroxide 10% solution in water . . . . . 20 ml	Attacks and darkens iron tungstide in carbon-free iron tungsten alloys. When carbon is present this solution darkens the compound (FeW <sub>2</sub> C?) in proportion to the amount of carbide present; tungsten carbide is darkened.	Must be fresh. Etching time 10-12 min.
24.	Ferriyanide solution	A. Potassium ferriyanide 1-4 g Potassium hydroxide . . . . . 10 g Water . . . . . 100 ml	Differentiates between carbides and nitrides; cementite is blackened, pearlite turned brown, and massive nitrides remain unchanged.	Must be freshly made; etch 15 min in boiling solution.



TABLE 9 (Continued)

No. Etching Reagent	Composition	Uses	Remarks
	B. Potassium ferricyanide. 10 g Potassium hydroxide. . . . . 10 g Water. . . . . 100 ml	Darkens carbide containing chromium, carbides and tungstides in tungsten and high-speed steels. At room temperature colors ternary carbides (Fe <sub>3</sub> W <sub>3</sub> C or Fe <sub>3</sub> W <sub>2</sub> C) in a few seconds, iron tungstide (Fe <sub>3</sub> W <sub>2</sub> ) in several minutes, and barely colors cementite.	May be used cold, but preferably hot, should be freshly made. Etching time 5-10 min. Murakami's reagent.
25. Sodium cyanide	Sodium cyanide. . . . . 10 g Water. . . . . 90 ml	Darkens carbides without attacking austenite or grain boundaries.	Used electrolytically, the specimen as anode, cathode, similar material about 1 in. apart; 6 volts (not less than 5). Etching time 5 min or more. W. B. Arnesen, <i>Trans. A.S.M.</i> , 1936, vol. 24, p. 701.
4. Chromic acid	Chromic acid. . . . . 10 g Water. . . . . 100 ml	Attacks carbides in stainless steels very rapidly; austenite less rapidly, and ferrite very slowly if at all. For various structures of stainless steels.	See solution No. 4 in Section I.
11. Oxalic acid	Oxalic acid. . . . . 10 g Water. . . . . 100 ml	To reveal carbides in stainless steels.	See No. 11 in Section II. If strongly etched general structure is revealed; therefore for study of carbides reduced voltage is used for etching, giving better control of etch.

TABLE 10. SOLUTIONS FOR MACRO-ETCHING\*

Purpose	Composition	Remarks	Uses
Blow holes	10% sulfuric acid in water.	Use cold on large sections for 24 hr. Surface B.	Shows blow holes, porosity, pipe, and inclusions.
Blow holes	50% hydrochloric acid in water.	Use at 160-175°F for ½ hr. Surface A.	Shows blow holes, porosity, pipe, and inclusions.
Carburized case	5% solution of nitric acid in alcohol.	Etch at room temperature. Surface B.	Shows depth of carburized case.
Contrast	1 part iodine; 2 parts potassium iodide; and 10 parts water.	Use at room temperature. Surface B.	Produces contrast for photographing.
Cracks	5% solution of nitric acid in alcohol.	Etch at room temperature. Surface B. within ½ hr. Surface B.	Detects fatigue, service, hardening and grinding cracks.
Cracks	Hydrochloric acid.	Apply cold with swab.	Detects embrittlement cracks in steam boiler drum.
Cracks	50% hydrochloric acid in water.	Use at 160-175°F for ½ hr. Surface B.	Detects fatigue, service, hardening, grinding, and internal cracks. If hardened, material should be softened prior to etching.
Cracks	Kerosene and whiting test.	Wash surface with kerosene. Wipe off. Paint with thin mixture of whiting and water. Let dry. Kerosene in cracks, if present, will discolor whiting. Surface B.	Detects fatigue, service, hardening and grinding cracks.
Cracks	120 g copper ammonium chloride; 50 cc concentrated hydrochloric acid, 1000 cc water.	Etch first with a neutral solution to remove machine marks. Use cold for 20 min to ½ hr. Surface B.	Produces a strong relief effect. Shows up dendrites and may indicate cracks.
Decarburization	5% nitric acid in alcohol.	Etch at room temperature. Surface C.	The decarburized areas will be light. Area not decarburized dark.
Defects	10% sulfuric acid in water.	Use cold on large sections for 24 hr. Surface B.	Shows porosity, pipe, blow holes, and inclusions.
Defects	50% hydrochloric acid in water.	Use at 160-175°F for ½ hr. Surface A or B.	Shows porosity, pipe, blow holes, and inclusions.

\* A.S.M. Metals Handbook, 1939, pp. 727-730.

TABLE 10 (Continued)

Purpose	Composition	Remarks	Uses
Defects	2 parts concentrated sulfuric acid; 1 part concentrated hydrochloric acid; 3 parts water.	Use at 160-175°F for at least ½ hr. Surface A.	Shows general structure and defects.
Dendrites	2 parts concentrated sulfuric acid; 1 part concentrated hydrochloric acid; 3 parts water.	Use at 160-175°F for at least ½ hr. Surface A.	Shows general dendritic structure and defects.
Dendrites	50% hydrochloric acid in water.	Use at 160-175°F for at least ½ hr. Surface A.	Shows general dendritic structure and defects.
Dendritic pattern	25% sulfuric acid in water.	Use cold, 8-16 hr. Surface B.	Shows dendritic pattern and flow lines.
Dendritic pattern	40 g ferric chloride; 3 g cupric chloric acid; 40 cc hydrochloric acid; 500 cc water.	Etch first with 10% nitric acid. Surface B.	Shows dendritic pattern or structure.
Etch, universal	500 cc hydrochloric acid; 70 cc sulfuric acid; 180 cc water.	Use at 160-175°F for 1-2 hr. Surface A.	Good universal etch.
Fiber	10-20% solution of ammonium persulfate in water.	Swab on freshly made solution for ½ min. Surface B.	Shows fiber and grain contrast.
Flow lines	25% sulfuric acid in water.	Use cold, 8-16 hr. Surface B.	Shows flow lines and dendritic pattern.
Flow lines	50% hydrochloric acid in water.	Use at 160-175°F. Surface A.	Shows flow lines.
Ghost lines	10-20% solution of ammonium persulfate in water.	Swab on freshly made solution for ½ min. Surface C.	Shows ghost lines.
Grain contrast	10-20% solution ammonium persulfate in water.	Swab on freshly made solution for 1-2 min. Surface B.	Shows grain contrast and fiber.
Grain contrast	1.5 g cupric chloride; 30 cc hydrochloric acid; 95 cc water; 30 cc ethyl alcohol.	Polish specimen carefully. Surface C.	Shows good grain contrast.
Grain size	10-20% solution ammonium persulfate in water.	Swab on freshly made solution for 1-2 min. Surface B.	Shows grain size especially in low-carbon steels, wrought iron, and welded sections.

TABLE 10 (Continued)

Purpose	Composition	Remarks	Uses
Hardness penetration	5% nitric acid in alcohol.	Etch at room temperature on smooth ground surface. Surface B.	Shows depth of hardness penetration of heat-treated samples.
Hardness penetration	50% hydrochloric acid in water.	Use at 160-175°F for about 15-60 sec. To preserve surface after etching, scrub in running water, dip in weak $\text{NH}_4\text{OH}$ , dip in solution of soluble cutting oil, dry with a rag and compressed air. Surface B or C.	Shows depth of hardening, especially carbon steels; produces distinct contrast between martensitic and troostitic zones.
Heterogeneity	50% hydrochloric acid in water.	Immerse specimen in solution at 160-175°F from $\frac{1}{2}$ -1 hr. Surface A.	Shows heterogeneity in general.
Heterogeneity	Undiluted hydrochloric acid.	Use hot (212°F). Surface A.	Shows heterogeneity in 3-3.5% nickel steels.
Impurities in ferrite	1 g cupric chloride; 0.5 g stannous chloride; 30 g ferric chloride; 30 cc hydrochloric acid; 500 cc distilled water; 500 cc ethyl alcohol.	Etch only well-polished surface which has been thoroughly dried. Surface C.	Plates out copper on ferrite containing impurities. Gives a good even etch.
Internal cracks	50% hydrochloric acid in water.	Use at 160-175°F for $\frac{1}{2}$ hr or longer. Surface B.	Shows internal cracks or thermal checks.
Inclusions	10% sulfuric acid in water.	Use cold on large sections for 24 hr. Surface B.	Shows inclusions, porosity, pipe, and blow holes.
Inclusions	10-20% sulfuric acid in water.	Use at 160-175°F. Surface B.	Etches sulfide inclusions.
Inclusions	50% hydrochloric acid in water.	Use at 160-175°F. Surface B.	Etches sulfide inclusions.
Pipe and porosity	10% sulfuric acid in water.	Use cold on large sections for 24 hr. Surface B.	Shows pipe, porosity, blow holes, and inclusions.
Pipe and porosity	50% hydrochloric acid in water.	Use at 160-175°F. Surface B.	Shows pipe, porosity, blow holes, and inclusions.
Rail sections	9 parts hydrochloric acid; 3 parts sulfuric; 1 part water.	Use at 160-175°F for 2 hr. Surface A.	Use for etching rail sections.

TABLE 10 (Continued)

Purpose	Composition	Remarks	Uses
Segregation	3% solution picric acid in ethyl alcohol.	Etch at room temperature for 4-5 hr. Surface B.	Shows segregation.
Segregation	1 g picric acid; 1 drop concentrated hydrochloric acid in 25 cc alcohol.	Use hot. Surface B.	Shows segregation.
Segregation	10-15% solution of nitric acid in water or alcohol.	Etch at room temperature. Surface B.	Shows heavy segregation.
Segregation	5% solution nitric acid in water or alcohol.	Etches within $\frac{1}{2}$ hr. Surface is black when etched. Surface B.	Shows segregation in low-carbon, low-chromium, nickel steels.
Segregation	2-10% solution nitric acid in water.	Etch first with weak acid to remove machine marks and then increase concentration for structure. Surface B.	Shows segregation in ingot sections and large pieces.
Segregation	50% hydrochloric acid in water.	Use at 160-175°F. Surface A.	Shows segregation in ingot sections and large pieces.
Segregation	1 g cupric chloride; 0.5 g picric acid; 1.5-2.5 cc hydrochloric acid; 10 cc water; 100 cc ethyl alcohol.	May be used for electrolytic etching. Surface B.	Shows segregation.
Segregation carbide	2% nitric acid in alcohol. For high-speed steel, use 5% nitric acid in alcohol.	Use cold on a polished, longitudinal section. For high-speed steel, etch until matrix is darkened. Surface C.	To detect carbide segregations, particularly in high-speed steels.
Segregation, carbon and phosphorus	1 part copper ammonium chloride, 12 parts water.	Immerse clean sample in solution for 1 min; wash with water, and rub off copper. Surface C.	Shows phosphorus and carbon segregation.
Segregation, phosphorus	0.5% solution picric acid in water.	Etch at room temperature until staining occurs. Surface C.	Uneven staining represents phosphorus segregation.
Segregation, phosphorus	30 g ferric chloride; 100 g hydrochloric acid; 1 g cupric chloride; 0.5 g stannous chloride; 1000 cc water.	Polish as for microscopic work, use etch cold for 10 sec to 2 min. Surface C.	Shows phosphorus segregation.

TABLE 10 (Continued)

Purpose	Composition	Remarks	Uses
Segregation, phosphorus	10 g cupric chloride; 40 g magnesium chloride; 20 cc hydrochloric acid; 1000 cc ethyl alcohol. (Stead's No. 1 reagent.)	Dissolve salts in small amount of hot water, then add alcohol. Apply solution to polished surface drop by drop. Surface C.	Areas not coated by copper show phosphorus segregation.
Segregation, phosphorus	5 g cupric chloride; 4 g magnesium chloride; 1 cc hydrochloric acid; 20 cc water; 100 cc alcohol. (Stead's No. 2.)	Etch for 1 min. Surface C.	Shows phosphorus segregation.
Segregation, phosphorus	4 g cupric chloride; 20 cc hydrochloric acid; 40 cc water; 20 cc ethyl alcohol.	Polish specimen carefully. Surface C.	Shows phosphorus segregation.
Segregation, phosphorus	1.5 g cupric chloride; 5 g nickel nitrate crystals; 6 g ferric chloride; 12 cc water.	Immerse specimen for 90 sec or more. Surface C.	Shows phosphorus segregation.
Segregation, sulfur	Soak ordinary sensitized photographic silver bromide paper in a 2% solution of sulfuric acid in water. Apply emulsion side of paper to smooth-ground, clean sample for a min or two. Rinse paper, fix in hypo, wash thoroughly.	The brown pattern formed on the paper indicates the relative distribution of sulfides. The darker and heavier the marks, the more sulfur is indicated to be present. Surface B. Best results are obtained only on first or second prints made from a surface.	Shows the distribution of sulfur.
Segregation, sulfide inclusions	10-20% sulfuric acid in water.	Use at 160-175°F. Surface A.	Etches sulfide inclusions.
Soft spots	5% nitric acid in alcohol.	Etch at room temperature. Surface B.	Nondestructive test for hardened tools.
Soft spots	50% hydrochloric acid in water.	Use cold on ground surface. Surface B.	Shows soft spots.
Strains	90 g cupric chloride; 120 cc hydrochloric acid; 100 cc water.	Copper does not precipitate with this etch. Heat specimen to 400-475°F for ½ hr, then etch ground surface for 1-3 min. Rub with powdered cupric chloride, then rinse with alcohol. Surface B.	Shows strain lines.

TABLE 10 (Continued)

Purpose	Composition	Remarks	Uses
Strains	6 g cupric chloride; 6 g ferric chloride; 10 cc hydrochloric acid; 100 cc ethyl alcohol.	Heat specimen to 400°F and immerse ground surface. Surface B.	Shows strain lines.
Strauss test	3% cupric sulfate; 10% sulfuric acid; 87% distilled water.	Specimen $\frac{1}{2} \times 1 \times 4$ in. is sensitized by actual welding, or artificially by heating to 900-1300° F (generally 1250°F). Immersed in the boiling cupric sulfate solution for 72 hr. Specimen is then bent 180° around $\frac{1}{2}$ -in. pin. Cracking indicates disintegration has taken place due to migration of carbides to grain boundaries. Surface B. (120° fine emery.)	To measure intergranular corrosion of 18-8 corrosion-resisting steel.
Structure	25% nitric acid in water.	Etch at room temperature. Surface B.	Shows general structure.
Structure	50% hydrochloric acid in water.	Use at 160-175°F for at least $\frac{1}{2}$ hr. Surface A.	Shows general structure and defects.
Structure	2 parts concentrated sulfuric acid; 1 part concentrated hydrochloric acid; 3 parts water.	Use at 160-175°F for at least $\frac{1}{2}$ hr. Surface A.	Shows general structure and defects.
Thermal cracks	50% hydrochloric acid in water.	Use at 160-175°F for $\frac{1}{2}$ hr or longer. Surface B.	Shows thermal checks or internal cracks.
Weld examination	50% hydrochloric acid in water.	When testing large sections, the acid may be added by building a dam with paraffin wax around the part to be tested. Surface A.	For testing the soundness of welds.

Surface A is saw-cut or machined surface.

B is average ground surface.

C is polished surface.

TABLE 11. SCHEME FOR ETCHING IDENTIFICATION TESTS\*

Appearance with Reflected White Light —  $\times 200$ ,  $\times 500$ ,  $\times 1000$ *Gray or Black Inclusions*

Etch 10 sec in 10% alcoholic nitric acid

More contrast  
a. FeO in FeO-FeS  
eutectic darkened

Unattacked  
Etch 5 min in 10% chromic  
acid in water

Etch 10 min in boiling alkaline sodium picrate solution

Attacked  
a. Removes FeS (pale yellow)

Unattacked  
Etch 10 min in a 20% aqueous  
solution of hydrofluoric acid

Attacked  
a. Removes FeS-MnS  
rich in MnS  
b. Darkens FeO-MnO

Unattacked  
Etch 5 min in boiling alkaline  
sodium picrate

Attacked  
a. Removes zirconium nitride  
(yellow cubes)  
b. Removes zirconium sulfide  
(tan crystals)

Unattacked  
a. Titanium nitride (yellow  
cubes)  
b. Titanium cyanonitride  
(violet) strongly angular,  
easily pitted in polishing  
c. Titanium carbonitride (blue  
cubes)

Attacked  
a. Removes FeS-MnS  
rich in MnS  
b. Removes FeO-MnO

Unattacked  
Etch 5 min in 5% alcoholic hy-  
drochloric acid

Attacked  
a. Removes FeO-FeS  
b. Removes FeO  
c. Removes balance FeO-MnO  
d. Removes MnO-SiO<sub>2</sub>

Unattacked  
Etch 10 min in a 20% aqueous  
solution of hydrofluoric acid

Attacked  
a. Removes FeO-SiO<sub>2</sub>  
b. Removes CaO-SiO<sub>2</sub>  
c. Removes some siliceous alu-  
mina

Unattacked  
a. Al<sub>2</sub>O<sub>3</sub>, FeO-Al<sub>2</sub>O<sub>3</sub> and (FeO,  
MnO) Al<sub>2</sub>O<sub>3</sub>  
b. Chromite (FeO-Cr<sub>2</sub>O<sub>3</sub>)  
Etch 5 min in boiling 10%  
H<sub>2</sub>SO<sub>4</sub> and 1% KMnO<sub>4</sub> and  
lightly repolish

Attacked  
a. Chromite (FeO-Cr<sub>2</sub>O<sub>3</sub>)  
Isotropic: red to brown  
by transmitted light

Unattacked  
a. Chromic oxide (Cr<sub>2</sub>O<sub>3</sub>) aniso-  
tropic: purplish gray by re-  
flected light, bright green by  
transmitted light  
b. Ferrous aluminates, (FeO-  
Al<sub>2</sub>O<sub>3</sub>) opaque isotropic:  
light gray

In stainless steel and ferrochromium — not applicable to ordinary alloys  
of lower Cr content.

\* A.S.M. Metals Handbook, 1939, p. 748.



TABLE 12. ETCHING SOLUTIONS  
I. For Aluminum Alloys\*

Etching Reagent	Concentration	Specific Use	Remarks	
1. Hydrofluoric acid	HF H <sub>2</sub> O	conc. 99.5 ml	General, microscopic	Swab with soft cotton swab for 15 sec.
2. Sodium hydroxide	NaOH H <sub>2</sub> O	1 g 99 ml	General, microscopic	Swab for 10 sec.
3. Sodium hydroxide	NaOH H <sub>2</sub> O	10 g 90 ml	Microscopic	Immerse 5 sec at 70°F; rinse in cold water
4. Sulfuric acid	H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> O	conc. 20 ml 80 ml	Separates Al-Cu-Fe-Mn from Al-Fe-Mn or αAl-Cu-Fe	Immerse 30 sec at 70°F; quench in cold water.
5. Nitric acid	HNO <sub>3</sub> H <sub>2</sub> O	conc. 25 ml 75 ml	αAl-Fe-Si from FeAl, microscopic	Immerse for 40 sec at 70°F; quench in cold water.
6. Keller's etch	HF HCl HNO <sub>3</sub> H <sub>2</sub> O	conc. 1.0 ml conc. 1.5 ml conc. 2.5 ml 95.0 ml	Microstructure of duralumin-type alloys	Immerse for 10-20 sec; wash in stream of warm water.
7. Flick's etch	HF HCl H <sub>2</sub> O	conc. 10 ml conc. 15 ml 90 ml	Macroscopic	Immerse for 10-20 sec; wash in warm water followed by dip in conc. HNO <sub>3</sub> .
8. Tucker's etch	HF HCl HNO <sub>3</sub> H <sub>2</sub> O	conc. 15 ml conc. 45 ml conc. 15 ml 25 ml	Macroscopic	Etch by immersion.
9. Viella's etch	HF HNO <sub>3</sub> Glycerine	conc. 2 pt conc. 1 pt 3 pt	General	Etch by immersion.

\* A.S.M. Metals Handbook, 1939, p. 1291.

TABLE 12 (Continued)  
II. For Copper and Its Alloys\*

Reagents	Concentration	Specific Use	Authorities
1. Ammonium hydroxide	Dilute	Polish attack, brass and bronze.	Hudson, Desch
2. Ammonium hydroxide plus hydrogen peroxide	NH <sub>4</sub> OH 5 parts H <sub>2</sub> O <sub>2</sub> 5 parts or H <sub>2</sub> O <sub>2</sub> (3%) 2-5 parts H <sub>2</sub> O <sub>2</sub> (9%) 1-2 parts	Copper and many of its alloys. Film on etched aluminum-bronze removed by weak Girard's solution.	Various
3. Ammonium hydroxide plus ammonium persulfate	NH <sub>4</sub> OH, 1-1, plus an equal part of 2½% solution (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> . 10% aqueous solution (cold)	Copper and some of its alloys polish attack.	Hudson
4. Ammonium persulfate	10% aqueous solution (boiling)	Copper, brass, bronze, nickel-silver, aluminum-bronze.	Law
5. Chromic acid	Saturated aqueous solution (CrO <sub>3</sub> ).	Copper, brass, bronze, and nickel-silver (plain etch).	Portevin Gulliver
6. Chromic acid plus hydrochloric acid	50 cc of 10-15% CrO <sub>3</sub> 1-2 drops HCl at time of use.	Copper, brass, bronze and nickel-silver (plain etch). Color by electrolytic etching (see below), or FeCl <sub>3</sub> reagents.	Vilella
7. Chromic acid plus nitric acid	A HNO <sub>3</sub> 50 cc H <sub>2</sub> CrO <sub>4</sub> 20 g H <sub>2</sub> O 30 cc B 5 cc 20 g 75 cc	Aluminum-bronze. Film from polishing removed by 10% HF.	Strauss
8. Copper ammonium chloride plus ammonium hydroxide	10% aqueous solution of copper ammonium chloride, plus NH <sub>4</sub> OH to alkalinity plus NH <sub>4</sub> OH to neutrality.	Best for darkening large beta areas in alpha-beta brass. Copper, brass, nickel-silver.	Heyn
9. Ferric chloride	FeCl <sub>3</sub> 5 HCl 50 H <sub>2</sub> O (Parts) 100 19 6 5 10 25 100 1 20 8 25 10 100 1 1 3 10	Copper, brass, bronze, nickel-silver, aluminum-bronzes. Darkens beta in brass; gives contrast following bichromate and other etches.	Am. Brass Co. Heycock and Neville Girard's No. 1 Girard's No. 2 Am. Brass Co. Am. Brass Co. Archbutt Rosenhain Pulsifer Rosenhain

\* A.S.M. Metals Handbook, 1939, p. 1472.

TABLE 12 (Continued)

Reagents	Concentration	Specific Use	Authorities
10. Nitric acid	Various dilutions	Deep etching.	Desch
11. Potassium bichromate	100 cc NaCl (sat. sol.)	Copper, copper alloys of beryllium, manganese, silicon, nickel-silver, bronzes, and other copper alloys. Followed by ferric chloride or other contrast etc.	Am. Brass Co. Vilella
	2 g H <sub>2</sub> SO <sub>4</sub> (sp. gr. 1.84)		
	or use in place of NaCl 1 drop HCl to 25 cc of solution just before using.		
	4 cc		
12. Electrolytic etching	30 g H <sub>2</sub> SO <sub>4</sub>	Darkens beta in brass, gives contrast following H <sub>2</sub> O <sub>2</sub> etch. Nickel-silver, bronze and other copper alloys.	Am. Brass Co.
	4 g H <sub>2</sub> O		
	100 cc		
	1900 cc		
	Current (0.1 amp, 8-10 volts)		
	Glacial acetic acid . . . . .	Employed for cupro nickel, particularly in avoiding the appearance of "coring."	
	Nitric acid . . . . .	Generally employed for alloys of copper with nickel.	
	Water . . . . .		
	5 parts		
	10 parts		
	85 parts		
	Various dilutions of		
	NaCl		
	NH <sub>4</sub> NO <sub>3</sub>		Desch
	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>		Hudson
	NH <sub>4</sub> OH		Le Chatelier
	Citric acid		Hudson
	Molybdic acid plus NH <sub>4</sub> OH		Adcock
	H <sub>2</sub> SO <sub>4</sub> plus H <sub>2</sub> O <sub>2</sub>		Adcock
			Archbutt

TABLE 12 (Continued)  
 III. For Lead and Lead Alloys\*

No.	Authority	Composition	Remarks
1.	Rutherford	3 parts glacial acetic acid 1 part 9% hydrogen peroxide	Etch for 10-30 min, depending on depth of flowed metal on the surface. Dry with alcohol and clean with concentrated nitric acid. The nitric acid is removed by sudden immersion in a large volume of water.
1a.	Lucas	3 parts glacial acetic acid 1 part 30% hydrogen peroxide	Etching time varies from 6-15 min. Used for lead, lead-tin, lead-antimony, and lead-calcium alloys.
2.	Vilella	1 part glacial acetic acid 1 part nitric acid 4 parts glycerol	Etching from 10-15 sec. Best results obtained when used in conjunction with method of alternate polishing and etching. For lead, lead-antimony, lead-calcium, and low-tin alloys. Use freshly prepared solution and discard after using.
2a.	Bassett and Snyder	3 parts glacial acetic acid 4 parts nitric acid 16 parts water	Used at a temperature of 40-42°C. Recommended for pure lead and lead-tin alloys up to 3% tin. Etching time depends on depth of distorted metal on prepared surface.
3.	Johnston	Concentrated nitric acid	Plunge specimen in concentrated acid. Wash in a rapid stream of water. Repeat operation as often as necessary. If acid becomes diluted by water carried by specimen it must be rejected and fresh acid used.
4.	Bassett and Snyder	60% solution of perchloric acid	For electrolytic etching. No. 6 dry cell used to supply energy. Also recommended by Dean, Zickrick, and Nix.

\* A.S.M. Metals Handbook, 1939, p. 1558.

TABLE 12 (Continued)

## IV. For Magnesium Alloys\*

A number of etching solutions have been recommended by various investigators who have worked with magnesium alloys. Many of the reagents and their specific applications have been reviewed in papers by Gann and by Pulsifer. At present practically all metallographic etching in these laboratories is done with a preparation known as the "glycol etch." Its composition is as follows:

Diethylene glycol	75% by volume
Distilled water	24% by volume
Concentrated nitric acid	1% by volume

The glycol etch permits a positive identification and separation of the constituents without severely attacking either the constituents or the matrix.

Some workers with magnesium prefer organic acid etches for grain boundary delineation in wrought alloys. Two of the suggested compositions are as follows:

<i>For wrought magnesium-manganese alloys</i>		<i>For wrought magnesium-aluminum alloys</i>	
5 g citric acid		5 g malic acid (inactive)	
95 cc distilled water		2 cc nitric acid (conc.)	
		93 cc ethyl alcohol	

## V. For Nickel and Its Alloys†

Nickel, monel metal, and other nickel-copper alloys may be most satisfactorily etched for microscopic examination with nitric acid solutions. The two solutions which give excellent results with both cast and wrought products are as follows:

*Flat Etching Solution*

50 cc of conc. nitric acid
50 cc of glacial acetic acid

*Electrolytic Contrast Etching Solution*

10 cc conc. nitric acid
5 cc glacial acetic acid
85 cc water

Use one 1.5 volts dry cell and platinum wires

The time of etching with the flat solution will vary from 5-20 sec, depending upon the nickel content of the alloy and the depth of etch required. The higher nickel content requires the longer time. Dilution with 25-50% of acetone is desirable when the nickel content of the alloy is less than 25%. The electrolytic contrast solution requires 20-60 sec. Overetching will invariably result in deep pitting.

\* A.S.M. Metals Handbook, 1939, p. 1591.

† A.S.M. Metals Handbook, 1939, pp. 1674-1676.

TABLE 12 (Continued)  
VI. For Tin and Its Alloys\*

Etching Reagent	Composition	Remarks	Use
No. 1. Nitral	$\left\{ \begin{array}{l} \text{HNO}_3 \\ \text{C}_2\text{H}_5\text{OH} \\ \text{Acidified dilute} \\ \text{solution} \end{array} \right.$	Swab or immerse for several minutes.	Tin-cadmium or tin-iron alloys Tin-cadmium alloys
No. 2. Potassium dichromate	$\left\{ \begin{array}{l} \text{HNO}_3 \\ \text{HC}_2\text{H}_3\text{O}_2 \\ \text{Glycerol} \end{array} \right.$	Immerse $\frac{1}{2}$ -10 min at 38-42°C.	A. Tin-lead alloys
No. 3. Mixed acids in glycerol	$\left\{ \begin{array}{l} \text{HNO}_3 \\ \text{HC}_2\text{H}_3\text{O}_2 \\ \text{Glycerol} \end{array} \right.$	Same as for A, above.	B. Pure tin
No. 4. Hydrochloric acid	$\left\{ \begin{array}{l} \text{HCl (conc.)} \\ \text{H}_2\text{O} \end{array} \right.$	Immerse for several seconds. Immerse $\frac{1}{2}$ -5 min following A.	To remove surface flow. Follow A.
No. 5. Ferric chloride	$\left\{ \begin{array}{l} \text{HCl} \\ \text{H}_2\text{O} \\ \text{FeCl}_3 \\ \text{HCl} \\ \text{H}_2\text{O} \end{array} \right.$	Electrolytic etch at low current density. Immerse $\frac{1}{2}$ -5 min at room temperature.	Tin-iron alloys Micro-etching tin-rich babbitt metal
No. 6. Nitric acid	$\left\{ \begin{array}{l} \text{HNO}_3 \\ \text{C}_2\text{H}_5\text{OH(abs)} \\ \text{Alcoholic solution} \end{array} \right.$	Immerse 20-30 min at room temperature.	Pure tin Tin-iron alloys
No. 7. Picric acid and nitric acid	Concentrated solutions	Immerse 20-30 min at room temperature. Blackens out the tin or tin alloy, leaving the compound as a bright contrasting layer.	Macro-etching of tin-rich babbitt metals Tin coatings on steel
No. 8. Ammonium polysulfide <sup>†</sup>	$\left\{ \begin{array}{l} (\text{NH}_4)_2\text{S}_2\text{O}_8 \\ \text{H}_2\text{O} \end{array} \right.$		Soldered joint
No. 9. Ammonium persulfate	$\left\{ \begin{array}{l} \text{HC}_2\text{H}_3\text{O}_2 \\ \text{H}_2\text{O} \\ \text{H}_2\text{O}_2 \end{array} \right.$		
No. 10. Acetic acid			

Note: Solutions of silver nitrate or 10% nitric acid plus 5% chromic acid are also occasionally used.

\* A.S.M. Metals Handbook, 1939, p. 1731.

TABLE 12 (Continued)

## VII. For Zinc and Zinc Alloys\*

The most useful etching composition for commercial grades of zinc is as follows:

*Solution 1*

200 g pure  $\text{CrO}_3$   
 15 g  $\text{Na}_2\text{SO}_4$  or 34 g  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$   
 1000 cc water

*Solution 2*

200 g pure  $\text{CrO}_3$   
 1000 cc water

Fifteen seconds immersion will be adequate for examination at 100 dia. At 1000 dia. etching for periods longer than one second will frequently cause too much relief.

Certain chromic anhydride-sulfate mixtures, some of which may be produced by diluting the reagent with water, produce a stain film on zinc. This film is soluble in a pure  $\text{CrO}_3$  solution which itself will not etch or stain. Use of solution 1 or others containing chromic anhydride should therefore be followed immediately by rinsing in solution 2. This rinse is followed by thorough washing in a strong stream of water, dipping in alcohol, then ether, and drying with a warm blast of clean air.

\* A.S.M. *Metals Handbook*, 1939, p. 1768.

### Metallurgical Microscopes

Metallurgical microscopes are used for examining and for recording photographically the structures of metal specimens. Since these are

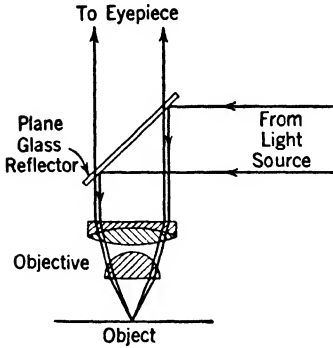


FIG. 47. Vertical illumination.

opaque and cannot be illuminated by transmitted light, a special type of illuminator must be used for all but very low magnifications where simple oblique illumination is occasionally useful. Ordinarily some form of vertical illuminator is used which reflects light to the specimen through the objective lens of the microscope, preferably the *plane-glass* type, illustrated in Fig. 47. The totally reflecting prism type is much less useful since it permits the use of only one side of the objective aperture with greatly reduced resolving power

and also gives a slightly oblique illumination.

Some of the large inverted metallurgical microscopes are also equipped with a *darkfield* illuminator which illuminates the specimen obliquely from all sides. Smooth surfaces appear dark and grain boundaries light under this illumination which finds very limited application in metallographic work. Another gadget sometimes provided is an opaque stop placed in the center of the beam of light coming to the plane-glass illuminator. It provides *conical* illumination which tends to emphasize a relief structure. Polarized light illumination is also provided occasionally and finds very limited application in the identification of partially transparent inclusions in steel.

### Optical Principles

The most important component of the microscope is the *objective*, the lens system nearest the object or specimen. The lens system nearest the eye is the *eyepiece* or *ocular* which serves to magnify the image of the objective for visual examination or to project it on a photographic plate or film.

**Chromatic and Spherical Aberration.** As the prime requisite of the objective is to resolve and magnify the details of the structure of the sample, it is necessary that it be corrected for two defects occurring in simple lenses which destroy sharp definition in the image: chromatic and spherical aberration. These are corrected by designing an objective made up of several lenses using different types of glass.



A simple lens not corrected for chromatic aberration brings images of different colors to a sharp focus at different distances from the objective, as shown in Fig. 48. The achromatic objective is corrected to bring images of two colors to a focus in the same plane, whereas the apochromatic objective is the most highly corrected and brings images of three colors to a sharp focus in the same plane.

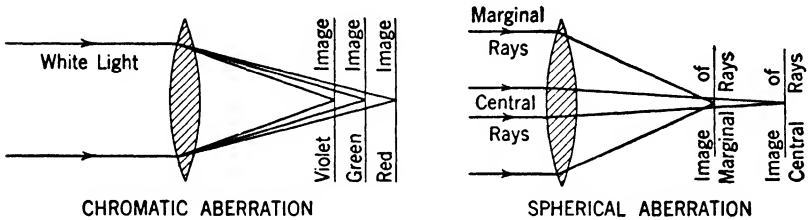


FIG. 48. Illustration of chromatic and spherical aberration in simple lens.

Spherical aberration (Fig. 48) ruins the definition of an ordinary uncorrected lens; it is caused by the fact that the rays coming through the center of the lens are focused in a plane farther away from the lens than the rays coming through the edges. This effect is distinct from and independent of chromatic aberration, but both are corrected in the design of the lens by similar means involving the use of several grades of optical glass varying in refractive index and dispersive power.

The simplest and cheapest lenses are nonachromatic and are not used with metallographic microscopes. The next higher grade is the achromatic lens, and the highest grade is the apochromatic lens; the fluorite or semiapochromat is intermediate in quality. All objectives are designed to give the best definition with one color of light (monochromatic), usually yellow-green to which the eye is most sensitive. Achromatic objectives are corrected for spherical aberration for one color of light only and give the best definition when used with monochromatic light of that color.

**Resolving Power and Numerical Aperture.** The resolving power of an optical system is its capacity to separate very close lines and show them clearly. The resolving power of an objective depends upon the angle of aperture (angle subtended between lines drawn from its focal point to the outer edges of the front lens of the objective). If the angle is wide more rays of light are collected and consequently a higher resolving power is obtained than with a narrow angle. The resolving power is proportional to the sine of half this angle and to the index of refraction of the medium between the objective and the specimen. The product

of these two factors is called the *Numerical Aperture* (N.A.).

$$\text{N.A.} = n \cdot \sin \frac{1}{2} \text{ angle of aperture}$$

$n$  = index of refraction

= 1 for air

= 1.515 for oil of cedar

Fig. 49 shows an objective with air for a medium on one side and oil for the medium on the other. The oil immersion lens collects a wider cone of light because of the higher index of refraction or bending power of oil of cedar as compared with air. Rays which would be lost by a dry lens ( $R_a$ ) are refracted within the angle of the oil immersion lens ( $R_o$ ). For the highest magnifications it is customary to use an oil immersion lens with a drop of oil of cedar between the specimen and the object. The highest numerical aperture of dry lenses is about 0.95 whereas good oil immersion lenses are usually rated at 1.3 N.A. or even 1.4 N.A.

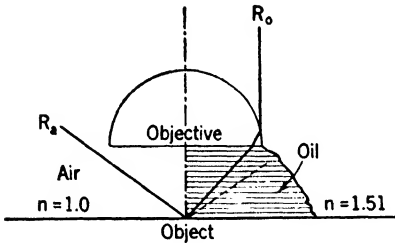


FIG. 49. Oil immersion lens collects a wider cone of light than a dry lens.

The resolving power also depends upon the wave length of light used, being greater for the shorter wave lengths such as violet or ultraviolet.

$$\text{resolving power} = \frac{\lambda}{\text{N.A.}} \text{ (with a narrow beam of light)}$$

$$\text{or} \quad = \frac{\lambda}{2\text{N.A.}} \text{ (with whole aperture filled with light)}$$

$\lambda$  = wave length of light used

$\lambda$  = 6470–7000 Å for red

$\lambda$  = 5750–5850 Å for yellow

$\lambda$  = 4000–4240 Å for violet

$\lambda$  = below 4000 Å ultraviolet (used with quartz lenses only)

These equations also show that the maximum resolving power is obtained by opening the aperture diaphragm until the entire objective

is filled with light, but to eliminate haze it is usually necessary to close the diaphragm down to about two-thirds of the full aperture. The theoretical limit of resolving power of an objective in terms of maximum number of lines per inch resolved is about 100,000 times the N.A., i.e., about 125,000 to 140,000 lines per inch.

The actual resolving power depends also upon the *definition* of the lens or the degree of correction for spherical and chromatic aberration for the particular wave length of light used. This limits the improvement in resolving power which can be obtained by using light of short wave length, such as blue or violet, since most objectives have better correction for green light.

Ultraviolet light of wave lengths down to 2750.Å has been used to obtain improved resolving power, but special quartz lens systems are necessary since ordinary glass absorbs ultraviolet light. Practical difficulties encountered, particularly in focusing an image which is not visible to the human eye, have definitely limited the usefulness of this type of microscope.

**Color Filters.** Since microscope objectives give the best definition with monochromatic light it is customary to use them with a light filter, particularly when photomicrographs are made. Light filters consist of colored glass, or a dyed gelatine film mounted between two glass slides, or a liquid cell filled with a colored solution, and are placed between the light source and the vertical illuminator. A good monochromatic yellow-green filter is now supplied with many microscopes. This color is used most commonly because the eye is most sensitive to it and most objectives, particularly achromats, are corrected for this wave length. Other colors are used mainly to improve contrast between colored constituents in the specimen. Blue, green, and yellow filters can be used when photomicrographs are made on orthochromatic plates or films and all colors can be used with the panchromatic type.

**Magnification.** The magnification of a microscope depends on the focal lengths of the objective and ocular, the tube length, and the bellows extension. Oculars are usually marked directly in terms of magnifying power, which is inversely proportional to focal length. Objectives are marked either in terms of focal length or in terms of their magnifying power when used for visual examination with a microscope of a definite tube length. The eye sees a *virtual image* which appears to be at a distance of 250 mm from the eyepiece, so the magnification is the same as would be obtained by projecting a real image on a ground glass located at the same distance from the ocular (250 mm). The initial magnification of the objective multiplied by that of the ocular gives the visual magnification or the magnification at 250 mm bellows extension.

For example, objective  $60\times$  · ocular  $10\times = 600\times$ . The microscope can be calibrated accurately by projecting the image of a stage micrometer on the ground glass and measuring the spacing of the ruled lines. If they are spaced 0.01 mm apart on the stage micrometer and 10 mm on the ground glass the magnification is  $(10/0.01) = 1000\times$ . For various objectives and eyepieces the magnification varies directly with the bellows extension and these can be plotted on a graph to give a straight-line calibration curve.

Table 13 gives the equivalent focal length, numerical aperture, initial magnification, and most useful range of magnification for a number of objectives.

TABLE 13. METALLURGICAL MICROSCOPE OBJECTIVES

Focal Length mm.	N.A.	Approx. Initial Magnif.		Most Useful Magnification
		160 mm. tube length	215 mm.	
<b>Achromats</b>				
32	0.10	3.5	5.0	35-100
24	0.20		8.0	75-200
16	0.25	9.0	12.5	100-250
8	0.50	20.0	26.0	200-500
5.5	0.65		37.5	350-750
<b>Apochromats</b>				
4	0.95	47.0	60.0	400-1000
3 (oil)	1.40		75.0	500-2000
2 (oil)	1.30	90.0	113.0	650-2000

The focal length of an objective is not the same as the working distance, but is much greater. A 2-mm oil immersion lens may have a working distance of only 0.13 mm. The rated focal length of a compound objective is the focal length of a single lens having the same magnification.

**Illuminating Power.** The intensity of illumination is proportional to the square of the numerical aperture,  $(N.A.)^2$ , of an objective.

**Depth of Focus.** A relief structure will not all focus in one plane if the objective lacks sufficient depth of focus. Depth of focus or depth of field is inversely proportional to both N.A. and magnification. For work at high magnification deep relief structures must be avoided by etching lightly and by polishing on a short-napped cloth for a minimum length of time. The magnification and numerical aperture should not be greater than necessary to resolve the structure. Closing the illuminator diaphragm increases depth of focus at the expense of resolving power.

**Flatness of Field.** The image formed by a simple lens comes to a focus on a curved field. This defect is not corrected in the design of microscope objectives since perfection in other corrections is more desirable and partial correction may be secured in the design of the ocular. The same factors which tend to improve depth of focus also tend to increase the diameter of the image that can be brought into sharp focus on the ground glass.

**Oculars or Eyepieces.** There are four important classes of oculars, each having special applications. The common Huygens ocular is the simplest in construction and is very satisfactory for visual examination with achromatic objectives. Apochromatic objectives are not corrected for chromatic difference of magnification so they require *compensating* oculars for visual work with white light to bring the images of various colors into coincidence. A third group of oculars known as Hyperplane, Periplan, etc., are designed to give partial correction for curvature of field, and can be used for both visual examination and photomicrography. A distinctly different type of ocular known as Homal or Ampliplane is a negative amplifier which does not form a virtual image so it can be used for photomicrography only. Its field is flat to the very edge, but the improvement is to some extent only apparent rather than real since its field is very limited in size, covering a relatively small area for a given magnification.

Micrometer eyepieces with measuring scales which coincide with the image of the specimen are very useful in measuring small objects and details. Greater accuracy can be obtained with a *Filar* micrometer eyepiece having a movable cross-hair and a calibrated dial. For grain-size determinations a special eyepiece is available with a grain-size chart mounted directly in the field of view.

## CHAPTER VIII

### COLD WORKING, PLASTIC DEFORMATION, STRAIN HARDENING

The plasticity of metals is attributed to slippage along specific crystallographic planes where all the atoms of one series of planes move as a block relative to a similar series of parallel planes. The reason slip takes place in the ductile crystals along the planes of highest atomic population is probably that they are farthest apart and have, therefore, the minimum of cohesion or restraining force.

The most plastic metals have the face-centered cubic and the hexagonal close-packed lattices. In each of these types there is dense packing of like atoms.

Single crystals of these metals are exceedingly soft, having low proportional limits and high plastic deformation. When slip planes are oriented at about  $45^\circ$  to the direction of pulling in tension, they will slide along their slip planes like a deck of cards. If the slip planes are not properly oriented to the axis of stressing the blocks may rotate considerably as they slip.

When slip has progressed far enough actually to cold work by deforming and straining the adjacent crystalline lattice, it stops on its original slip planes and slippage begins on other parallel planes. With single crystals, slip does not take place on each and every slip plane properly oriented to the stress, but usually in blocks of approximately equal thickness.

Single crystals of copper about one-quarter inch in diameter and several inches long can be bent easily with three fingers but ordinarily they cannot be bent back with both hands. This example shows the effect of work hardening by what is known as *slip interference*. Jeffries and Archer<sup>1</sup> state that "cold working introduces slip interference by change of orientation of the small grain fragments between intersecting slip planes and, to a lesser extent, by the disorganization of atomic arrangement at slip planes and at original grain boundaries."

Face-centered cubic metals have four sets of 111 planes (the eight planes forming an octahedron) called octahedral planes. This lattice also has twelve sets of 110 planes, making this lattice the most plastic

<sup>1</sup> Z. Jeffries and R. S. Archer, *The Science of Metals*, p. 412.

and easily deformed of any lattice. Metals like copper, gold, silver, aluminum, platinum, etc., have this lattice. They are good conductors of heat and electricity and will take the maximum amount of cold working without annealing because there are more potential slip planes.

In the body-centered cubic lattice the main slip plane is 110 and there are six sets of these planes, but the slip is not too well defined on them so it also takes place on planes 112 and 123, depending on the direction of stress. This lattice is not so conducive to the plastic flow characterized by F.C.C. lattices.



FIG. 50. Brass wire, 70% copper-30% zinc. Cold drawn 30%. Etched with concentrated  $\text{HNO}_3$ ; showing transgranular slip in polycrystalline solid solution. Ordinary slip lines are rather fine lines.  $\times 100$ .

In the hexagonal close-packed lattice the basal planes are the planes of easy slip and there are only three directions for slip which are parallel to the sides of the hexagonal prism. Slip does not take place in this lattice with the freedom it does in the face-centered cubic.

Many metals of industry are important because of their ductility. They are in the cubic and hexagonal systems, whereas those in the orthorhombic, monoclinic, and triclinic systems do not have the close-packed planes and easy direction of slip and, therefore, are relatively brittle.

Plastic deformation in a polycrystalline material is shown in Fig. 50. Here the various grains have a restraining force on each other because their slip planes are in different orientations. Slipping does not take place on each potential slip plane but over relatively large numbers of unit cells and, when the slip stops, the orientation of all unit cells within the block is about the same as when it started. When mechanical twinning takes place, each plane of atoms shifts only a small but definite

fraction of the atomic spacing with respect to adjacent planes and mechanical twins are formed as shown in Fig. 51 and Fig. 52.

Along the twinning plane the lattice on one side is a mirror image of the lattice on the other side. Hexagonal close-packed and face-



FIG. 51. Annealing twins in aluminum bronze containing Cu 93%-Al 7%. Treatment: cold worked 50%; annealed 20 hr at 1650°F. Etchant:  $\text{FeCl}_3$  in HCl. Annealing twins are mechanical twins and the bands are known as slip bands or twin bands and are wider than slip lines.  $\times 100$ .



FIG. 52. Neumann bands in mild steel, etched with picric acid. Neumann bands in ferrite are mechanical twins formed by impact and occur primarily on 211 planes.  $\times 1000$ .

centered cubic metals twin frequently and these twins are usually found on annealing after cold working and so are often called *annealing twins*.

The plastic flow of polycrystalline metals is exceedingly complicated because of readjustments in strain and restraint by other grains as



slipping progresses. The slip lines are frequently bent and the movement is not confined to the preferred slip plane but extends to several other families of planes.

Since slipping from grain to grain involves a change in direction at grain boundaries, it follows that there is less plasticity and greater hardness and strength with a small-grained than with a large-grained material. When polycrystalline, body-centered cubic materials are drastically cold worked, as in wire drawing, the 110 planes line up in the direction of working and two cube faces, 100, are parallel to the surface; the other four cube faces are perpendicular to the surface and make angles of  $45^\circ$  with the direction of working.



*Courtesy Pulsifer*

FIG. 53. Lüders' lines or stretcher strains.

**Self-Stopping Slip Planes.** One of the theories advanced in Beilby's amorphous metal hypothesis postulates that atoms are removed from their unstrained positions to form superficial films of noncrystalline material along the slip planes and at grain boundaries, thereby increasing the resistance to slip.

Rosenhain modified Beilby's hypothesis and postulated this amorphous metal at grain boundaries even with unworked metals. In the slip interference theory of Jeffries and Archer, a modification of the fragmentation theory, it is postulated that fragments of crystals or disarranged material interfere with slip. Of late, lattice distortion has been held to cause a roughening of slip planes, thereby lessening the slip. It may be stated that work hardening results in the formation of disarranged material as shown by microscopic and x-ray investigations. It is known that polished metal samples exhibit considerable disarrangement of structure at the surface.

**Lüders' Lines or Stretcher Strains.** On large-grained mild steels having much plastic flow (elongation) at the yield point, it is frequently found that there is considerable block slipping that cuts across many grains (Fig. 53), when the material is stretcher-straightened or tested in tension or compression. This is troublesome in automotive sheets requiring deep forming because these wide bands destroy the surface

flatness necessary for a good appearance. They are ordinarily eliminated by cold rolling the sheet, about 1 to 3 per cent reduction in thickness, to decrease the plastic flow and break it up into more directions.

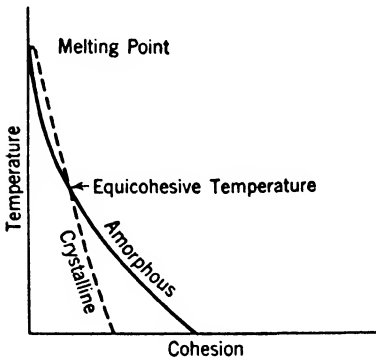


FIG. 54. Relation between mechanical properties of the crystalline phase of metals and the disarranged intergranular material to temperature. (After Jeffries and Archer.)

### Effect of Temperature on Metals

In considering the effect of temperature on metals the reader is referred to Fig. 54. When metals fail at ordinary temperatures in static tests or by fatigue, fracture takes place through the grain or crystal itself failing on slip planes when the slip-plane shearing strength has been exceeded. Failure at the grain boundaries occurs only when

the metal is exceptionally full of inclusions located at grain boundaries. The strength of the amorphous or intergranular material, which the authors prefer to call disarranged material, is high at low temperatures and, consequently, the metals do not begin to fail at the grain boundaries. At the *equicohesive* temperature the relative strengths are equal and at the melting point about zero.

Above the equicohesive temperature the crystalline phase is stronger than the disarranged material. For any particular metal the equicohesive temperature depends on the rate and duration of loading and corresponds closely to the *recrystallizing* or *annealing* temperature.

In copper, and probably most metals, when tested above the equicohesive temperature in creep or at ordinary rates of loading in a short time test, the fracture will be intercrystalline. If tested quickly, however, the fracture will be transcrystalline because amorphous substances like pitch and glass are stronger when loaded quickly, but when loaded slowly fail almost one atom at a time. The mechanical properties of metals, at both high and low temperatures of testing, behave as if the grain boundary material were totally amorphous.

## Recrystallization

When metals are cold worked drastically at temperatures below the equicohesive temperature, they become harder and more brittle as the grains are broken up and deformed almost beyond recognition through a microscope. In order to relieve the strain hardening most effectively the metals are *strain relieved* or *annealed* by heating for sufficient time to a temperature just above the recrystallizing temperature, which corresponds closely to the equicohesive or annealing temperature. Recrystallization gradually takes place with the formation of new equiaxed grains and the metal is again soft, stress relieved, and ready for further cold work if desired.

The recrystallizing temperature is not always the same for a given metal or alloy but is lower,

- (1) the greater the amount of cold working;
- (2) the lower the temperature of working;
- (3) the purer the metal;
- (4) the smaller the grain size before cold working;
- (5) the longer the time at the annealing temperature.

The lowest temperature at which new grains are visible with the microscope may be called the recrystallizing temperature and these approximate temperatures are shown in Table 14. Examination of this table shows that the annealing temperature, equicohesive or recrystallizing temperature, increases as the melting point of the metal increases.

Temperatures above the equicohesive temperature of the various metals correspond to hot-working temperatures and recrystallization takes place simultaneously with working. Metals like tin, cadmium, and lead cannot be work hardened materially at ordinary temperatures because they self-anneal.

Strain hardening takes place at all temperatures below the recrystallizing temperatures. The strain-hardening or cold-working effect is greater the lower the temperature of working.

After cold working, high-purity copper softens completely in a few days at about 150°C, but when it contains only 0.034% silver it will not anneal in about a year at the same temperature. Likewise 0.25% tin in nickel increases the annealing temperature of nickel over 200°C above its ordinary recrystallizing temperature.

The apparent mechanism of recrystallization is that an increase in temperature increases the atomic mobility of a strained and distorted lattice which has a high energy content. When the temperature is

sufficiently high the strained lattice is relieved by the formation of more stable unstrained grains.

The finest grain size in the wrought nonferrous metals is obtained by giving the maximum cold work possible, without rupturing, and annealing at a minimum temperature for the necessary time. Usually the annealing time is about one-half hour at temperatures slightly above the equicohesive temperature. On heating to temperatures considerably above the annealing temperature, softening progresses at a faster

TABLE 14. RECRYSTALLIZING TEMPERATURES AND MELTING POINTS OF SEVERAL METALS

Metal	Approx. Recrystallizing Temperature		Melting Point	
	°C	°F	°C	°F
Tin	Below room temperature		232	449
Cadmium	Room temperature		321	609
Lead	Below room temperature		327	621
Zinc	Room temperature		419	787
Magnesium	150	302	651	1204
Aluminum	150	302	660	1214
Silver	200	392	961	1761
Gold	200	392	1063	1945
Copper	200	392	1083	1981
Nickel	600	1112	1452	2646
Iron	450	842	1535	2795
Platinum	450	842	1773	3224
Molybdenum	900	1652	2620	4748
Tantalum	1000	1832	2850	5162
Tungsten	1200	2192	3370	6098

Lowest recrystallizing temperature for cold-worked metals corresponds closely to equicohesive temperature.

rate and the grain size is much larger. With nonferrous metals having no phase changes on cooling from the annealing temperature to room temperature, the rate of cooling is immaterial, as would be expected. Ordinarily, slow cooling from the annealing temperature is desirable with many alloys for the best softening treatment in order to coagulate any precipitating phase to larger particles and prevent age hardening.

Recrystallization cannot be discussed without mentioning grain growth because recrystallization is actually grain growth on a small scale. There is a strong tendency for grains to have the lowest energy content and, therefore, to assume the most stable state, which is the large equiaxed grain having the minimum surface area. A simple proof of this is that under identical conditions of electrolysis the small-

grained material will be anodic to the large-grained material. Likewise, cold-worked material is anodic to strain-relieved material.

**Grain Growth.** When cast metals are heated for long periods of time high above the equicohesive temperature but below the melting point there is very little grain growth. Ordinarily, when wrought metals are likewise treated there will be a larger grain size the longer the time of exposure and the higher the temperature of exposure (Fig. 55).

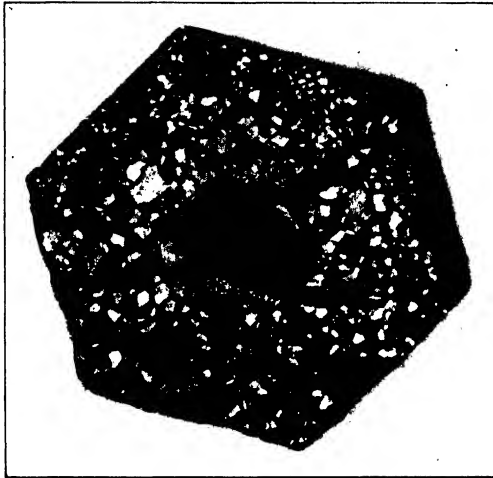


FIG. 55. Fracture grain of 1% carbon tool steel, heated 15 min just below solidus. Before treating the wrought steel was fine grained.  $\times 2$ .

In order to produce abnormally large grains (*germination*) it is customary to cold work a metal so that it will have a *strain gradient* throughout the section. With most metals this means a permanent elongation, in tension, of about 2 per cent, but this critical deformation varies with different metals. After the permanent stretching, followed by annealing, the unstrained and more stable grains grow by gradually absorbing the strained grains, probably atom by atom, as growth proceeds by boundary migration. This is one of the methods for making single crystals and is commonly used (Fig. 56). Germination is common with many "deep-drawn" metals because at certain locations in the stamped or drawn article there is found the critical degree of strain for the particular annealing temperature. When cold-worked articles must be annealed after forming operations, such as alpha brass cartridge cases, they should be heated as fast as possible through any germinative temperature range to avoid abnormally large grains. Ordinarily the germinative temperature increases as the degree of strain decreases.

Also, the grain size produced at the germinative temperature is larger the higher the germinative temperature.

The abnormal grains, on annealing, are favored by (1) strain gradient, (2) temperature gradient, (3) obstruction, and (4) grain-size contrast.

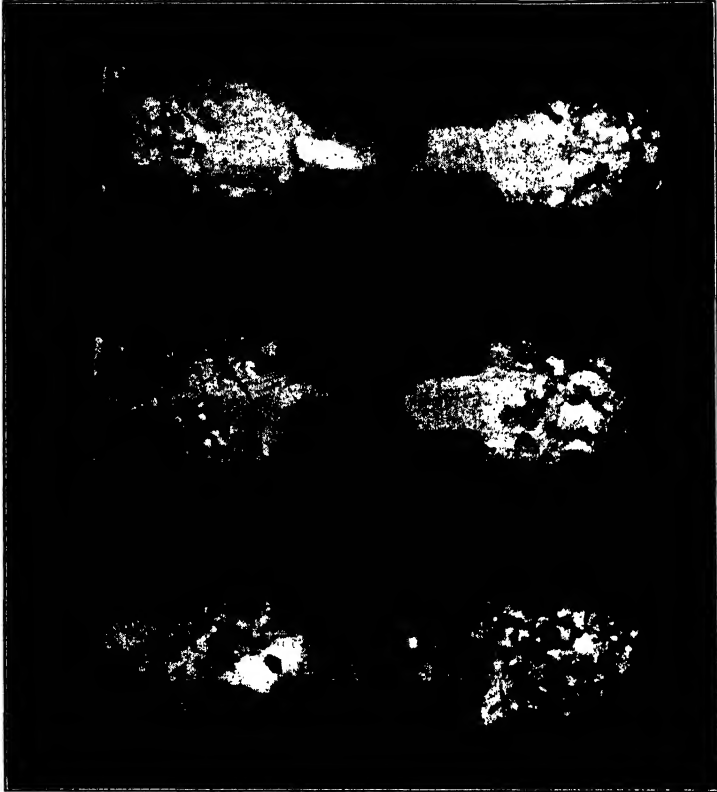


FIG. 56. Grain growth in high-purity aluminum. Equiaxed fine-grained specimens stressed to 2% permanent elongation in tension followed by heating to 475°C and gradually raising temperature to 555°C over 4 days. Temperature raised to 600°C for 1 hr. Treatment resulted in single grains within gage of specimens.  $\times 1$ .

By obstruction is meant inclusions which are sometimes sufficient to maintain a fine grain throughout heat-treating cycles and these metals are known as "inherently fine-grained" metals. Examples of these are: the sodium treatment of cast aluminum-silicon alloys producing fine particles of  $\text{Na}_2\text{O}$  as grain-growth inhibitors, and  $\text{Al}_2\text{O}_3$  particles in killed steels.

In tungsten with thorium nitrate additions, Jeffries found a strong

germinative condition between about 2.5 and 4% thoria. Above and below the critical amounts, a sintering temperature of 3200°C for 12 minutes in a hydrogen atmosphere gave a normal grain size.

Usually cold work followed by recrystallization is a grain-refining process and, in certain cases, a specific grain size is produced in metal stocks, especially sheet, by the manufacturer. When the grain is too coarse some forming operations cause a roughening resembling an "orange peel" pattern. If too small a grain it may work harden too rapidly and require annealing before further work hardening, so the specification of grain size in metals for specific purposes is becoming more common.

**Annealing.** Annealing is a strain-relieving treatment which softens metals when heated to their particular recrystallizing temperature for sufficient time. With most metals it is immaterial as to the rate of cooling from its annealing temperature. Most steels, however, having solid state transformations must be cooled slowly from above their critical points for complete annealing. The 18-8 stainless steels and other austenitic steels ( $\gamma$  solid solutions) are best annealed by quenching from about 2100°F; this treatment is called the "stainless anneal."

Copper-gold alloys and others having superlattice structures at ordinary temperatures, formed by slow cooling, are likewise annealed by quenching from above their critical points so as to retain the solid solution at ordinary temperature.

**Age Hardening.** Duralumin, beryllium bronze, and other alloys having a constitution similar to the Type II-*b* system have structures of two phases if cooled slowly. When these are heated to temperatures high enough to be homogenized (one phase), the resulting solid solution can be retained at some predetermined lower temperature after quenching. Most of these alloys are softer and more workable in the quenched state and they will precipitate the *supersaturated* phase on aging at a temperature above the lowest temperature at which the solid solution was stable. Some age at room temperature. This phenomenon is called *age hardening*.

The constant temperature process of hardening with time is also called *aging*. Naturally, if the aging temperature is increased above room temperature the precipitation of the second phase will take place in less time. When the precipitated phase is a compound in a fine "critical" dispersion, or perhaps in the "knot" state before actual precipitation, there is a marked increase in hardness, tensile strength, and yield point, and the elongation usually decreases. This is in accord with the slip-interference theory of hardness, and the hardest state appears to be when the lattice is strained to the maximum amount

before the precipitated phase can be recognized with a microscope of high resolving power.

Aging at too high a temperature or for too long a time results in the *coagulation* or coalescence of the precipitated particles to a size easily recognized with the microscope. At this stage, however, the hardness and tensile strength have decreased considerably and the alloys are spoken of as *overaged*. (See "Duralumin.")

In the early stages of precipitation the electrical conductivity is lower than for the original solid solution alloy. This would indicate that the high electrical resistivity found in the precipitating stage might be caused by lattice strain or distortion interfering with the transfer of electrons.

The changes occurring during the early stages of precipitation in age hardening alloys appear as follows:

- (1) a specific volume decrease or a density increase,
- (2) an increase in tensile strength, proportional limit, and hardness,
- (3) an increase in electrical resistivity.



# CHAPTER IX

## IRON AND STEEL

### High-Purity Iron

The element iron is the most useful metal to man. Its abundance and geographical distribution, the ease with which it can be produced in commercial purity, its desirable mechanical and physical properties, and the alloys it makes with other elements have all contributed to make it an extremely useful metal.

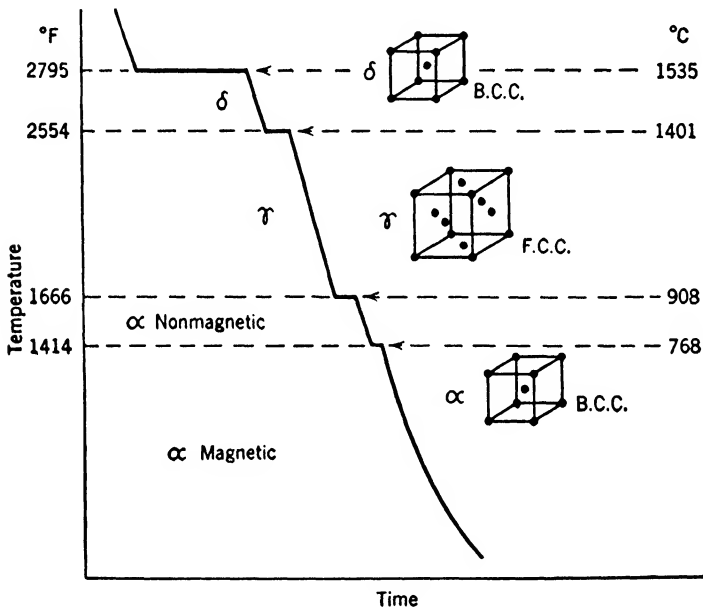


FIG. 57. Temperature-time cooling curve and allotropic modifications of high purity iron.

Iron is allotropic and the transformations in the solid state have been determined by many investigators. Thermal analysis is the usual method for determining transformation points although dilatation has been used successfully in the solid state. Fig. 57 represents the result of a temperature-time cooling curve showing the temperature of each transformation and also the crystalline arrangement stable at the various temperatures.

The general procedure for naming allotropic forms of metals or compounds has been to start at room temperature with alpha ( $\alpha$ ) and continue to higher temperatures with beta ( $\beta$ ), gamma ( $\gamma$ ), delta ( $\delta$ ), etc., to the melting point. In the case of pure iron  $\alpha$  represents the form which is stable at room temperature. It crystallizes in the isometric (cubic) system as the body-centered cubic (B.C.C.) arrangement having two atoms in the unit cube. At approximately 1414°F (768°C)  $\alpha$ -iron becomes nonmagnetic on heating and the reaction is endothermic. This nonmagnetic  $\alpha$ -iron was called  $\beta$ -iron until it was established that no crystalline change occurs. The so-called beta transformation in no way affects the heat treatment of steel and modern metallurgists call the nonmagnetic form  $\alpha$ -iron also. Alpha iron, upon being heated to about 1670°F (910°C), transforms to  $\gamma$ -iron which is face-centered cubic (F.C.C.), having four atoms in the unit cube.

**Volume.** Face-centered cubic arrangement allows closer packing of the atoms than body-centered cubic; this results in  $\gamma$  having a smaller volume and higher density than  $\alpha$ . Gamma-iron is stable from about 1670°F (910°C) to about 2554°F (1401°C), where  $\delta$  is formed which is body-centered cubic similar to  $\alpha$ .

These allotropic modifications absorb heat (endothermic) when being heated through the transformation and give off heat (exothermic) when cooled. The change occurs at almost constant temperature, both forms coexisting during transformation. When heating pure iron, however, unless the rate is extremely slow, the  $\alpha \rightarrow \gamma$  transformation is always higher than the corresponding cooling reaction  $\gamma \rightarrow \alpha$ . Further reference to these points will be made in the study of critical points in steel.

Iron, because of its high chemical activity and high melting point, is relatively difficult to produce in a state of high purity. Several methods have been used to produce iron of high purity; the mechanical properties of these products are listed in Table 15. The quantities of carbonyl, hydrogenated, and electrolytic iron produced are small and, for the most part, used in laboratory research.

A typical analysis of commercial low-carbon iron (ingot iron) made by the open-hearth process is about as follows:

Silicon	0.005
Manganese	0.02
Carbon	0.02
Phosphorus	0.005
Sulfur	0.025
Iron oxides and alumina and iron	remainder

The alpha solid solution of iron with the usual amounts of manganese, silicon, phosphorus, sulphur, and small amounts of carbon, is called

*ferrite*. The structure of ingot iron, as given in Fig. 58, is polygonal, having somewhat the same appearance as most other pure metals.

A high phosphorus content in ferrite lowers its ductility at ordinary temperatures and makes it "cold short" or brittle when cold. It is also a contributing factor in ferrite banding (ghost lines) in mild steel. Phosphorus is a more potent hardener of ferrite than is carbon in like amounts. High-phosphorus iron possesses improved resistance to corrosion.

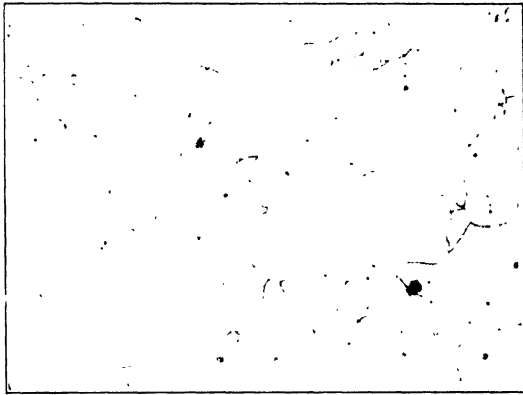


FIG. 58. Ingot Iron. Ferrite in typical polyhedral grains. Etchant: picric acid in alcohol.  $\times 100$ .

When sufficient manganese is present, sulfur occurs as inclusions of  $MnS$ . With insufficient manganese, and sulfur more than about 0.02%, there is a tendency toward "hot shortness" and the steels have poor hot-working qualities, being brittle at forging or rolling temperatures. This is because the sulfur is in the form of  $FeS$  which is molten at about  $1800^{\circ}F$ , below hot-rolling temperatures of  $2100$ – $2300^{\circ}F$ , and has a tendency to form a network structure (continuous envelopes around the grains of iron).

### Wrought Iron

Wrought iron was one of the first commercial irons and was used very widely before the advent of the open-hearth and Bessemer steel-making processes. It was originally produced by the hand puddling process, later by mechanical puddling, and recently also by the Byers or Aston process. Mechanical properties of these grades are given in Table 16, and are compared with those of ingot iron and mild steel in Table 17.

The structure of wrought iron is similar to that of high-purity iron except that slag inclusions in long stringers in the direction of rolling are



WROUGHT IRON

	As deposited	Electrolytic Iron	Fused and annealed	Hydrogenized Iron	Carbonyl Iron
Compression					
Elastic limit					
Proportional limit					
Yield strength					
Tensile					
Elastic limit					
Proportional limit					
Yield strength			10,000-20,000	7,000	15,000-24,000
Tensile strength		55,000-113,500	35,000-40,000	14,000	28,000-40,000
% elongation		25-3	40-60		30-40
Gage length, in.		2	1.5		$L = 10d$
% reduction of area			70-90		70-80
Torsion					
Proportional limit					
Yield strength					
Hardness					
Brinell Hardness No.					
Rockwell B			45		
Scleroscope			90	B-10-B10	56-80
Fatigue					
Reversed bend					
Reversed torsion					
Axial stress					
Impact					
Charpy, kg-m					
Izod, ft-lb			21.2*		

\* A.S.M. Metals Handbook, 1939, p. 443.  
 † 25 hr at 1650°F slow cool.  
 ‡ Cold-worked iron has no sharp yield point. The stress corresponding to the arbitrarily chosen strain of 0.5% on a 2-in. gage length can be distinguished up to about 15% cold reduction beyond which this value coincides with the tensile strength.  
 § Hot-rolled ingot iron. Tested at 20°C. Test specimen 60 X 10 X 10 mm.  
 ¶ Hot-rolled ingot iron. Tested at 20°C. Type of specimen, probably large Charpy.

easily observed with the microscope at  $100\times$ . The total amount of slag present varies between about 2 to 4 per cent. Its structure is shown in Fig. 59.



FIG. 59. Wrought Iron. Showing ferrite and slag constituents. Etchant: Nital.  $\times 100$ .

Wrought iron resists grain growth at elevated temperatures much better than pure iron or low-carbon steel. This resistance is attributed to oxides and the interference of the slag, which also aids in fluxing it during scarf welding in the open fire.

## Steel

**Types of Steel.** There are three main types of steel, classified as to melting and deoxidation technique as follows.

*Rimming* steel or *open* or *effervescent* steel usually contains less than 0.15 per cent carbon and generally not over 0.40 per cent manganese. Fig. 60 shows the result of a heat properly handled. The outside section is free from blow holes; this insures a good surface on the finished sheet or plate. The blow holes in the section are deep seated, of uniform size, well distributed, and they weld together during rolling. This type is used mostly for sheet where a good surface is required.

*Semideoxidized* steel comprises about 40 per cent of the annual production. This type of steel is used for commercial products where specifications on strength and surface are not too strict. It finds its application as structural shapes, concrete-reinforcing bars, fence wire, etc.

*Fully deoxidized* or *killed* steel is of the soundest quality. Its final deoxidation is with aluminum, which reduces the FeO, forming  $Al_2O_3$  in

TABLE 16. TYPICAL COMPOSITION OF WROUGHT IRONS\*

Type of Iron	C	Mn	Si	P	S	Slag by Weight
Byers No. 1	0.08	0.015	0.158	0.062	0.010	1.20
Mechanical iron	0.08	0.029	0.183	0.115	0.015	2.85
Hand puddled iron	0.06	0.045	0.101	0.068	0.009	1.97

*Carbon.* A carbon content over 0.10% is usually construed to mean imperfect refining or awakens the suspicion that steel scrap has been used in making up the customary "piles."

*Manganese.* Well-made wrought iron has a manganese content below 0.10%. If in excess of that amount imperfect refining may be indicated, or adulteration by use of steel in bushelling or piling.

*Phosphorus.* The phosphorus content of wrought iron is largely in the incorporated slag. Good wrought iron will contain from 0.08–0.160%, of which from 40–60% will be combined with the slag.

*Sulfur.* High-grade wrought iron contains up to 0.035% sulfur. Higher amounts are known to produce "red shortness" and also indicate imperfect refining.

*Silicon.* The amount of silicon is usually from 0.10–0.20%. The proportion associated with the base metal is practically nil. Silicon under 0.10% indicates either that there is not the normal amount of slag, or that the composition of the slag is not normal for properly refined wrought iron. Silicon content about 0.20% may indicate poor slag distribution, probably due to improper mechanical working.

\* A.S.M. Metals Handbook, 1939, p. 460.

TABLE 17. COMPARATIVE MECHANICAL PROPERTIES OF WROUGHT IRON, INGOT IRON, AND MILD STEEL\*

Materials	Endurance Limit Rotating beam, psi	Limit Axial, psi	Tensile Strength, psi	Charpy Notched Bar, ft-lb	Brinell Hardness No.
Wrought iron, longitudinal	23,000	16,000	46,900	17.5	105
Wrought iron, transverse	19,000	11,000	34,400	4.8	105
Ingot iron, as rolled	26,000	17,000	42,400	19.3	69
Structural steel, C 0.18% (as rolled)	28,000		61,500		

\* A.S.M. Metals Handbook, 1939, p. 463.

small particles, some of which are eliminated by rising to the slag but some also remain. Most structural alloy steels and tool steels are of this type.

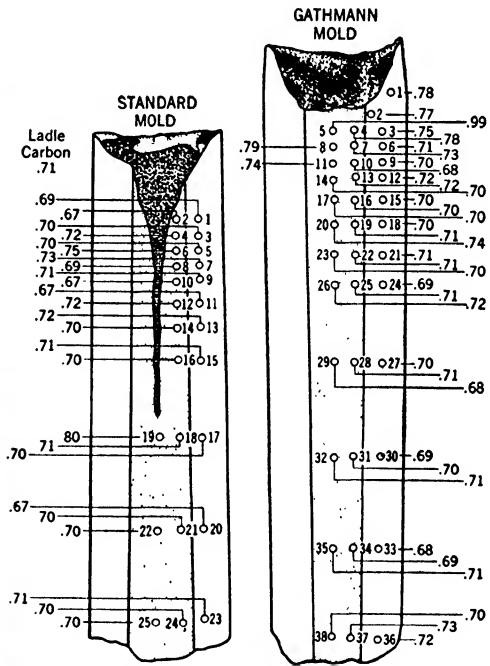
Steel is essentially an alloy of iron and carbon but it also contains small percentages of manganese, sulfur, and phosphorus. In the liquid state the metal is homogeneous but, since solidification takes place over a range of temperatures, the composition of the first solid to form is vastly different from the last. This change in composition, or segregation, varies in accordance with the composition of the alloy. In general, the first crystals forming at elevated temperature are high in iron whereas the last are higher in carbon and other elements such as sulfur and phosphorus. In most cases areas of segregation will be

higher in the last three elements than the ladle composition and will be located along the central longitudinal axis of the ingot. In sampling, therefore, the worst condition in a bloom, billet, or bar will be found at the center and the average composition will be found somewhere between the center and the outside edge. Examples of carbon segregation are given in Fig. 61.

The production of quality steel is the result of constant and intelligent con-



FIG. 60. Section of big-end-down rimming steel ingot.



Courtesy Gathmann Engineering Co.

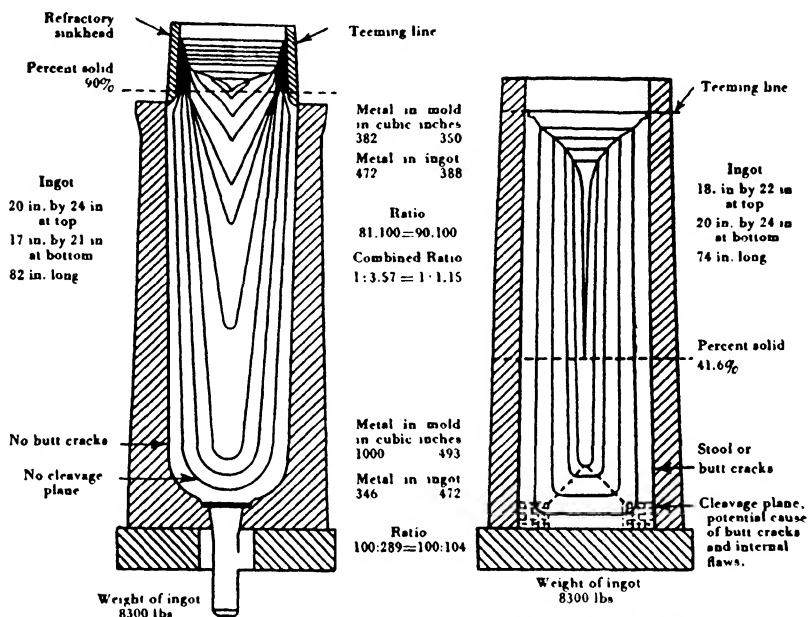
FIG. 61. Carbon segregation in fully deoxidized ingots. Left, " pipe cavity " about halfway from top to bottom as dark triangular portion.

trol, the purpose being to prevent or in some way compensate for some of the defects known as columnar structure, segregation, piping, blow holes, internal fissures, shatter cracks, scabs, checks, and inclusions. Some of these defects may be and are largely eliminated whereas others are kept within limits. Where control is not practiced, failure in the



finished product is too often traced to one or more of the above-mentioned defects.

Ingot molds, made of cast iron, are of two general types known as "big end down" or "big end up." The taper of the individual mold varies with the size, shape, use, and composition of the metal cast. Such molds may have a square or rectangular cross section with filleted



Courtesy Gathmann Engineering Co.

FIG. 62. Ingot molds for big-end-up and big-end-down practice.

or rounded corners, having either straight or corrugated sides. The cross section of the ingot mold will have a direct influence on the formation of planes of weakness in the ingots.

Fig. 62 shows two molds, one with big end down, the other with big end up, including the sink head or hot-topped portion. Big-end-down ingot molds are extensively used for semikilled and rimmed steel whereas the big-end-up type with sink heads are most satisfactory for the production of sound ingots from various killed steels, especially those having high carbon and/or high alloy contents.

Ingot is reduced to commercial sizes or shapes by rolling or forging. The choice between these two operations depends on the type of steel and its particular application. For example, the highest quality tool steels, especially the high alloy grades, are hammered and usually cogged

so the outside and part of the inside portion of ingots are mechanically mixed so as to have less segregation. Large and irregular forgings are made with the forging press; regular sections such as blooms, billets, bars, structural shapes, etc., are usually rolled. At the completion of this preliminary working operation (whether it is rolling, hammering, or pressing) and before reheating for finishing, the product is inspected by various macro-inspection methods for soundness, segregation, seams, etc. (See Chapter VII.)

### IRON-IRON CARBIDE CONSTITUTION DIAGRAM

(Usually known as iron-carbon diagram)

Alloys of iron and carbon plus small amounts of other elements are used commercially in larger quantities than any other type of alloys. The system has been studied in detail and many variations of the constitution diagram have been proposed. In many cases the alloys studied were not made from iron of high purity and for that reason the results represent the commercial alloys rather than the simple binary system. The iron-Fe<sub>3</sub>C constitution diagram, as shown in Fig. 63, represents data from a number of sources but preference has been given to data obtained when high-purity elements were used.<sup>1</sup>

Carbon and iron, when combined in the proportion of 6.68% carbon to 93.32% iron by weight, either by melting or diffusion, unite to form a chemical compound represented by the formula Fe<sub>3</sub>C. This compound is referred to as iron carbide or cementite. There are no commercial alloys of over 6.68% carbon so this range of composition is not ordinarily included in published Fe-C diagrams.

The diagram (Fig. 63) represents the melting points, the phases stable at various temperatures in both the liquid and solid states, and transformations that take place under conditions of very slow cooling or heating. The system is made up of five stable phases: liquid, delta ( $\delta$ ), gamma ( $\gamma$ ), alpha ( $\alpha$ ), and the compound iron carbide (Fe<sub>3</sub>C). The first three are stable only at high temperature whereas the last two are stable at room temperature. (The instability of Fe<sub>3</sub>C at elevated temperatures in high-carbon alloys will be discussed later.) These phases should not be confused with the microconstituents given at the bottom of the diagram (Fig. 63) and discussed in detail later.

A discussion of the cooling of an alloy from the liquid state to room temperature will be used to explain the various phase changes. Assume an alloy of 0.35% C which is represented by alloy No. 1 (Fig. 63). An alloy of such composition would begin to solidify at a temperature corre-

<sup>1</sup> R. F. Mehl and C. Wells, *Trans., A.I.M.E.*, Vol. 125, 429-472 (1937).

sponding to point *c*. The composition of the first solid would be represented by point *b*. With further decrease in temperature the composi-

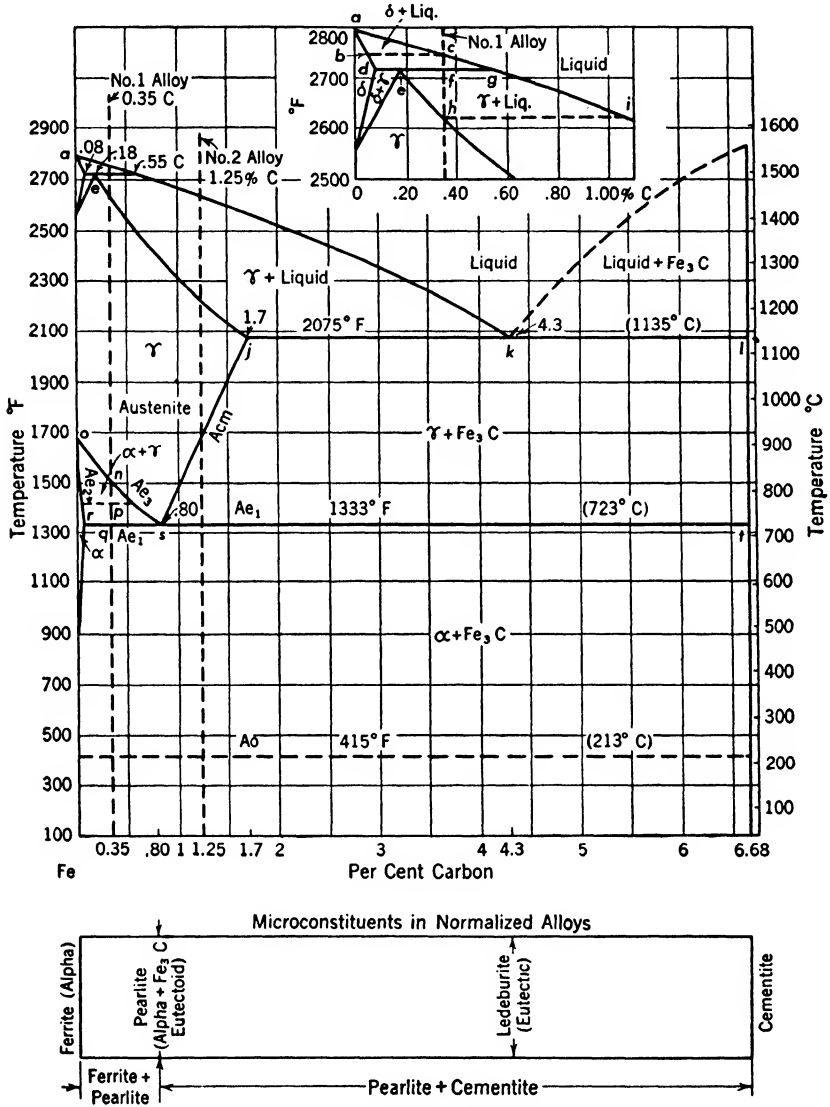


FIG. 63. Iron-iron carbide constitution diagram.

tions of the solid and liquid in equilibrium at any temperature between points *c* and *f* would vary along the lines *bd* and *cg* respectively. At point *f* a peritectic reaction occurs in which  $\delta$  of composition *d* reacts

with the remaining liquid and is changed to  $\gamma$  of composition  $e$ . The alloy under consideration being of higher carbon content than  $e$ , the reaction can be written  $\delta + \text{liquid} = \gamma + \text{liquid}$ . As cooling continues the composition of the phases  $\gamma$  and liquid for any temperature between points  $f$  and  $h$  varies along the lines  $eh$  and  $gi$ , respectively. Below temperature  $hi$  the alloy is solid solution gamma ( $\gamma$ ). No further phase change occurs until point  $n$  is reached where nonmagnetic  $\alpha$  begins to separate from  $\gamma$ . This separation continues with drop in temperature until at point  $p$  the  $\alpha$  becomes magnetic. As  $\alpha$  continues to separate from  $\gamma$  between the points  $p$  and  $q$  the composition of  $\alpha$  varies along the line  $or$ , reaching maximum solubility of carbon at  $r$ , whereas the composition of  $\gamma$  varies along the line  $ns$ , reaching saturation of carbon at a point  $s$  (0.80% C). At the temperature  $rq$ s the eutectoid reaction occurs and  $\gamma$  transforms to  $\alpha$  and iron carbide as a typical eutectoid mixture called pearlite. This reaction is reversible and can be written  $\gamma \rightleftharpoons \alpha + \text{Fe}_3\text{C}$ . In addition, it can be stated that regardless of the composition under consideration between the limits  $r$  and  $t$   $\gamma$  will always transform according to the above reaction and will contain 0.80% C when the transformation begins. Further cooling to room temperature results in a small amount of  $\text{Fe}_3\text{C}$  being precipitated from  $\alpha$  because of a change of solubility of carbon in  $\alpha$ -iron from maximum at the eutectoid temperature of about 0.04% to about 0.007% at 75°F. At  $A_0$  (415°F) the compound  $\text{Fe}_3\text{C}$  becomes magnetic.

Alloys in excess of 0.80% C can be conveniently discussed under three groups, according to carbon content, as follows: (a) 0.80 to 1.7, (b) 1.7 to 4.3, and (c) 4.3 to 6.68.

(a) **Alloys of 0.80–1.7% C.** Phase changes in alloys of this range can be discussed by taking an example such as alloy No. 2 (Fig. 63), containing 1.25% C. Upon cooling from the liquid state the first phase change taking place is the formation of  $\gamma$  which starts separating from the liquid when a temperature of about 2560°F is reached. With further drop in temperature,  $\gamma$  continues to separate until the solidus line  $ej$  is reached, at which temperature solidification is complete. No further phase change takes place by cooling until the line  $js$  is reached, where  $\text{Fe}_3\text{C}$  begins to precipitate and collect around the gamma grains and also along crystallographic planes within the gamma phase. This reaction continues until the eutectoid temperature  $rqst$  is reached, at which the remaining  $\gamma$  of composition 0.80% C transforms to  $\alpha + \text{Fe}_3\text{C}$  at constant temperature. Further changes are identical with alloy No. 1.

(b) **Alloys of 1.7–4.3% C.** During the cooling of alloys in this range primary  $\gamma$  separates first and this is surrounded by the eutectic

of  $\gamma + \text{Fe}_3\text{C}$  having the composition of 4.3% C. Upon further cooling the composition of  $\gamma$  again varies along the  $A_{cm}$  line ( $js$ ) by precipitation of  $\text{Fe}_3\text{C}$  at the grain boundaries until the eutectoid composition is again reached, where  $\gamma$  containing 0.80% C transforms to  $\alpha + \text{Fe}_3\text{C}$ . Further changes on cooling are identical with alloys No. 1 and No. 2.

(c) **Alloys of 4.3–6.68% C.** In alloys in this range primary  $\text{Fe}_3\text{C}$  separates first in dendritic form; this is followed by the freezing of the eutectic at temperature  $jkl$ . Below the eutectic all transformations are identical with (b).

**Critical Points in Steel.** As has been previously stated the element iron has two allotropic changes. On heating, the first change ( $\alpha \rightarrow \gamma$ )

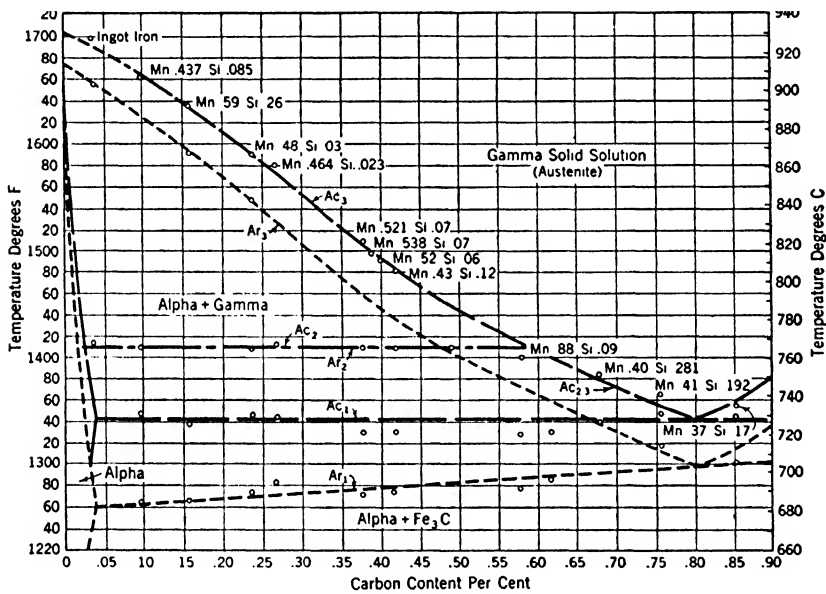


FIG. 64. Hypoeutectoid portion of iron-iron carbide constitution diagram enlarged to show critical points. (University of Minnesota.)

takes place at about 1670°F (910°C) and the second ( $\gamma \rightarrow \delta$ ) at 2554°F (1401°C). Both reactions are reversible and when the heating and cooling rates are very slow each transformation takes place at almost constant temperature. For the present we shall deal only with the  $\alpha \rightarrow \gamma$  transformation since it is of more commercial importance.

Iron in the gamma form has the property of dissolving a maximum of 1.7% carbon whereas in the alpha form the maximum solubility is about 0.04%. The effect of adding carbon is to lower the  $\gamma \rightarrow \alpha$  transformation temperature until a minimum is reached at 0.80% C. Further-

more, it has been found that the rate of heating or cooling has a pronounced effect on the temperature at which transformation occurs and as a result the transformation on heating is higher than the corresponding one on cooling. Fig. 64 shows the results obtained by thermal analysis of a series of commercial carbon steels when the heating and cooling rate averaged 11°F (6°C) per minute. Thus the difference or lag between corresponding transformation temperature is about 50°F.

Carbon steels containing less than 0.80% C are often referred to as *hypoeutectoid* steels and steels over 0.80% C as *hypereutectoid*.

The symbols represent the following abbreviations of French words: *A* from *arret* meaning arrest or stop; *c* from *chauffage* which means heating; *r* from *refroidissement* which means cooling. The combination *Ac*, therefore, designates arrest on heating and *Ar* arrest on cooling. The figures in subscript, 0, 1, 2, and 3, indicate the order of transformation beginning with the low temperature.

SUMMARY OF THE TRANSFORMATION POINTS IN STEELS  
(Critical Points)

- A*<sub>0</sub> Fe<sub>3</sub>C becomes magnetic at 415°F on cooling, and on heating becomes non-magnetic.
- A*<sub>1</sub> Pearlite transformation according to reaction  $\gamma = \alpha + \text{Fe}_3\text{C}$ .  
*Ac*<sub>1</sub>  $\alpha + \text{Fe}_3\text{C} \rightarrow \gamma$   
*Ar*<sub>1</sub>  $\gamma \rightarrow \alpha + \text{Fe}_3\text{C}$   
*Ae*<sub>1</sub> Equilibrium temperature for slow rates of heating and cooling for the *A*<sub>1</sub> transformation.
- A*<sub>2</sub> Magnetic transformation of  $\alpha$   
*Ac*<sub>2</sub>  $\alpha$  on heating becomes nonmagnetic  
*Ar*<sub>2</sub> Nonmagnetic  $\alpha$  on cooling becomes magnetic.  
*Ae*<sub>2</sub> Equilibrium temperature for *A*<sub>2</sub> transformation.
- A*<sub>3</sub> Solid solution transformation  
*Ac*<sub>3</sub> On heating all  $\alpha$  is transformed to  $\gamma$  and forms a solid solution.  
*Ar*<sub>3</sub> On cooling  $\gamma$  becomes supersaturated and  $\alpha$  precipitates out around the  $\gamma$ .  
*Ae*<sub>3</sub> Equilibrium transformation.
- A*<sub>4</sub>  $\gamma$  to  $\delta$  transformation, reversible at about 2554°F.
- A<sub>cm</sub>* Cementite solubility line, *sj* in Fig. 63.  
 Above the line Fe<sub>3</sub>C is dissolved in  $\gamma$ ; on cooling alloys with above 0.80% C, Fe<sub>3</sub>C begins to precipitate from the supersaturated solution  $\gamma$ .

In the foregoing discussion only one name was used for each phase although several of these are known by various names. An effort was also made to avoid confusion between phases and microconstituents, since some microconstituents contain more than one phase. The iron-carbon diagram given in Fig. 63 is labeled in terms of phases only, and a

separate diagram at the foot of the page gives the names of the microconstituents present in slowly cooled alloys.

Commercial alloys of iron and carbon, such as steels and cast irons, contain appreciable amounts of manganese, silicon, phosphorus, and sulfur. Table 18 gives not only the various names by which the phases and microconstituents in steel are known but also the composition of phases in commercial alloys.

**TABLE 18. NAMES AND COMPOSITIONS OF PHASES AND MICROCONSTITUENTS IN SLOWLY COOLED COMMERCIAL IRON-CARBON ALLOYS**

<i>Phases</i>	<i>Microconstituents</i>
$\alpha$ or $\alpha$ solid solution (or ferrite*). A solid solution of C (0.04% max), Mn, Si, P, S in $\alpha$ iron.	Ferrite or free ferrite or proeutectoid ferrite or excess ferrite are names frequently used for this constituent.
$\gamma$ or $\gamma$ solid solution (or austenite*). A solid solution of C (1.7% max), Mn, etc., in $\gamma$ iron.	Austenite. Not stable at room temperature in plain carbon-steels.
$\text{Fe}_3\text{C}$ or iron carbide (or cementite*). A compound of iron and carbon. May also contain Mn, etc.	Cementite or carbide. Sometimes described as "massive" or network or proeutectoid or free cementite.
(Pearlite is not a phase.)	Pearlite. A two-phase eutectoid mixture. At high magnifications can be resolved as alternate plates of $\text{Fe}_3\text{C}$ and $\alpha$ solid solution.

\* It is suggested that the terms ferrite, austenite, and cementite might be used for microconstituents only.

## STEEL CASTINGS

### Types of Cast Steel

There are three general types of cast steel: ingots, fusion welds, and castings. In each the laws of solidification and crystallization play an important part and in certain cases may be reflected in the properties of the finished product.

Ingots, as such, are seldom used commercially but are rolled or forged or pressed into a great many parts and certain characteristics of the ingot such as soundness, grain size, segregation, impurities, etc., may remain unchanged by fabrication once they are formed. Fusion welds are always produced by the use of molten metal even though definite molds may not be employed. Thermit welds are very closely related to metal castings since a refractory mold is employed. In welds, the quantity of metal in the liquid state at any one time during welding would correspond to a very small casting. Crystallization takes place according to the same laws (Fig. 65) although the cooling rate is much more rapid and the properties of the weld metal may not be comparable

to metal of the same composition in the form of castings. Soundness and the absence of inclusions is of major importance in welds just as in castings, and adequate control is essential.

**Steel Castings.** The term steel casting is a very broad one and includes a great variety of sizes and shapes as well as different chemical compositions. Castings are made in steel foundries by both acid and basic melting practice, in open-hearth furnaces, electric furnaces, and,

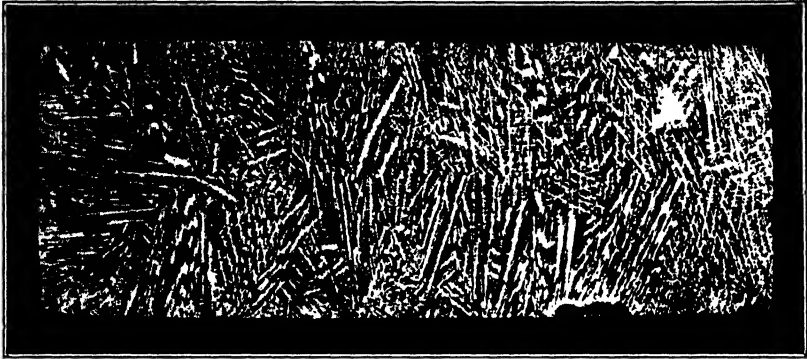


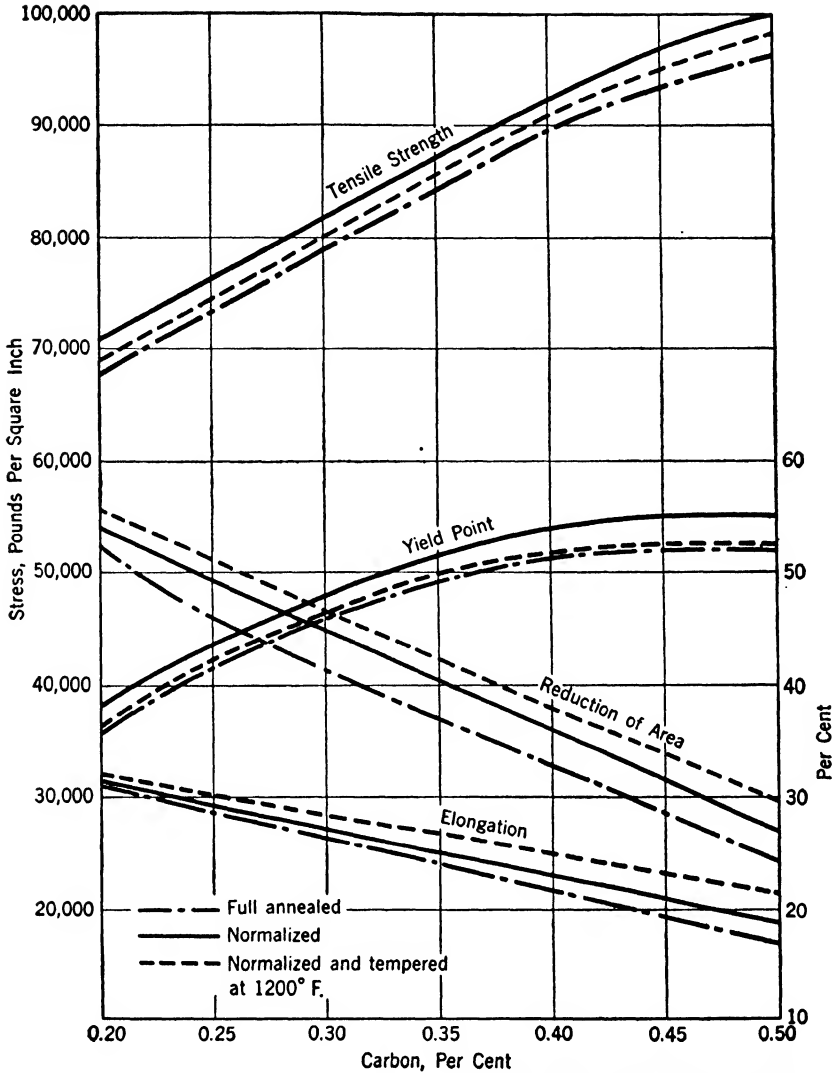
Fig. 65. Steel casting of mild steel, showing a dendritic structure in rectangular section of casting made in green sand.  $\times 1$ .

in some cases, Bessemer converters. The molten steel is poured into molds made of green sand, dry sand, or skin-dried sand. Some castings are small and relatively simple whereas others may be any shape or size within the limits of good foundry practice. Castings weighing over 200 tons have been cast successfully. One of the largest on record weighed 460,000 lb and was used as a cylinder jacket for a 14,000-ton forging press.

The mechanical properties of the casting depend for the most part on composition, technique of melting, design of the casting, and heat-treatment. The technique of melting cannot be discussed here, but must be in accordance with accepted standards. Under these standards certain chemical compositions have been found to produce certain average properties. Normal values for mechanical properties of various compositions are given in Fig. 66.

After casting and during cooling there are two types of metallic shrinkage that take place: one during solidification which is called "solidification shrinkage"; the other after solidification which is called "thermal contraction." To control the former effectively, all solidification in the mold should be progressive. It should begin at the bottom so that as crystallization progresses molten metal from above will flow





*Courtesy Steel Founder's Society of America*

FIG. 66. Normal mechanical properties of medium-carbon cast steel and effect of various heat treatments.

down and thus prevent the formation of cavities or porosity. This is assured by proper design and proper placing of risers, gates, and chills. (A simple example is seen in a big-end-up ingot with hot top, Fig. 62).

Thermal contraction is compensated for by increasing the dimensions of the pattern by about one-fourth inch per foot. This can be roughly

calculated from the average coefficient of expansion of a 0.20% C steel between room temperature and its melting point.

coeff. = about 0.00000811 per °F per in.

temp. change = about 2630°F

Therefore

total contraction = 0.02133 in./in.

or

0.2556 in./ft

It must be remembered, however, that every composition has a slightly different coefficient of contraction which also changes with temperature. In castings this theoretical amount of contraction may be altered by interference due to design and the position and size of cores.

**Cooling and Cleaning.** After the castings have been poured they may be handled in one of two ways. The first and most common procedure is to allow them to cool below the lower critical temperature in the mold. They are then shaken out and cleaned; the gates and risers are removed and they are heat treated.



FIG. 67. Medium-carbon cast steel as cast. Etchant: picric acid. Widmanstätten structure showing ferrite which separated between  $A_{r3}$  and  $A_{r1}$  (light); the dark structure is pearlite not resolved into  $\alpha$  and  $Fe_3C$  at this magnification.  $\times 150$ .

The second possibility is to shake out the castings hot, remove as much sand as possible and then charge into an annealing furnace operated at a temperature approximately the same as that of the castings and then gradually raise the temperature and hold as required. The saving in annealing time and expense by this method is considerable when applied to large simple castings such as rolls where long annealing cycles are

necessary. Internal stresses are largely avoided and there is much less danger of cooling cracks.

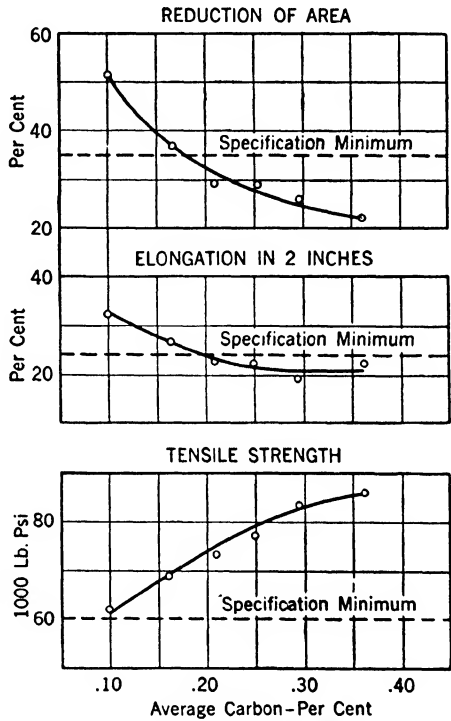
**Composition and Properties.** The bulk of the tonnage of carbon steel castings falls within the relatively narrow range of carbon content of about 0.15 to 0.35% carbon. The castings receiving no heat treatment (Fig. 67), or only a simple treatment such as an anneal, will usually be on the low side of this range (between 0.15 and 0.25% C) because of their natural toughness and relative ease of production. The castings which are to be heat treated (normalized and tempered, or quenched and tempered) usually have a higher carbon content since response to heat treatment depends largely on carbon content.

Fig. 66 (mentioned previously) presents the compositions, properties, and effect of heat treatments for a selected group of carbon steel castings. From this data it is possible to get a general idea of the effect of composition and heat treatment on the physical properties. Values obtained from such curves are only approximate and depend on the size of the casting.

Fig. 68 represents the effect of carbon content on physical properties of test bars from 100 consecutive heats to show the variations in meeting specifications in plant production. Treatment normalized 2 hr—1650°F, air cooled. Average composition: Mn 0.75%, P 0.017%, S 0.049%.

It is advisable to keep carbon on the low side of the range in order to have high elongation and reduction of area.

**Heat Treatment.** Normalizing, annealing, quenching, and tempering are the principal treatments used in the production of finished steel castings. In some cases only one treatment is necessary whereas in

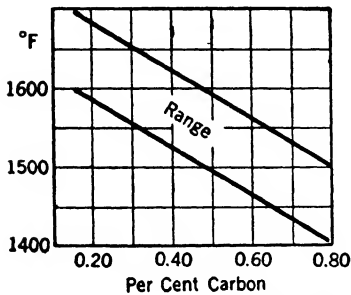


Courtesy National Bureau of Standards

FIG. 68. Effect of carbon content on physical properties of test bars from 100 consecutive heats to show the variations in meeting specifications in plant production. Treatment normalized 2 hr—1650°F, air cooled. Average composition: Mn 0.75%, P 0.017%, S 0.049%.

others two or more may be required to improve the mechanical properties.

**Simple Normalize or Simple Anneal.** The castings are properly supported in the furnace and the heating gases are allowed to circulate



*Courtesy A.S.M.*

FIG. 69. Temperature range for the heat treatment of steel castings.

freely. They are then heated uniformly, with minimum lag between inside and outside sections, to the temperatures given in Fig. 69. They are heated above the upper critical temperature of the composition under consideration so that dendritic or cored structures may be eliminated and a homogeneous  $\gamma$  solid solution formed. Just above  $A_{c3}$  the rate of diffusion of carbon and other elements is slow but increases as the temperature is raised. The time at temperature is judged by the size, and a rough guide is one hour per inch of heaviest section. It is known that little benefit is obtained after ten or twelve hours at temperature for any size.

The castings are air cooled in normalizing or cooled slowly in the furnace in annealing. The general benefits to be derived from normalizing or annealing steel castings are higher percentage of elongation and reduction of area in addition to an appreciable increase in yield strength. Annealing produces softer castings with more freedom from stresses but with slightly lower strength than can be obtained by normalizing.

**Double Treatment.** The purpose of this treatment is twofold: to obtain a homogeneous distribution of the diffusible elements (primarily carbon, manganese, and silicon), and the development of a fine grain size in the finished casting.

The first is accomplished by reheating to high temperature, as much as  $200^{\circ}\text{F}$  above  $A_{c3}$ , where diffusion is rapid. The castings are then cooled in air or in the furnace. The second step produces further grain refinement and consists of reheating,  $25\text{--}50^{\circ}\text{F}$  above  $A_{c3}$ , holding only until uniformly heated through and air cooling or quenching, and reheating to  $800\text{--}1250^{\circ}\text{F}$  (tempering).

Such long heat-treating cycles, however, are costly and are used only in special cases. A common commercial cycle would be to heat to a temperature high above  $A_{c3}$ , homogenize, cool in air, then temper at  $1200\text{--}1250^{\circ}\text{F}$ . This produces high ductility, the property most frequently required, and the specification most difficult to meet.

**Quenching and Tempering.** When exceptional or special physical properties are required the castings may be heat treated by quenching followed by tempering. It is recommended that normalizing or annealing precede the quenching operation to insure maximum refinement and to minimize danger from cracking during quenching. The possibility of cracking should be carefully considered since very fine cracks (invisible to the eye without deep etching) may eventually cause failure. Quenching, therefore, is resorted to only when the properties are not readily obtained in other ways.

The common quenching media are water and oil. Immediately after quenching the casting should be tempered, thus again minimizing the danger of cracking due to quenching stresses. It is most effective to have the temperature of the tempering furnace approximately the same as that of the castings and then uniformly reheat as required to obtain the desired properties. (See Table 19.)

Differential quenching is followed when only certain parts of the casting require special properties. Thus certain sections will be quenched by submersion in a liquid bath or by sprays and followed by tempering.

TABLE 19. QUENCHING AND TEMPERING OF CARBON STEEL CASTINGS\*

Carbon Range	Quenching Temp., °F	Time at Heat	Tempering		
			Quenching Medium and Temp., °F	Tempering Temp., °F	Time at Heat
0.15-0.30	1600-1650	¼ hr for every in. of diam or thickness	Water at 70	800-1250	At least 2 hr
0.30-0.40	1550-1600	¼ hr for every in. of diam or thickness	Water at 125	800-1250	At least 2 hr
0.40-0.60	1500-1550	¼ hr for every in. of diam or thickness	Water at 125 or oil	800-1250	At least 2 hr

These temperatures are based on the assumption that the castings were first annealed.

\* *A.S.M. Metals Handbook*, 1939, p. 961.

**Tempering or Stress-Relief Annealing.** Castings may be tempered after the normalizing operation as well as after quenching. In either case the temperature would be between 800° and 1250°F, as given in Table 19. The purpose is to remove stresses set up by nonuniform cooling and to improve impact resistance and ductility, which automatically reduces the tensile strength slightly. The temperature range for stress-relief annealing is usually between 500° and 1000°F. There is very little effect below 500°F but around 750°F about half of the stresses are eliminated.

**Structure.** The changes in mechanical properties from the original casting to the finished heat-treated casting are primarily accomplished by structural changes. The raw castings, after being cooled in the

sand, are dendritic (cored structure) and will exhibit crystalline weakness at corners as illustrated in Fig. 65. Proper normalizing or annealing, or both, will break up most or all of the dendritic structure and produce uniformly finer-grained ferrite and pearlite. Still further treat-

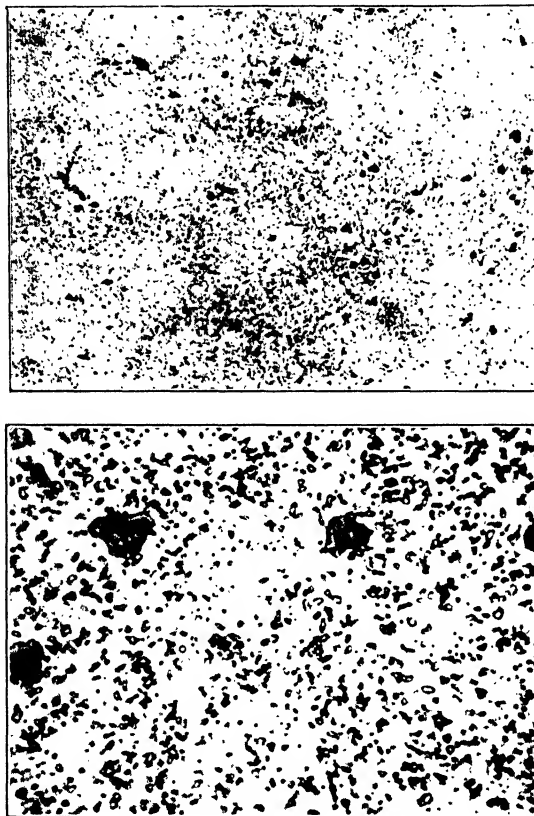


FIG. 70. Steel castings. *Above*, microstructure showing MnS inclusions located at grain boundaries. Treatment: quenched and tempered to 1250°F.  $\times 100$ . *Below*, same as above at higher magnification. Composition: C 0.24%, Mn 1.00%, Ni 0.67%, S 0.045%. Properties: Y.P. 62,050 psi; elong. 25.5% in 2 in.; R.A. 47%; T.S. 83,150 psi; B.H. 170; Charpy 37 ft-lb.  $\times 1000$ .

ment by quenching and tempering will give structures similar to those discussed later under heat-treated wrought steels.

**Inclusions.** A large number of inclusions around the grain boundaries is detrimental to ductility and favors fatigue failure. If, on the other hand, the inclusions are large, well-rounded, and uniformly spaced the effect does not seem to be detrimental.

The well-rounded inclusions in steel castings appearing as "bull's eyes" are usually silicates high in silica. When sulfur and manganese are relatively high, it is common to find MnS inclusions, and with aluminum-killed castings it is claimed that AlS predominates.

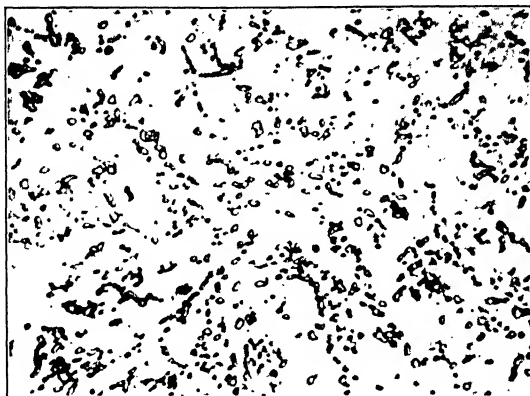


FIG. 71. Steel casting. Microstructure showing spheroidized cementite. No MnS inclusions. Treatment: quenched and tempered to 1250°F. Composition: C 0.24%, Mn 1.02%, Ni 0.67%, S 0.023%. Properties: T.S. 80,450 psi; Y.P. 59,300 psi; elong. 33.5% in 2 in.; R.A. 66%; B.H. 156; Charpy 50 ft-lb.  $\times 1000$ .

Figs. 70 and 71 show the effect of sulfur on the ductility of steel castings in the quenched and tempered state.

## HEAT TREATMENT OF STEELS

By heat treatment it is possible to produce in steels certain specified mechanical and physical properties for a definite purpose. Such changes in properties for the most part are dependent on the rearrangement and recrystallization of phases and require a thorough understanding of phase diagrams.

**Definition.** S.A.E., A.S.T.M., and A.S.M. have adopted the following definition for heat treatment of steel: "Heat Treatment— an operation, or combination of operations, involving the heating and cooling of a metal or an alloy in the solid state for the purpose of obtaining certain desirable conditions or properties." *Note:* Heating and cooling for the sole purpose of mechanical working are excluded from the meaning of this definition. It should be said in connection with this note that cooling in air, as from the rolling or forging operation, may give the desired structure and in most cases structure identical to what would be obtained by reheating for the purpose of cooling in air.

**Heating.** Steels to be heat treated are first heated uniformly to a temperature usually above the critical range (above  $A_{c3}$ ), although in some special cases lower temperatures may be used. Steels above the upper critical ( $A_{c3}$ ) are austenitic and capable of dissolving carbon along with other elements to form a homogeneous solid solution.

Steels may be heated in air, controlled atmospheres, molten salt baths, molten lead, or packed in containers surrounded by solid materials such as carburizing compounds, cast iron borings, mica, etc. The *safe rate* of heating varies with the alloy under consideration. Ordinary steels of the carbon and low alloy type may be heated quite rapidly, in a molten salt bath, without damage, but some alloy tool steels must be heated slowly and carefully to avoid cracking. This is especially true of steels with low coefficients of thermal conductivity. Sufficient time at temperature should be allowed to obtain a homogeneous austenite. The general rule is one-half to one hour per inch of section for wrought steel but may vary with composition of steel and its structure. Both time and temperature must be considered since solution and diffusion are much more rapid at high temperature.

Excessively high temperatures and extremely prolonged heating are usually avoided as they tend to produce a coarse grain structure. The amount of grain growth is dependent not only on the degree of overheating above the  $A_{c3}$  and the time at temperature, but also on the type of steel. Castings show very little tendency toward grain growth and certain fine-grained steels (deoxidized or killed with aluminum) become coarse grained only at relatively high temperature, in some cases 400°F or more above the  $A_{c3}$ . These steels are said to have a high coarsening temperature.

**Cooling.** The rate at which steel is cooled from temperatures above the upper critical is responsible for a wide variety of microstructures and each structure possesses its own characteristic combination of mechanical properties. The very slow rates produce microstructures which are softer and more ductile whereas rapid rates yield harder and more brittle structures. Slow cooling results in microstructures which correspond very closely to stable equilibrium (ferrite plus pearlite, or spheroidal cementite) whereas rapid rates of cooling produce microstructures that are not closely related to the stable iron-iron carbide diagram.

**Annealing.** The term annealing usually implies the heating of iron-base alloys above the critical temperature range, holding for the proper period of time (usually not less than one-half to one hour per inch of heaviest section), followed by slow cooling to below that range. Such a cycle should be referred to as "full annealing" but that term is often shortened to annealing.



The purpose<sup>2</sup> of annealing may be to (a) remove stresses, (b) induce softness, (c) alter ductility, toughness, electrical, magnetic or other physical property, (d) refine grain size, (e) remove gases, (f) produce a definite microstructure.

The usual temperature range for annealing is shown in Fig. 76.

Two other annealing processes, occasionally used in special cases are: (1) *process annealing* (sometimes called low anneal or stress-relieving anneal) is heating steels to a temperature below or close to the lower limit of the critical temperature range,  $A_{c1}$ , followed by cooling as desired. It is commonly applied in the sheet and wire industries after cold working and the temperature generally used is 950–1300°F; (2) *spheroidizing* is any process of heating and cooling steel to produce a rounded or globular form of cementite. This may be accomplished by either of two ways: (a) prolonged heating at a temperature just below the lower critical; (b) in high-carbon steels the result is accomplished more rapidly by prolonged heating to temperatures first within and later slightly below the critical temperature range.



FIG. 72. Spheroidized carbide produced by very slow cooling of a previously normalized 1.00% C steel. Cooled from 1400 to 1200°F in 10 hr.  $\times 1000$ .

Annealing in all cases implies a relatively slow rate of cooling, produces a soft, easily fabricated structure, and prepares the alloys for further treatment.

Illustrations of structures formed on slow cooling are shown in Figs. 72, 73, and 74.

**Normalizing.** Normalizing implies a faster rate of cooling than annealing and is defined as the heating of steel to about 100°F above

<sup>2</sup> A.S.M. Handbook, 1939, Definitions, purpose, p. 3.

the critical temperature range followed by cooling to below that range in still air. The temperature range recommended for annealing and for normalizing steels of various carbon contents is shown in Fig. 76. A representative structure of a normalized steel is reproduced in Fig. 75.



FIG. 73. Coarse lamellar pearlite produced by slow cooling of 0.80% C steel in the furnace from above  $A_{c1,2,3}$ .  $\times 1000$ .

The phases in Fig. 75 are  $\alpha$  and  $Fe_3C$ , and the microconstituents are ferrite and pearlite. Ferrite and cementite, after being etched in picric acid in alcohol or in 2% nitric acid in water, are both light in color. Ferrite appears rougher and darker than  $Fe_3C$  because it etches faster, and with deep etching becomes wavy in appearance. The dark lines are the boundary contact between the phases.

Annealing steels having less than 0.80% carbon produces structures containing the microconstituents ferrite and pearlite except when the cooling rate is slow enough to spheroidize the  $Fe_3C$ . If hypereutectoid steels are slow cooled from a temperature above the  $A_{cm}$  line the cementite forms around the pearlite grains and increases the brittleness of the steel owing to the more or less continuous network of this brittle constituent (Fig. 77). In typical structures of normalized steel the pearlite is finer than in structures of annealed steel of similar carbon content.

Normalizing is done for several reasons and in many cases is a final heat treatment. In carbon steels below 0.80% C (hypoeutectoid) the normalizing treatment increases the tensile and yield strength over annealed steel and retains sufficient ductility for many commercial parts. This combination of mechanical properties lies between those



C = 0.20



C = 0.28



C = 0.54



C = 0.63



C = 0.72



C = 0.90



C = 1.10



C = 1.18



C = 1.31

FIG. 74. Annealed carbon steels with increasing carbon content. Showing pearlite together with hypoeutectoid ferrite or hypereutectoid cementite depending on carbon content. Treatment: annealed by cooling in furnace from austenitic state.  $\times 500$ . *Reduced 20% in copying.*

produced by oil quenching and by annealing and satisfies many requirements.

By normalizing hypereutectoid carbon steels (above 0.80% C) the separation of cementite at the austenite grain boundaries between

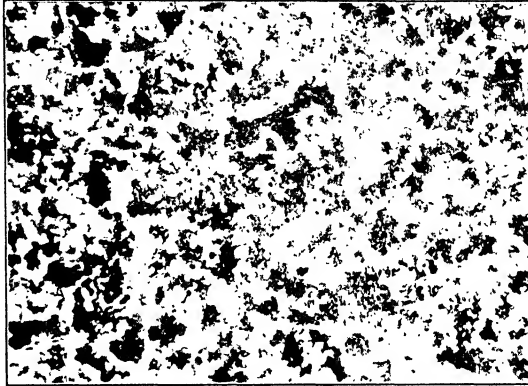
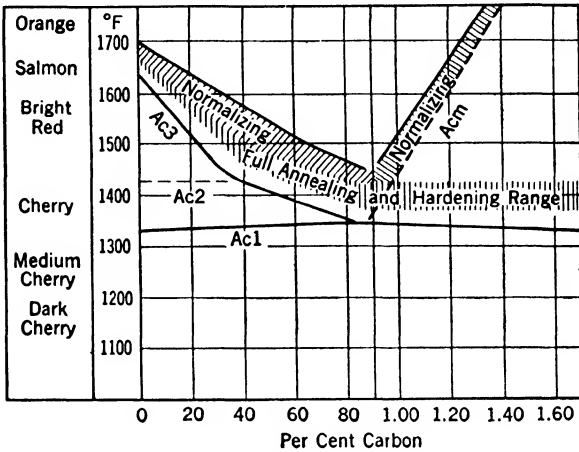


FIG. 75. *Above*, normalized carbon steel, showing pearlite and ferrite. C = 0.54%. Etchant: picric acid in alcohol. Treatment: 1-in. round air cooled.  $\times 100$ .  
*Below*, same as above,  $\times 1000$ .

$A_{cm}$  and  $A_{r1}$  is suppressed; this results in a much tougher steel than if the cementite had formed a continuous network as it does when these steels are cooled very slowly. Furthermore, when such steels are reheated for hardening the excess cementite is more easily spheroidized and a more uniform structure produced. Mechanical properties of carbon steels in the annealed state are given in Fig. 78.<sup>3</sup>

<sup>3</sup> F. T. Sisco, *Alloys of Iron and Carbon*, Vol. II, p. 177, Engineering Foundation.

More rapid cooling rates than those used in annealing or normalizing can be obtained by air blast, quenching in oils of various viscosities, sodium silicate solutions, water at various temperatures, and aqueous



*Courtesy A.S.M. Handbook, 1933, p. 779.*

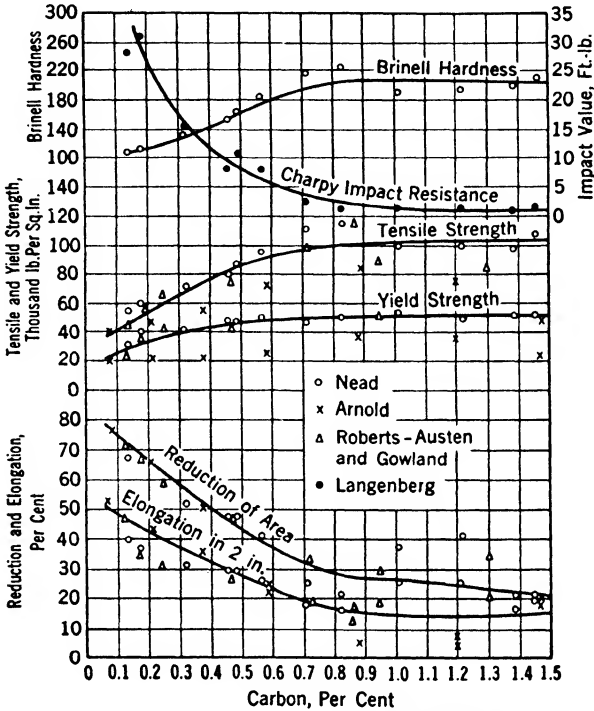
FIG. 76. Normalizing, annealing, and hardening temperature range for carbon steels of various carbon contents. (Spheroidizing is usually at temperatures slightly below  $A_{r1}$ .)



FIG. 77. Annealed carbon steel (1.18% C) showing coarse pearlite and network cementite. Treatment: annealed from 1800°F by cooling in furnace as so to produce the undesirable network carbide separation between  $A_{cm}$  and  $A_{r1}$ . Etchant: picral.  $\times 1000$ .

solutions containing 5-10% NaCl or NaOH. These media are named in order of increased rate of cooling and will cool similar samples at increasingly faster rates.

**Hardening.** A rapid and continuous quenching of carbon and most low-alloy steels in water will harden them and the hardness will increase up to a certain limit as the velocity of quench increases. This increase in hardness is accompanied by a change in the structure of the steel and



*Courtesy Engineering Foundation*

FIG. 78. Mechanical properties of carbon steels in the annealed state.

the two are very closely related. To complete successfully the hardening cycle for any part, however, there are several very important variables or factors to be considered. The most important of these are:

1. Composition, carbon and alloy content.
2. Homogeneity of the austenite.
3. Grain size of the austenite.
4. The quenching temperature.
5. The quenching medium.
6. The size (mass) of the part;
  - a. Very small samples cool rapidly all through whereas large pieces cool fairly rapidly on the outside but more slowly in the center.
  - b. Thermal conductivity of the steel.
7. Surface condition, whether clean or with thick scale.

Rapid cooling of small sections of steel from above  $A_{c3}$ , such as quenching in water, gives high hardness and martensitic structure characterized by acicular or needle-like markings and light color after etching (Fig. 79). Slower velocities of cooling, such as quenching in oil, often give mixed

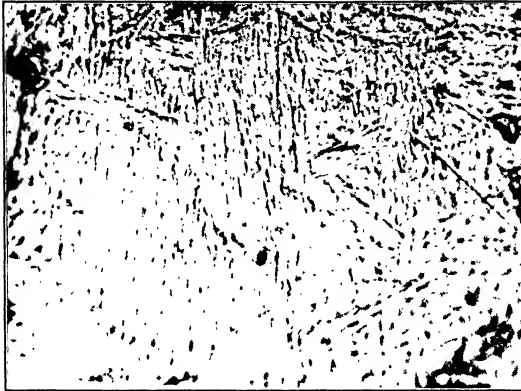


FIG. 79. Martensite. Composition: 0.35% carbon. Treatment: quenched in water from just above  $A_{c3}$ .  $\times 1000$ .

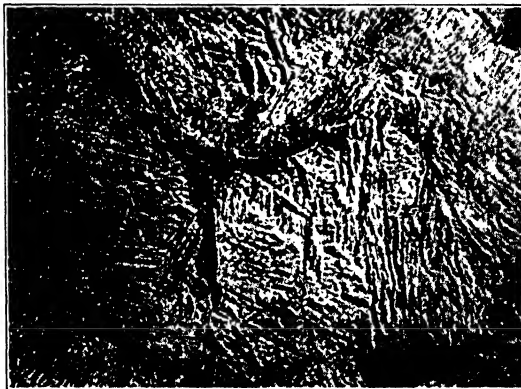


FIG. 80. Martensite and primary troostite at grain boundaries. Composition: 0.20% carbon. Treatment: water-quenched from just above  $A_{c3}$ .  $\times 1000$ .

structures composed of martensite and a much softer constituent which is dark after etching and cannot be resolved with an oil immersion lens of high resolving power. This fine pearlitic structure, known to form at a temperature below  $A_{r1}$  (designated  $A_{r'}$ ), is often called primary troostite (Fig. 80) because it appears similar to the structure obtained by tempering martensite. It is now known, however, that the transfor-

mation  $Ar_1$  can be suppressed by rapid cooling and that  $Ar_1$  and  $Ar'$  are similar physically. Steel having this fine pearlitic structure is much stronger than the coarse type produced by slower cooling.

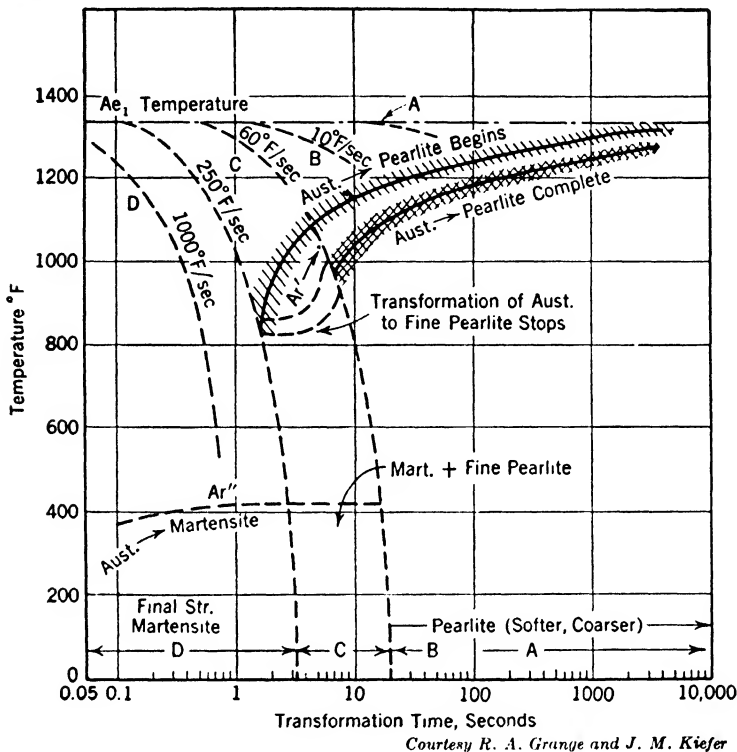


FIG. 81. Schematic sketch for eutectoid steel showing the relationship between microstructure and quenching velocity.

In 1919 Portevin and Garvin<sup>4</sup> presented the first comprehensive data on the cooling velocities required to produce definite structures as well as the temperatures at which they were formed. They further reported that the rates required to produce similar structures varied for different carbon steels.

The results of recent investigators are presented by the sketch in Fig. 81, which shows that with slow cooling velocities of about  $\frac{1}{10}^{\circ}\text{F}$  per second (A) austenite begins to transform very close to the  $Ar_1$  and also that the reaction is completed within a very narrow range of temperature. The product is coarse lamellar pearlite (see Fig. 73). If the cooling rate is increased to about  $10^{\circ}\text{F}$  per second (B) the transformation

<sup>4</sup> A. Portevin and M. Garvin, *J. Iron & Steel Inst.*, Vol. 99, p. 469-563 (1919).



of austenite is slightly suppressed; thus according to the sketch the average austenite begins to transform to pearlite at about 1150°F and is complete at about 1060°F. The structure is a finer pearlite having higher hardness than that produced by the slower cooling rate. The



FIG. 82. Austenite and martensite, showing martensite plates in relief in austenite matrix. Composition: 1.31% carbon. Treatment: quenched in ice water from 2100°F. (Note: Not a commercial heat treatment for carbon steel; represents maximum amount of austenite that may be retained by quenching.)  $\times 1000$ .



FIG. 83. Tempered martensite (acicular troostite) in matrix of austenite. Composition: 0.80% carbon. Treatment: quenched in ice water from 2100°F and tempered 1 hr at 300°F. (Note: This structure has also been called black martensite in austenite matrix. It can be formed also by interrupted quenching and holding at  $Ar''$ .)  $\times 1000$ .

temperature of the  $Ar''$  is almost independent of the cooling rate but varies with carbon content from approximately 900°F for 0.20% C and 425°F for 0.80% C to approximately 275°F for 1.3% C.

Still faster cooling velocities, such as would be obtained by a slow quench and which would correspond to cooling rates between 60 and 500°F per second, depending on the type of steel, causes austenite to begin to transform between 1100 and 840°F ( $Ar'$ ), depending on the cooling velocity. The transformation, only partly completed, stops somewhere between 840 and 950°F. When the untransformed austenite is cooled to below 400°F it changes into martensite at the  $Ar''$ . The structure is a mixture of primary troostite (fine pearlite of about 100 uu between laminations) and martensite (Figs. 80 and 81).

Very rapid cooling suppresses all transformations at high temperatures and austenite is retained until the temperature has dropped to about 400°F or lower, where it transforms to martensite (Figs. 81 and 79). The critical cooling rate is the slowest cooling rate (velocity) which will suppress the formation of primary troostite and produce only martensite. This cooling velocity for a  $\frac{3}{4}$ -in. round of steel containing about 1% carbon is about 7 sec from 1300 to 390°F as reported by Portevin and Garvin.

Martensite is the hardest decomposition product of austenite and, for high-carbon steels, usually varies between 64 and 70 Rockwell C. Rapid, continuous cooling to room temperature or below gives the highest hardness and is most liable to cause cracking. To avoid cracking the first stage of cooling may be done rapidly and the later stage more slowly. Rapid cooling of austenite to  $Ar''$  prevents the austenite to pearlite transformation and slower cooling below  $Ar''$  prevents cracking. This is often accomplished commercially by quenching from above the upper critical ( $A_{c3}$ ) in cold water, brine, or caustic for sufficient time and finishing the quench in oil. Cracking usually occurs when the steel is at a temperature below 212°F.

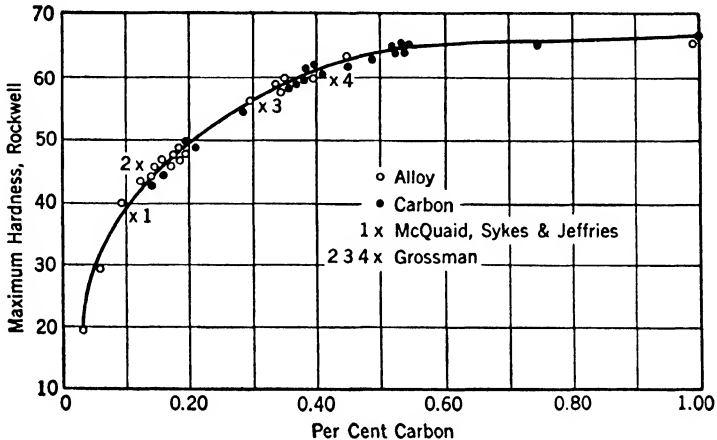
**Mechanism of Hardening by Quenching.** When austenite is quenched drastically it reaches the transformation  $Ar''$  and, being metastable and supersaturated with carbon atoms in its interstitial solid solution, it starts to recrystallize. Recrystallization takes place in acicular plates on the 111 planes of the austenite with the formation known as martensite and with an increase in volume. These martensite plates etch white and are in relief in any residual austenite matrix. Freshly formed martensite is a phase composed of a supersaturated solid solution of carbon atoms in a body-centered tetragonal lattice. When austenite is quenched to  $Ar''$  and slowly cooled from there, these white needles are tempered so they etch dark and are composed of a matrix of ferrite and extremely fine unresolved particles of  $Fe_3C$ . This is called tempered martensite or acicular troostite and the hardness is lowered by 5 to 10 points Rockwell C below that of martensite formed by quenching drastically to room temperature.

**Probable Reasons for the High Hardness of Martensite in High-Carbon Steels.** 1. Supersaturation of carbon atoms in a strained body-centered tetragonal iron.

2. Fine recrystallization product martensite within the austenite grain.

3. Reinforcement of structure or the resistance to slip caused by the martensite plates in the austenite grain.

4. Lattice distortion.



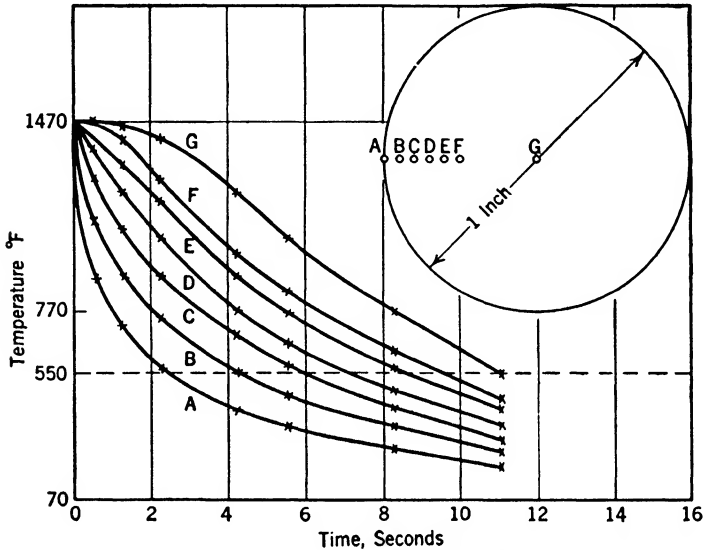
*Courtesy Burns, Moore, Archer, Grossman, A.S.M.*

FIG. 84. Hardness vs. carbon content. Steels water quenched.

The most important variable in the heat treatment of steel is chemical composition, and small variations in carbon and alloy content produce important changes in critical cooling rates, hardness, and other properties. It is generally agreed that low-carbon steels (hypoeutectoid) require higher critical cooling rates and must be quenched more rapidly than eutectoid steels, other variables being constant. From the data available, hypereutectoid steels appear to have critical cooling rates very close to or only slightly faster than eutectoid steels. The effect of carbon on the maximum hardness is clearly shown in Fig. 84.

Low-carbon steels do not respond to heat treatment sufficiently to warrant hardening commercially. As the carbon content is increased the hardness obtainable by quenching is rapidly increased to about 0.60% carbon, beyond which further increase is gradual. Increased amounts of carbon when dissolved in gamma-iron to form austenite retard the transformation of austenite to martensite sufficiently to allow lower cooling rates and still produce martensitic structure of high hardness. Critical cooling rates may be lowered still further by alloying elements dissolved in austenite and by coarse austenitic grain size.

**Surface Scale.** The presence of a thick layer of scale on a steel, due to heating in an oxidizing atmosphere, will lower the speed at which the steel can be cooled and result in lower hardness. Areas from which the scale cracks off during quenching of course will be much harder than those protected. The quenching of steel covered with heavy scale will result in an unreasonable number of soft spots.



Courtesy M. A. Grossman, *The Heat Treatment of Steel*, 1940

FIG. 85. Time-temperature cooling curves at different positions in a 1-in. diameter bar quenched drastically in water.

**Size or Mass of the Piece.** It is obvious that a small piece (1 in. diam by  $\frac{1}{8}$  in. thick) will cool much faster than a large piece (1 in. diam by 6 in. long) when quenched in water, but it is not easy to visualize or predict the difference in cooling rate between the outside and the inside. The outside is cooled more rapidly than the inside, as shown by Grossmann-Russell in Fig. 85. The general form of these curves has been confirmed by experiment.

The circle in the upper right represents the cross section of a one-inch steel bar and A, B, C to G the points taken. The curves A, B, C to G (lower left) show the actual cooling rate for the various distances from the outside to the inside of the bar. The outside, having a much faster cooling rate, will become much harder during quenching than the inside where the cooling rate is slower. The outside will be martensite whereas the inside will be a mixture of martensite and primary troostite (unre-

solved pearlite). In accordance with this principle some special steels with very low critical cooling rates will harden completely through heavy sections, whereas steels with high critical cooling rates can be hardened throughout only in small sections.

**Homogeneity of Austenite.** In order to obtain homogeneous austenite the steel must be heated to the proper temperature above the upper critical and held at constant temperature until a solution and diffusion of the carbon has taken place. Immediately above the upper critical the rate of diffusion is somewhat slow but increases rapidly as the temperature is increased. Austenite grains low in carbon content have high critical cooling rates and therefore may not be completely hardened when quenched. Homogeneous grains, on the other hand, are more sluggish, more easily hardened, and produce more uniform hardness.

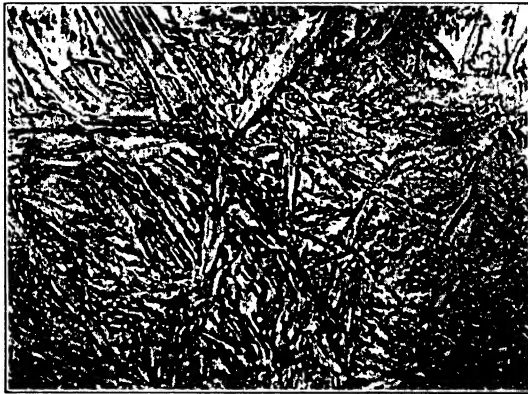


FIG. 86. Overheated steel. Martensite and austenite, showing martensite plates in relief in austenitic matrix. Composition: 0.86% carbon. Treatment: heated to below the solidus and held for coarsening the grain and then drastically quenched in ice water.  $\times 1000$ .

**Grain Size of Austenite.** Steels heated to far above the upper critical will tend toward large austenitic grain size (Fig. 86). This tendency for grain growth is the greatest in homogeneous structures. The so-called fine-grained steels, usually deoxidized by aluminum, are more resistant to grain growth because of many small particles of  $\text{Al}_2\text{O}_3$  in the grain boundaries of the austenite which are not soluble. This insoluble buffer retards grain growth until quite high temperatures are reached. In general, steels with large austenite grains harden more deeply than those having fine grains but are not so tough.

**Quenching Media.** From a practical standpoint high quenching velocity can be obtained by the use of rather limited number of quenching

media. The most important are listed below in order of descending rapidity of quench.

NaOH, up to 10% in water  
NaCl, up to 10% in water  
Water at various temperatures  
Oil of various kinds

The temperature of the quenching media should be maintained within relatively close temperature limits to insure uniform quenching rates. This is accomplished by having a large volume of liquid and a circulating system. With oil the temperature should never be allowed to reach, or even approach, the flash point because of danger of fire. Aqueous solutions are the most effective for quenching and most common, primarily because of the property of high heat of vaporization.

**Tempering.** Steels are seldom used in the "as quenched" condition since most steel parts would be too brittle in this state and would have considerable internal stress. Tempering or drawing is usually essential before suitable properties are obtained. This operation consists of reheating a hardened steel to some temperature below the lower critical, holding a sufficient period of time, and cooling as desired, usually in air. Quenching from tempering temperature is sometimes employed to prevent aging or temper brittleness in certain alloy steels.

The purpose of tempering steel is to toughen it, but increasing the toughness is usually accompanied by a drop in hardness. If hardened steel parts are reheated at low temperatures such as 300°F for periods of one or two hours, very little change in hardness takes place but the increase in toughness is appreciable. On the other hand, if the time is long, such as in die steels which are used day after day at 300°F, the hardness will gradually decrease. Increasing the tempering temperature to between 350 and 375°F for one to two hours will cause a very appreciable increase in toughness and a decrease in hardness. Further increase in the tempering temperature will continue to increase the toughness and decrease the hardness. The results are represented clearly in Fig. 87. It should be pointed out that there is a range between about 450-650°F in which both hardness and toughness drop off.

The changes in properties of hardened steel brought about by tempering are due directly to precipitation and coagulation of  $Fe_3C$  to larger particles. Microscopic examination offers a very useful means of checking the degree of tempering and gives an indication of the mechanical properties which might be expected. Micrographs shown in Figs. 88, 89, and 90 illustrate the changes that take place at different tempering temperatures.

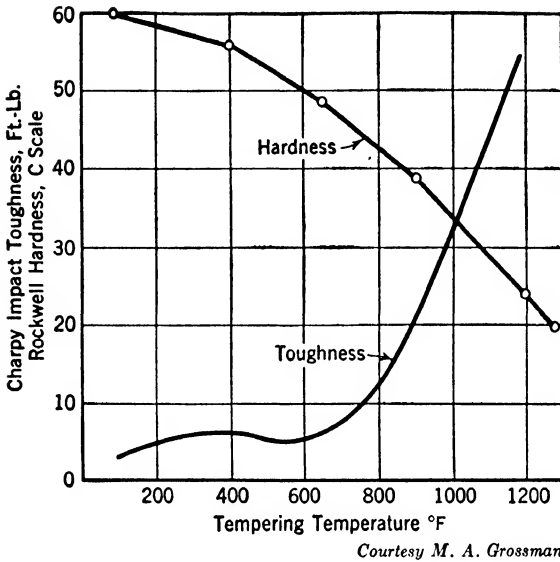


FIG. 87. Hardness and impact toughness of hardened carbon steels when tempered at various temperatures for 1 hr.

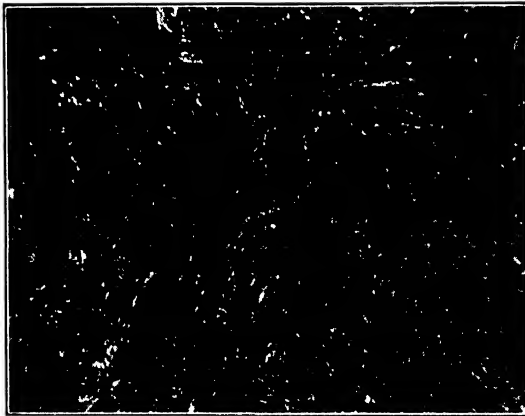


FIG. 88. Troostite. Composition: Carbon 0.90%. Etchant: picral. Treatment: quenched from above  $A_c3$  and tempered at 800°F for 1 hr.  $\times 1000$ .

The effect of different heat treatments upon the mechanical properties of medium carbon steel is shown in Table 20.

Usually carbon tool steels used for machining or punching soft steels are tempered for one hour between 350–500°F. When martensite is

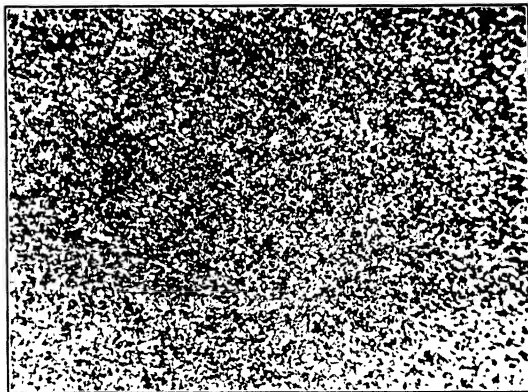


FIG. 89. Sorbite. Composition: Carbon 0.86%. Treatment: Quenched from above  $A_{c3}$  and tempered at 1100°F for 1 hr.  $\times 1000$ .

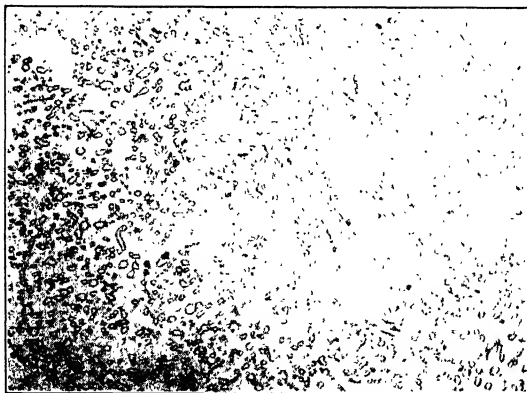


FIG. 90. Spheroidized carbide. Composition: Carbon 0.86%. Treatment: quenched from above  $A_{c3}$  and tempered at 1300°F for 10 hr.  $\times 1000$ .

tempered at temperatures as low as 212°F there is an increase in density and the white acicular structure precipitates  $Fe_3C$  and tempers to troostite over a period of about 1000 hours. This tempering lowers the Brinell hardness by about 100 points, or from 850 to 750.

**Austenite Transformation at Constant Temperature.** If a steel specimen is quenched in a molten alloy bath at some temperature below the critical such as 500°F and held at this temperature until all the



TABLE 20. THE EFFECT OF VARIOUS HEAT TREATMENTS UPON THE MECHANICAL PROPERTIES OF MEDIUM-CARBON STEELS\*

Chemical composition: C .38%, Mn .55%, Si .05%, P .024%, S .050%.

Description of pieces treated: 1-in. rounds, 29 in. long; 14 pieces, all from same billet.

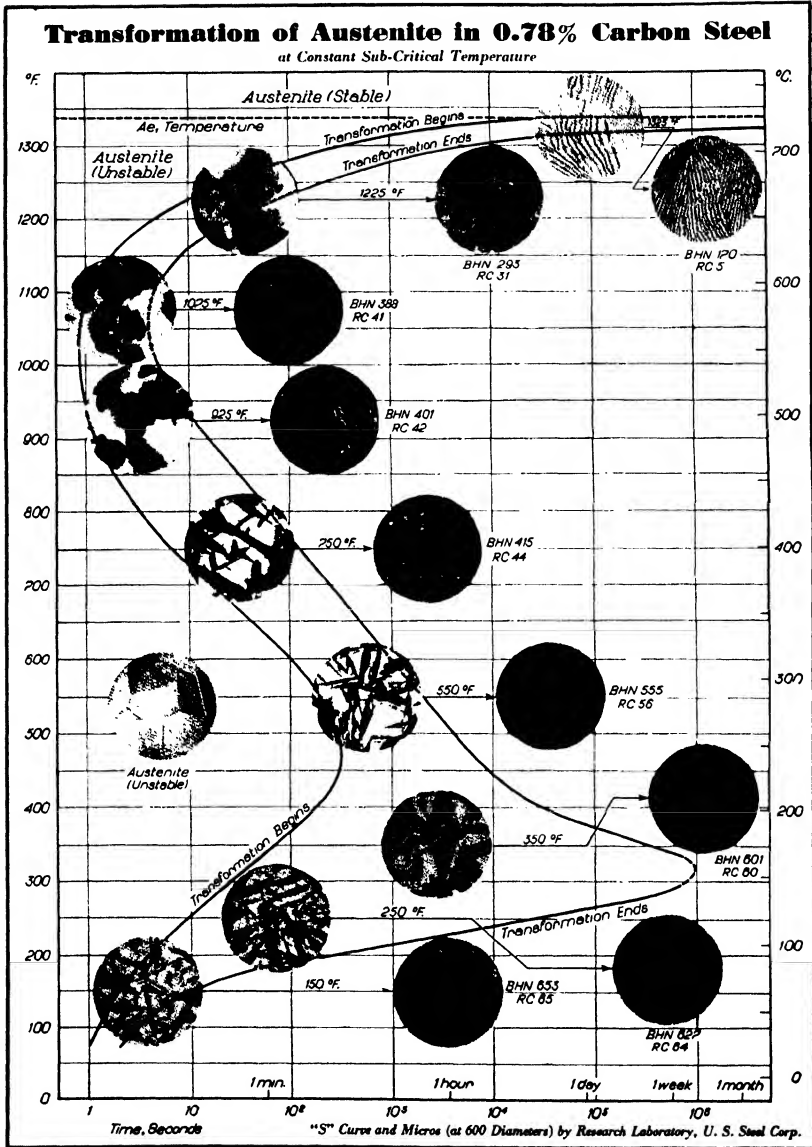
Description of test pieces: One test piece from each of the 14 pieces, turned to a diameter of  $\frac{1}{2}$  in.

Heat Treatment		Physical Tests					
Hardening and refining, °C	Anneal and draw, °C	Tensile strength	Elastic limit	Elong. in 2", %	R.A. %	Brinell number	Sclero-scope test
As rolled		85,000	50,000	30.0	48.9	163	25
Heated to 760° and cooled in furnace		74,000	42,500	32.0	54.7	134	23
Heated to 815°; quenched in oil		100,000	67,000	21.0	53.9	179	30
	427	98,000	66,000	23.5	52.8	170	29
	538	90,000	59,000	26.5	54.7	170	29
	593	89,000	58,000	26.5	63.5	170	29
	649	75,000	53,000	33.5	64.7	156	27
	704	71,000	51,000	34.0	59.3	137	25
Heated to 815°; quenched in water		110,000	81,000	19.0	46.0	223	33
	427	103,000	71,000	22.5	54.7	192	35
	538	95,000	68,500	23.5	61.6	187	32
	593	89,000	63,000	28.5	63.0	179	29
	649	82,000	57,500	30.5	65.4	156	26
	704	73,000	51,000	34.0	59.8	143	25

\* Camp and Francis, *The Making, Shaping and Treating of Steel*, 5th ed., 1940, p. 885.

austenite is transformed, the product will not be exactly the same as would be obtained by quenching in water and tempering at 500°F. The results of the transformation of austenite at constant temperature (isothermal transformation) are shown in Fig. 91. Such a chart, or S-curve as it is often called, represents the data for a single steel which in this case was a carbon steel of eutectoid composition. Each steel has a characteristic austenite decomposition rate and will, therefore, have a different S-curve. It should be noted that temperature in degrees Fahrenheit has been plotted against time in seconds on a logarithmic scale.

Such a curve is worked out experimentally by determining the time required for austenite to begin to transform and the time at which transformation is complete at each temperature level. For example, suppose the temperature of 500°F is selected. Two furnaces are required, one at a high temperature within the austenitic field, and the second at a low temperature having a salt bath or low fusing alloy held constant at 500°F. Several small pieces of steel are heated to the austenitic condition. The first piece is quenched in the 500° bath, held at this temperature for a short interval of perhaps five seconds, and again quenched



Courtesy Bain and Davenport

FIG. 91. Isothermal transformation of eutectoid carbon steel.

in water. The second specimen is quenched to the same temperature but held longer, about ten seconds, and quenched in water. Each successive piece is held a slightly longer period of time at 500° before quenching in water. All samples are then examined with the microscope. The first samples that have not begun to transform at 500° are completely martensitic in structure and in partly transformed specimens all austenite remaining at 500° when quenched in water is also changed to martensite. By estimating the relative amount of martensite in each specimen it is possible to determine the time required for the beginning and completion of the transformation of austenite at any temperature level. All other temperature levels are handled in the same manner as the one discussed.



FIG. 92. Tempered martensite or acicular troostite or bainite in a martensitic matrix. Treatment: quenched from 1650°F in salt quenching bath maintained at 350°F; held 1 hr to obtain about 50% transformation of austenite to bainite and quenched in water to transform remaining austenite to martensite.

The temperature of transformation has a pronounced effect on the properties of the steel. When austenite of eutectoid composition transforms at high temperature, for example about ten degrees below the  $A_{e1}$ , the structure is coarse lamellar pearlite which has a hardness of about 170 Brinell. When the steel is transformed at 1000–1100°F the structure is very fine. It can be resolved only with great difficulty but has been shown to be fine pearlite. The transformed patches make their appearance as nodular patches which etch dark. The hardness is about 401 Brinell (42 Rockwell C). At about 850°F the transformation product is of the acicular type which persists to low temperatures where martensite is formed. This structure is acicular troostite or tempered martensite and has been called Bainite (Fig. 92). Its hardness gradually increases as the temperature of transformation is lowered from about 850 to 400°F.

An advantage of such a treatment (Austempering) over the conventional method of quenching and tempering seems to be in increased toughness in the high hardness range without any danger from cracking; however, it takes about a week for a plain carbon steel of 0.80% C to transform to its maximum hardness of 60 Rockwell C at about 350°F, so the long time involved limits its application. Small sizes only can be successfully or economically treated. If sections are too large they partly transform to fine pearlite between 1000° and 1100°F and consequently there is less austenite remaining for the low temperature transformation between 250° and 350°F. The shape of an isothermal curve is materially affected by both the carbon and the alloy content. Curves for many types of steels have been published and are available in the literature.

In summarizing the heat treatment of carbon steel the reader is referred to Fig. 93 which summarizes the microstructures formed when a carbon steel of eutectoid composition is given various heat treatments.

#### ALLOY STEELS

Alloy steels contain one or more alloying elements, other than carbon, in sufficient proportion to modify or improve substantially some of its physical or mechanical properties.

Usually alloying elements are added to steels in order to

1. Improve strength at ordinary temperatures.
2. Increase depth of hardening so larger sections can be treated.
3. Refine grain size and obtain higher impact toughness.
4. Improve strength at high temperatures.
5. Increase resistance to corrosion.
6. Increase resistance to abrasion for wear resistance.
7. Improve magnetic properties.

The trends of influence of various alloying elements and also their specific effects are shown in Table 21(a).

Table 22 gives the general classes of S.A.E. structural alloy steels recognized in industry. In the automotive and tractor fields there is considerable overlapping of different steels for the same usage, but this is not surprising because the S.A.E. structural steels are all substantially equivalent on the basis of mechanical properties, provided:

1. The sections are so chosen that they are hardened throughout on quenching.
2. They are tempered to the same tensile strength irrespective of the tempering temperature necessary to produce that tensile strength.
3. A tensile strength of 200,000 psi is not exceeded.

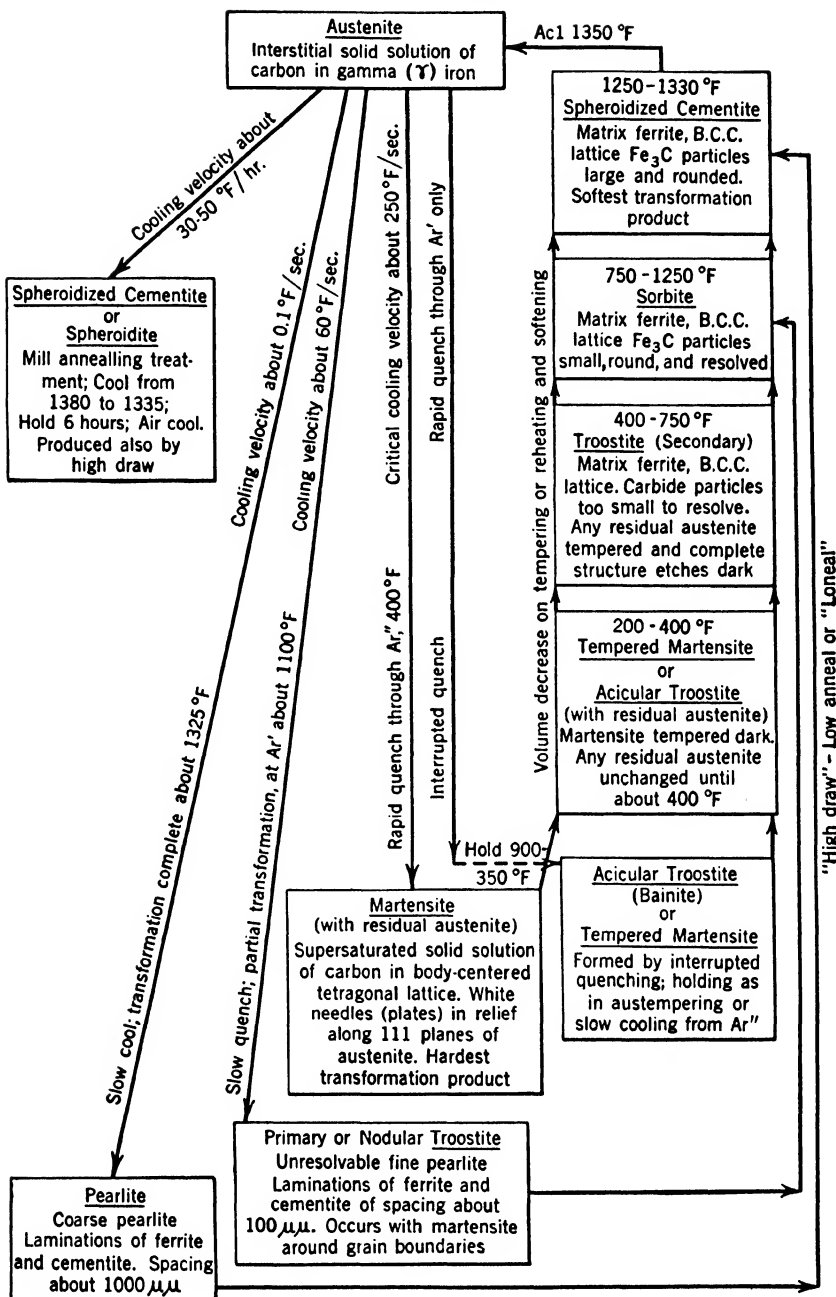


FIG. 93. Austenitic transformation of eutectoid carbon steel.

TABLE 21(a). SPECIFIC EFFECTS OF ALLOYS IN STEEL\*

Element	Solubility		Influence Exerted Through Carbides			Influence on ferrite	Principal Functions
	In gamma iron	In alpha iron	Carbide-forming tendency	Effect on hardenability	Action during tempering		
Aluminum Al	1.1% (Increased by C)	30% ±	Less than Fe (graphitizes)	Mildly positive (if any dissolved in austenite)		Harden considerably by solid solution.	1. Deoxidizes efficiently. 2. Restricts grain growth (by forming dispersed oxides or nitrides). 3. Alloying element in nitriding steel.
Chromium Cr	12.8% (20% with 0.5% C)	Unlimited	Greater than Mn. Less than W	Moderate (up to 1% more effective than Mn)	Mildly resists softening.	Hardens slightly (increases corrosion resistance).	1. Increases corrosion and oxidation resistance. 2. Increases hardenability. 3. Contributes some strength at high temperatures. 4. Resists abrasion and wear (with high carbon).
Cobalt Co	Unlimited	80% ±	Similar to Fe	Negative (that is, decreases it)	Sustains hardness by solid solution.	Hardens by solid solution.	1. Contributes to red hardness by hardening ferrite.
Manganese Mn	Unlimited	15 to 18%	Greater than Fe Less than Cr	Moderate (Ni < Mn < Cr) (retains austenite)	Very little, in usual percentages.	Hardens markedly and reduces plasticity.	1. Counteracts embrittlement by inevitable sulfur. 2. Increases hardenability inexpensively. 3. Forms batter-resistant steel (high Mn, high C).
Molybdenum Mo	3% ± (8% with 0.30% C)	32% (less with lower temperatures)	Strong Greater than Cr	Great (when dissolved) Mo > Cr	Opposes softening by secondary hardening.	Gives age hardening systems in high Mo-Fe alloys.	1. Raises coarsening temp nature of austenite. 2. Deepens hardening. 3. Raises hot strength, creep resistance, and red hardness. 4. Enhances corrosion resistance in stainless.
Nickel Ni	Unlimited	25% ± (irrespective of carbon content)	Less than Fe (graphitizes)	Mild (retains austenite in medium-carbon steels)	Very little in small percentages.	Strengthens and toughens by solid solution.	1. Strengthens unquenched or annealed steels. 2. Toughens pearlitic-ferritic steels (especially at low temperature). 3. Renders high chromium-iron alloys austenitic.

\* Courtesy of *Metal Progress*, 1940 Reference Issue, p.386, adapted from Edgar C. Bain, *The Functions of the Alloying Elements in Steel*, A. S. M.

TABLE 21(a). (Continued)

Element	Solubility		Influence Exerted Through Carbides			Influence on ferrite	Principal Functions
	In gamma iron	in alpha iron	Carbide-forming tendency	Effect on hardenability	Action during tempering		
Phosphorus P	0.5%	2.5% (irrespective of carbon content)	Nil	Moderate	Sustains hardness by solid solution.	Effective hardener by solid solution effect.	1. Strengthens low-carbon steel. 2. Increases resistance to corrosion. 3. Improves machinability in free-cutting steels.
Silicon Si	2% ± (9% with 0.35% C)	18.5% (even with considerable carbon)	Negative (graphitizes)			Hardens with loss in plasticity. Mn < Si < P	1. Used as general-purpose deoxidizer. 2. Alloy for electrical and magnetic sheet. 3. Improves oxidation resistance. 4. Increases hardenability of steels carrying nongraphitizing elements.
Titanium Ti	0.75% (1% with 0.20% C)	6% ± (less with lower temperatures)	Maximum (2% Ti renders 0.50% carbon steel unhardenable)	Strong, if dissolved (persistent carbides restrain grain growth and withhold carbon; therefore reduce hardenability).	Persistent carbides probably unaffected.	Age-hardening systems in high Ti-Fe alloys.	Strengthens low-alloy steels. 1. Fixes carbon in inert particles. (a) Reduces martensitic hardness and hardenability in medium-chromium steels. (b) Prevents formation of austenite in high-chromium steels. (c) Prevents localized depletion of chromium in stainless steels during long heating.
Tungsten W	6% ± (11% with 0.25% C)	32% (less with lower temperatures)	Strong	Considerable, especially in small percentages	Opposes softening by secondary hardening	Age-hardening systems in high W-Fe alloys.	1. Forms hard, abrasion-resistant particles in tool steels. 2. Promotes red hardness and hot strength.
Vanadium V	1 to 2% (4% with 0.20% C)	Unlimited	Very strong (V < Ti or Cb)	Marked (when dissolved)	Maximum for secondary hardening.	Hardens moderately by solid solution.	1. Elevates coarsening temperature of austenite (promotes fine grain). 2. Increases hardenability (when dissolved). 3. Resists tempering. 4. Gives marked secondary hardening.

TABLE 21(b). RELATIVE MERIT OF ALLOYS IN STEEL AS REGARDS INFLUENCE ON SPECIFIC PROPERTIES OR RESPONSES\*

Carbon 0.10 to 0.30%	Carbon 0.30 to 0.85%	Manganese 0.25 to 2.00%	Phosphorus up to 0.15%	Sulfur up to 0.30%	Silicon up to 2.00%	Chromium up to 1.10%	Nickel up to 5.00%	Molybdenum up to 0.75%	Vanadium up to 0.25%	Copper up to 1.10%
ABRASION RESISTANCE; Steel as rolled, as forged, or normalized										
+3 L	+10 P	+8 L	0	0	+2 P	+7 P	+3 P	+4 P	0	+1 P
WEAR RESISTANCE; Steel fully hardened (no free ferrite) to C-60, drawn at 300 to 400°F										
0	+10 P	+6 P	+1 P	0	+2 P	+8 P	+3 L	+5 P	+2 P	+
ANNEALING; Degree of accuracy necessary to control temperature when annealing to lamellar pearlite										
+3 L	+5 P	-2 L	0	0	-2 P	+3 P	-5 P	-3 L	+2 P	-
CARBURIZING; Depth of case only										
0	-4 P	+5 P	0	0	-10 L	+2 P	-3 P	-2 P	+2 P	-10 L
CORROSION in atmosphere or weakly corrosive liquids										
-3 P†	-6 P	0	+10 P	-10 P	+2 P	0	+6 L	+2 P	0	+10 S
CREEP RESISTANCE at temperatures up to 950°F; Steels drawn at higher temperatures										
+2 I	-3 P	0	0	0	0	+1 P	0	+10 P	?	?
DISTORTION ON OIL QUENCHING, and susceptibility to quench cracks (effect of volume change at transformation)										
-1 P	-2 P	-4 P	-3 P	0	-1 P	-4 P	-2 P	-3 P	-1 I	0
DISTORTION ON WATER QUENCHING and drawing (and susceptibility to quench cracks)										
-2 P	-4 P	-7 P	-6 P	0	-3 P	-7 P	-7 L	-5 P	-2 I	-
FABRICATION IN DEEP DRAWING; Breakage of strip or sheet										
-4 P†	-10 P	-10 P	-10 P	-10 P	-10 S	-10 S	-10 S	-10 P	-	-10 P
FABRICATION IN COLD BENDING										
-2 L	-10 P	+2 I	-10 L	-7 P	-6 P	-10 P	+5 S	+3 S	+3 P	+2 P
HOT WORKABILITY; Formation of seams, scale, decarburized skin, resistance to flow										
+2 P	-7 P	+7 S	-10 S	0	-5 P	0	-6 P	-3 P	0	-10 S
HARDENABILITY or hardness penetration (Basis: Steel with 0.70 to 1.00% manganese)										
+1 P	+2 P	+10 P	+3 P	-2 P	+2 S	+7 S	+10 L	+7 S	+5 I	+
MACHINABILITY; Steel as rolled, as forged, or normalized										
+2 P	-2 P	-6 P	+6 P	+10 P	-2 P	-2 P	-10 P	-5 P	0	-

\* Courtesy John Mitchell, *Metal Progress*, July, 1942, p. 56.

† Rating based on carbon range of 0.0 to 0.30%. Code:

Zero to +10 for strongest favorable effect.

Zero to -10 for strongest unfavorable effect.

P means effect is proportional to amount of alloy.

S means small quantities are most effective.

L means large quantities near the top of the range, are needed.

I means intermediate amounts are most effective.

+ (?) means probable positive influence.

- (?) means probable negative influence.



TABLE 21(b). (Continued)

Carbon 0.10 to 0.30% 0.30%	Carbon 0.30 to 0.85%	Manganese 0.25 to 2.00%	Phosphorus up to 0.15%	Sulfur up to 0.30%	Silicon up to 2.00%	Chromium up to 1.10%	Nickel up to 5.00%	Molybdenum up to 0.75%	Vanadium up to 0.25%	Copper up to 1.10%
MACHINABILITY; Steel annealed to maximum lamellar pearlite										
+2 P	+3 I	-2 L	+6 P	+10 P	-2 L	-2 P	-10 P	-4 P	-1 P	-(?)
MACHINABILITY; Steel quenched and drawn to 300 Brinell										
0	0	-2 L	+4 P	+8 P	-2 P	0	-10 P	-4 P	0	-(?)
MACHINABILITY; Steel quenched and drawn to 400 Brinell										
0	0	-4 L	+2 P	+3 P	-2 P	0	-10 P	-4 P	?	-(?)
STRENGTH; Steel as rolled, as forged, or normalized										
+4 P	+10 P	+5 P	+5 P	-2 P	+7 P	+5 P	+5 P	+5 P	0	+1 P
TOUGHNESS AT ROOM TEMPERATURE (as judged by reduction of area in the tensile test or by notched bar impact test); Steel as rolled, or as forged										
-3 P	-8 P	+2 I	-8 P	-6 P	-2 P	-8 P	+10 P	+3 S	+2 P	+1 L
TOUGHNESS; Steel as normalized										
-2 P	-6 P	+3 I	-6 P	-4 P	-2 L	-6 P	+10 S	+5 P	+5 P	+2 P
TOUGHNESS; Steel fully quenched and drawn to 300 Brinell										
0	-1 P	0	-5 P	-3 P	0	0	+6 P	+2 S	+1 P	+(?)
TOUGHNESS; Steel fully quenched and drawn to 400 Brinell										
0	-2 P	0	-6 P	-3 P	0	0	+7 P	+4 S	+2 S	+(?)
TOUGHNESS; Steel fully quenched and drawn to 300 to 400°F										
0	-8 P	-4 L	-10 P	-5 P	+2 L	-8 P	+10 S	+4 S	+3 S	+(?)
TOUGHNESS AT ROOM TEMPERATURE; Steel fully quenched and drawn to 400 to 600°F										
0	-2 P	-4 P	-4 P	0	0	-5 P	-2 I	0	0	?
TOUGHNESS AT -50°F; Steel as rolled or as forged (Basis: Notched bar impact test, specimen at -50°F)										
-3 P	-10 P	+2 I	-10 S	-6 P	-1 P	-10 P	+10 S	+3 S	+3 P	+(?)
TOUGHNESS AT -50°F; Steel as normalized at 1650°F, but below grain-coarsening temperature										
-3 P	-10 P	+2 I	-8 P	-4 P	-1 L	-8 P	+10 S	+5 S	+5 P	+(?)
TOUGHNESS AT -50°F; Steel fully quenched and drawn to 300 Brinell										
0	-2 P	0	-5 P	-3 P	0	0	+10 P	+2 S	+1 P	+(?)
TOUGHNESS AT -50°F; Steel fully quenched and drawn to 400 Brinell										
0	-6 P	0	-7 P	-4 P	+2 P	0	+10 S	+4 S	+2 S	+(?)
TOUGHNESS AT -50°F; Steel fully quenched and drawn at 300 to 400°F										
0	-10 P	-8 L	-10 P	-6 P	+2 L	-10 P	+10 S	+4 S	+4 S	+(?)
WELDABILITY; Susceptibility to small ruptures when fusion welding without preheating or post heating										
-2 L	-10 P	-10 L	-7 L	-3 P	-6 L	-10 L	-10 L	-10 L	+1 P	-4 L

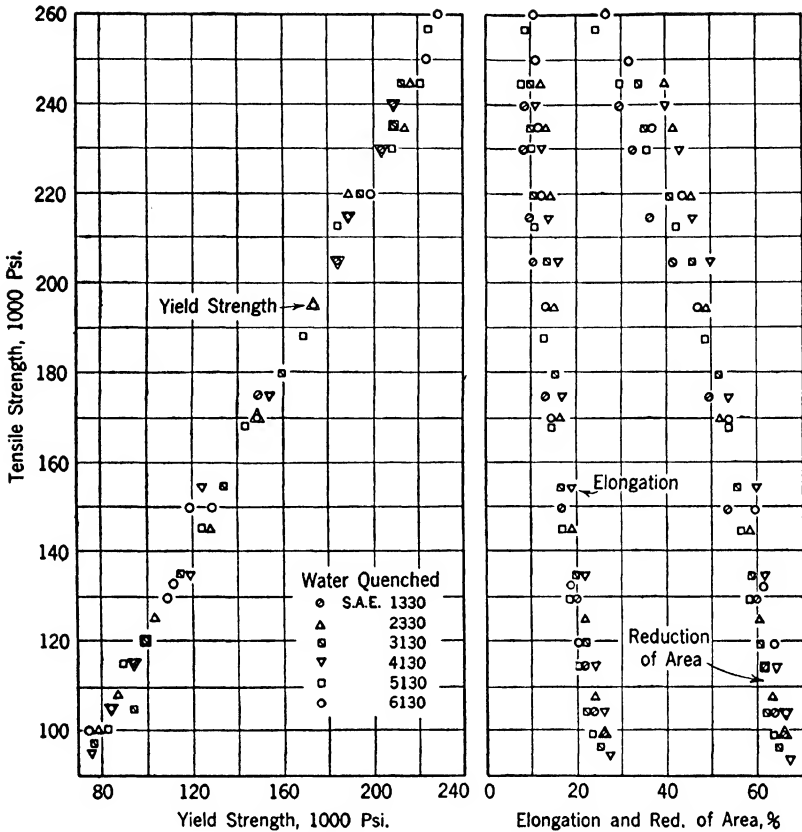
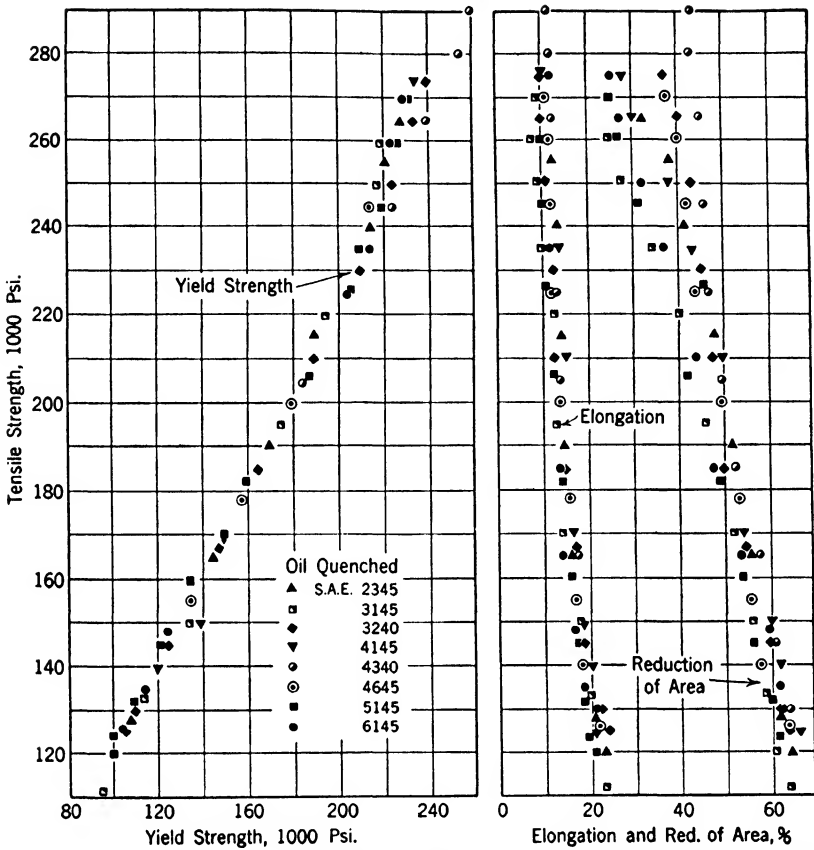


FIG. 94. Data on the tensile properties of several S.A.E. water-hardened steels. One-inch round bars were normalized, hardened according to S.A.E. recommendations, then tempered at various temperatures from 400–1300°F.

Fig. 94 and Fig. 95 give the relationship of mechanical properties of these tempered steels after water or oil quenching. Fig. 96 shows that low alloy steels are more resistant to tempering than the 1300 series, which are essentially carbon steels.

In general it may be said that alloying elements having a crystal structure similar to that of gamma-iron (f.c.c.), and which are completely soluble in  $\gamma$ , will cause retention of a comparatively stable austenite at room temperature if present in sufficient quantities. These elements are manganese and nickel.

**Hardenability.** One of the most important reasons for using alloy steels instead of carbon steels is for an increase in depth of hardening.



Courtesy E. J. Janitzky and M. Baeyerz, A.S.M. Handbook, 1939.

FIG. 95. Data on the tensile properties of several S.A.E. oil-hardening steels. One-inch round bars were normalized, hardened according to S.A.E. recommendations, then tempered at various temperatures from 400–1300°F.

Larger sections can be hardened to a greater depth and consequently greater strength is obtained throughout the thicker sections than obtains with carbon steel.

A list of elements affecting hardenability of steel is arranged in the following decreasing order of effect:

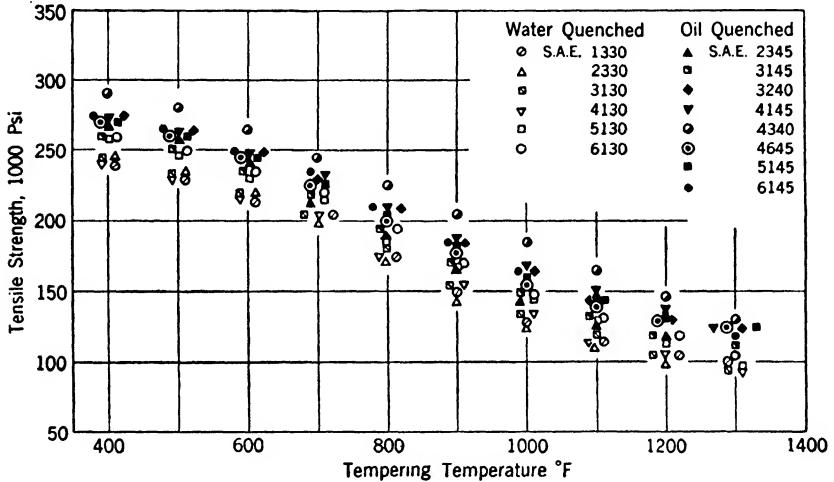
- Highest Hardenability and Poorest Weldability
- C   P   S   Mo   V   Si   Cr   Mn   Cu   Ni

A recent view of weldability is that it is the reverse of hardenability. This does not mean that there is difficulty in melting or fusion, but that unannealed welds with large amounts of elements on the left end of the

series will be harder and less ductile as welded than if the elements are lower and toward the right.

The Bethlehem Steel Company suggested a list of alloying elements with a factor for each 0.01 per cent of the given element for calculating the strength of alloy steels in the same condition of heat treatment. The list is similar to one used by the Ryerson Company.

P	C	V	Mo	S	Mn	Cr	Si	W	Ni	Cu
40	30	20	16	16	8	5	5	4	4	4



Courtesy E. J. Janitzku and M. Baeyerz, *A.S.M. Handbook*, 1939.

FIG. 96. Change in tensile strength with increase in tempering temperature for water- and oil-hardening steels. Specimens were held at tempering temperatures for 30 min.

Another series of elements for hardenability was proposed by Burns, Moore, and Archer:

C	Cr	Mn	Ni	Cu	
1000	500	400	100	100	(for 0.45% C steels)

Recently Burns and Riegel rated hardenability as follows for three different carbon contents:

C	Cr	Mn	Ni	Cu	
2000	500	500	100	25	(for 0.10–0.35% C steels)
1000	500	500	100	25	(for 0.35–0.50% C steels)
500	500	500	100	25	(for 0.50–1.00% C steels)

The proper order of elements for a hardenability rating depends on grain size, carbon content, combinations with other elements, etc., and it may be a long time before metallurgists are in agreement on this

important question. The hardenability effect of the various elements mentioned is supposed to be proportional to the numerals accompanying them.

The elements having a strong influence for grain refining are aluminum as  $\text{Al}_2\text{O}_3$ , zirconium as  $\text{ZrO}_2$ , chromium as  $\text{Cr}_2\text{O}_3$ , and titanium, aluminum, and zirconium as nitrides. The elements classed as ferrite formers, which are not in the carbide phase ( $\text{Fe}_3\text{C}$ ), are phosphorus, silicon, copper, nickel, and aluminum. Manganese is a weak carbide former and also strengthens ferrite. The carbide-forming elements which are present in annealed steels mainly as carbides, if sufficient carbon is present, are titanium, vanadium, tungsten, molybdenum, and chromium to some extent.

The amounts of alloying elements commonly used in commercial alloy steels are given as follows<sup>5</sup> with only slight modifications:

- P Under 0.04% in heat-treated steels; around 0.10% in some free-machining steels; up to 0.15% in low-carbon, high-yield-strength steels.
- S Under 0.055% in heat-treated steels; 0.10–0.30% in some free-machining steels in conjunction with high manganese. (Not an alloying element.)
- C 0.10–0.20% in carburizing, and 0.07–0.15% in high-yield-strength steels for welding; 0.20–0.40% in most constructional steels and castings; 0.40–1.20% in various spring and tool steels.
- Mn Over 0.25% and under 2% in most structural steels; 12–14% in austenitic castings.
- Si Very low in rimming steels; from 0.10–0.30% in most S.A.E. steels; around 0.50% in castings; up to 0.75% in high-yield-strength steels; 1–1.75% in graphitic steels; up to 2% in spring steels; still higher in low-carbon steels for electric uses.
- Cu About 0.20% in “copper-bearing” atmospheric-corrosion resistant steels; up to 1% in high-yield-strength steels; to 2% in steels for precipitation hardening.
- Ni Usually 2.50–3.50% when used alone; up to 5% in carburizing steels; 0.50–3.75% in complex steels. 7% or more added to corrosion-resistant Cr austenitic steels. Special uses for higher Ni steels.
- Cr Under 1.50% in most structural steels for heat treatment; 0.50–4% in tool steels, larger amounts in still-tube steels; 12–30% in corrosion-resistant “stainless” steels.
- Al 0.01–0.10% for grain-size control. Seldom used as ordinary alloying element, save 1–2% in special nitriding and up to 5% in special heat-resisting steels.
- Ti 0.01–0.20% for grain-size control; up to 0.80% in austenitic stainless steels to stabilize carbides, and in nonhardening 5% Cr steels.
- V 0.01–0.20% for grain-size control and slight alloying effect; 0.25–5% in tool steels.
- Mo About 0.20% in constructional steels, smaller amounts in high-yield-strength steels; 0.50–1.50% in steels for high temperature service, up to 9% in tool steels.
- W Very rarely used in constructional steels. Around 1–2% in steels for high temperature service; 0.50–20% in tool steels; 5.00–9.00% in magnet steels.

<sup>5</sup> Bullens-Battelle, *Steel and Its Heat Treatment*, Vol. II, 4th ed., pp. 178–179, 1939.

In general, the alloying elements lower the eutectoid composition to less than 0.80% C. The austenite formers lower the critical points and the carbide formers raise the critical points, with the exception of chromium if the carbon is low.

The effect of carbon is far greater than the effect of like amounts of alloying elements on the physical properties of hot-rolled steels if phosphorus is excluded as the element having the most potent effect.

With most S.A.E. steels,

0.1% carbon lowers	$Ac_3$ about 4°F; increases tensile strength.
0.01% Mn lowers	$Ac_3$ about 0.5° ; increases T.S. about 110–250 psi.
0.01% Ni or Cu lowers	$Ac_3$ about 0.4° ; increases T.S. about 100 psi.
0.01% P raises	$Ac_3$ about 8°
0.01% Si raises	$Ac_3$ about 0.5°
0.01% V raises	$Ac_3$ about 0.6°
0.01% Mo raises	$Ac_3$ about 1.3°
0.01% W raises	$Ac_3$ about 0.5°
0.01% Cr raises	$Ac_3$ with high C; increases T.S. about 60–200 psi.
0.01% Sn	increases T.S. about 1000 psi.

**Gamma Loops.** When a number of alloying elements, ferrite and carbide formers, such as Si, P, Mo, W, V, Cr, are added to iron, individu-

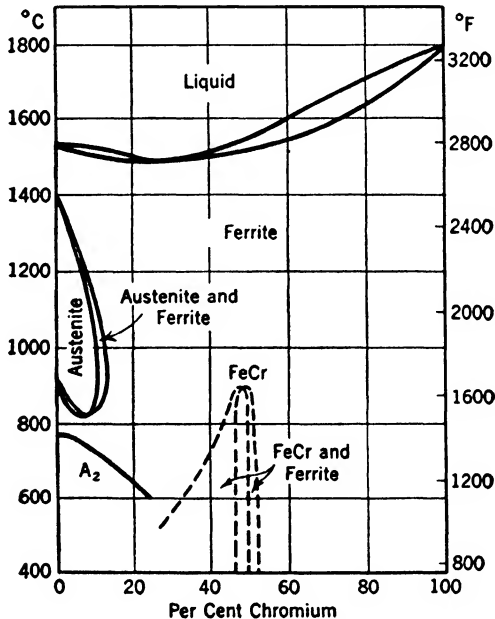


FIG. 97. Iron-chromium constitution diagram.

ally or in combination, they form the so-called  $\gamma$ -loop, illustrated in Fig. 97.

In these cases the elements raise the  $A_3$  transformation and with increased carbon the loops are enlarged by extension of the  $\gamma$  field to the right. Alloys having composition just beyond the nose of the loop remain ferritic and are not capable of hardening by quenching because

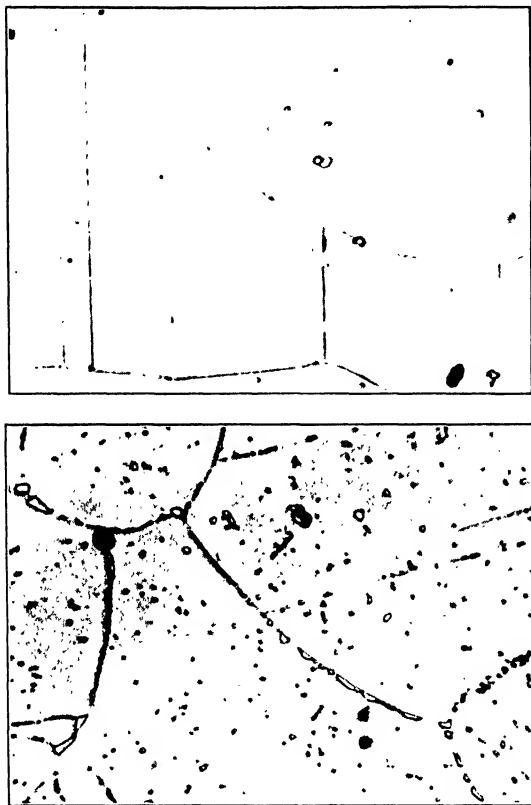


FIG. 98. Stainless steel. *Above*, 18% Cr, 8% Ni, 0.08% C. Structure is twinned austenite. Treatment: water-quenched from 2100°F.  $\times 1000$ . *Below*, same after heating 1000 hr at 1600°F. Showing precipitation of chromium carbide at grain boundaries which aids in intergranular embrittlement and decreases corrosion resistance.  $\times 1000$ . Mo bearing stainless steels not susceptible to this type of corrosion at same heat treatment.

$\delta$ - and  $\alpha$ -irons are the same modification; i.e., the 18 per cent chromium steel of low carbon is ferritic and strongly magnetic. On the other hand, a low carbon alloy of 18% Cr and about 8% Ni can be made about 100% austenitic ( $\gamma$ -solid solution) and nonmagnetic by quenching (Fig. 98). In the first case the composition falls outside the nose of the loop and in the second case the  $\gamma$  field is extended by the addition of nickel.

The  $\alpha$ - $\delta$  steels are very susceptible to grain growth at elevated temperatures because they have no transformation to the face-centered lattice and, therefore, cannot recrystallize. All grain refining must, therefore, be done by the cold-working and annealing process the same as for copper and brass.

A classification of commercial steels, including plain carbon, alloy, and some special alloys, is given under the following headings and is based on service classification.

1. Structural steels
  - S.A.E. steels
  - A.I.S.I. standard steels
  - National Emergency alloy steels
  - Stainless steels
  - Low alloy high-yield-strength steels
  - Hadfield manganese steels — austenitic, high manganese
2. Tool steels
  - Carbon, alloy, and high-speed steels
  - Graphitic steel
3. Magnetically soft steels
4. Permanent magnet steels and alloys
5. High temperature steels
6. Valves and valve seat steels
7. Low expansion steels
8. Low temperature steels (below room temperature)

TABLE 22. CLASSIFICATION OF STEELS

1. Structural Steels

- (a) *S.A.E. Steels*; carbon, free-cutting, medium-alloy, and corrosion- and heat-resisting steels.

*Authors' note:* Free-cutting steels (screw stock) with higher P and S are for breaking the chips easier by lowering the ductility. Lead additions to free-machining steels, between 0.10–0.25%, appear to increase machinability about 20%. Also added to alloy grades. Segregation of lead in stringers is common. Mechanical properties as follows:

	Hot-Rolled S.A.E. 1020 (No lead)	Hot-Rolled S.A.E. 1020 (Same heat + 0.25% Pb)
Tensile strength	58,000 psi	58,500 psi
Yield point	39,500	39,500
Elongation, %	31	28.5
Reduction in area, %	56	51
Charpy impact	36.5	35
Brinell hardness	106	106

- (b) *A.I.S.I. Steels*; standard steel compositions were proposed by the American Iron and Steel Institute and the Society of Automotive Engineers in January,



1942, to simplify the several thousand different types of steel made up to that time and these organizations have made a great forward step toward simplification.

See Table 22(a).

- (c) *Stainless Steels*; martensitic, ferritic, austenitic. Chromium is the main element for corrosion resistance by film effect of  $\text{Cr}_2\text{O}_3$ . Nickel also increases corrosion resistance and improves hot-working characteristics. Mo improves corrosion resistance. Cb ten times carbon content and Ti minimum four times carbon content improves corrosion properties after welding and largely eliminates intergranular corrosion adjacent to welds.

See Tables 22(b) and 22(c).

- (d) *Low-Alloy High-Yield-Strength Steels*.

Trade names: Cor-Ten, Man-Ten, Sil-Ten, Yoloy, R.D.S., Hi-Steel, H.T.50, A.W.Dyn.El., Jal-Ten, Konik, Mayari R, etc.

Yield point raised from 30–40,000 psi for carbon steels to 45–65,000 psi.

Comp: Carbon 0.10–0.30, Mn 0.10–1.75, Si 0.10–1.00, Cu 0.10–1.50, Ni 0–2.00, Mo 0–0.40, P 0.035–0.20, Cr 0–1.50, V 0–0.20. Cu, P, and Cr added for corrosion resistance and increased strength.

- (e) *Hadfield Manganese Steel* (mostly cast).

Austenitic — high manganese.

Comp: C 1.00–1.40, Mn 10.00–14.00, Si 0.30–1.00, S 0.05 max, P 0.10 max.

Tensile strength 130,000–160,000 psi.

Proportional limit 40,000–60,000 psi (No Y.P.).

Elongation in 2 in. 60–70%.

Reduction of area, 60–70%.

Brinell hardness 200–230.

Austenitized 1830–1940°F by water quenching.

Wear resistant under heavy abrasion only by recrystallization  $\gamma \rightarrow \alpha$ , increasing BHN 450–550.

Uses: rail crossings, dipper teeth, rock-crushing machinery.

## 2. Tool Steels

- (a) *Carbon, Alloy, and High-Speed Steels*.

See Tables 22(d), 22(e), and 22(f).

- (b) *Graphitic Tool Steels*.

Recommended by F. R. Bonte and Martin Fleishmann, Timken Roller Bearing Co.

Graph-Sil: Si 1.00, C 1.50, combined C < 0.90%.

See Table 22(g).

Graph-Mo: Similar to Graph-Sil with Mo 0.25–0.30.

Advantages claimed: easy machining in annealed state; increased life for drawing dies, punches, coining dies, etc.

Treatment: After annealing, quench in water or oil from 1450°F, temper 300°F.

Structure: Martensite matrix and free graphite.

Rockwell "C" hardness 61–62 for production without chipping, dulling or spalling.

Hot roll or forge < 2000°F without difficulty.

**3. Magnetically Soft Steels**

Carbon preferred 0.005%; should not be over 0.01%.

See Tables 22(*h*), 22(*i*), and 22(*j*).

**4. Permanent Magnet Steels and Alloys**

See Tables 22(*k*) and 22(*l*).

**5. High Temperature Steels**

Service at 750–1100°F.

See Tables 22(*m*) and 22(*n*).

**6. Valves and Valve Seat Steels and Alloys**

See Table 22(*o*).

**7. Low Expansion Steels**

Low carbon, high alloy, mostly nickel.

See Table 22(*p*).

**8. Low Temperature Steels**

See Table 22(*q*).

TABLE 22(a). STANDARD STEEL COMPOSITIONS

Jointly Issued, January 21, 1942. Revised, Feb. 1, 1943, by American Iron &amp; Steel Institute and Society of Automotive Engineers

OPEN-HEARTH ALLOY AND ELECTRIC FURNACE CARBON AND ALLOY STEELS (Blooms, Billets, Slabs, Bars, and Hot-Rolled Strip)									
A.I.S.I. No.	C	Mn	P Max*	S Max*	Si*	Ni	Cr	Mo	1942 S.A.E. No.
A	1330	0.28-0.33	1.60-1.90	0.040	0.040	0.20-0.35			1330
A	1335	0.33-0.38	1.60-1.90	0.040	0.040	0.20-0.35			1335
A	1340	0.38-0.43	1.60-1.90	0.040	0.040	0.20-0.35			1340
A	1345	0.43-0.48	1.60-1.90	0.040	0.040	0.20-0.35			
A	1350	0.48-0.53	1.60-1.90	0.040	0.040	0.20-0.35			
A	2317	0.15-0.20	0.40-0.60	0.040	0.040	0.20-0.35	3.25-3.75		{2315 2317
A	2330	0.28-0.33	0.60-0.80	0.040	0.040	0.20-0.35	3.25-3.75		2330
A	2335	0.33-0.38	0.60-0.80	0.040	0.040	0.20-0.35	3.25-3.75		
A	2340	0.38-0.43	0.70-0.90	0.040	0.040	0.20-0.35	3.25-3.75		2340
A	2345	0.43-0.48	0.70-0.90	0.040	0.040	0.20-0.35	3.25-3.75		2345
E	2512	0.09-0.14	0.45-0.60	0.025	0.025	0.20-0.35	4.75-5.25		
A	2515	0.12-0.17	0.40-0.60	0.040	0.040	0.20-0.35	4.75-5.25		2515
E	2517	0.15-0.20	0.45-0.60	0.025	0.025	0.20-0.35	4.75-5.25		
A	3115	0.13-0.18	0.40-0.60	0.040	0.040	0.20-0.35	1.10-1.40	0.55-0.75	3115
A	3120	0.17-0.22	0.60-0.80	0.040	0.040	0.20-0.35	1.10-1.40	0.55-0.75	3120
A	3130	0.28-0.33	0.60-0.80	0.040	0.040	0.20-0.35	1.10-1.40	0.55-0.75	3130
A	3135	0.33-0.38	0.60-0.80	0.040	0.040	0.20-0.35	1.10-1.40	0.55-0.75	3135
A	3140	0.38-0.43	0.70-0.90	0.040	0.040	0.20-0.35	1.10-1.40	0.55-0.75	3140
A	3141	0.38-0.43	0.70-0.90	0.040	0.040	0.20-0.35	1.10-1.40	0.70-0.90	{X3140 3141
A	3145	0.43-0.48	0.70-0.90	0.040	0.040	0.20-0.35	1.10-1.40	0.70-0.90	3145
A	3150	0.48-0.53	0.70-0.90	0.040	0.040	0.20-0.35	1.10 1.40	0.70-0.90	3150
A	3240	0.38-0.45	0.40-0.60	0.040	0.040	0.20-0.35	1.65-2.00	0.90-1.20	3240
E	3310	0.08-0.13	0.45-0.60	0.025	0.025	0.20-0.35	3.25-3.75	1.40-1.75	{3310 3312
E	3316	0.14-0.19	0.45-0.60	0.025	0.025	0.20-0.35	3.25-3.75	1.40-1.75	
A	4023	0.20-0.25	0.70-0.90	0.040	0.040	0.20-0.35		0.20-0.30	4023
A	4024	0.20-0.25	0.70-0.90	0.040	(a)	0.20-0.35		0.20-0.30	
A	4027	0.25-0.30	0.70-0.90	0.040	0.040	0.20-0.35		0.20-0.30	4027
A	4028	0.25-0.30	0.70-0.90	0.040	(a)	0.20-0.35		0.20-0.30	
A	4032	0.30-0.35	0.70-0.90	0.040	0.040	0.20-0.35		0.20-0.30	4032
A	4037	0.35-0.40	0.75-1.00	0.040	0.040	0.20-0.35		0.20-0.30	4037
A	4042	0.40-0.45	0.75-1.00	0.040	0.040	0.20-0.35		0.20-0.30	4042
A	4047	0.45-0.50	0.75-1.00	0.040	0.040	0.20-0.35		0.20-0.30	4047
A	4063	0.60-0.67	0.75-1.00	0.040	0.040	0.20-0.35		0.20-0.30	4063
A	4068	0.64-0.72	0.75-1.00	0.040	0.040	0.20-0.35		0.20-0.30	4068
A	4119	0.17-0.22	0.70-0.90	0.040	0.040	0.20-0.35	0.40-0.60	0.20-0.30	4119
A	4120	0.17-0.22	0.70-0.90	0.040	0.040	0.20-0.35	0.60-0.80	0.20-0.30	
A	4125	0.23-0.28	0.70-0.90	0.040	0.040	0.20-0.35	0.40-0.60	0.20-0.30	4125
A	4130	0.28-0.33	0.40-0.60	0.040	0.040	0.20-0.35	0.80-1.10	0.15-0.25	{X4130 4130
A	4131	0.28-0.33	0.50-0.70	0.040	0.040	0.20-0.35	0.80-1.10	0.14-0.19	
E	4132	0.30-0.35	0.40-0.60	0.025	0.025	0.20-0.35	0.80-1.10	0.18-0.25	

\* Lowest standard maximum phosphorus or sulfur content for acid open-hearth or acid electric furnace alloy steel is 0.05% each; silicon is 0.15% min.

NOTE (a): Sulfur range: 0.035 to 0.050%.

CODE: A is basic open-hearth alloy steel.  
 B is acid bessemer carbon steel.  
 C is basic open-hearth carbon steel.  
 D is acid open-hearth carbon steel.

E is electric furnace steel.  
 Q is forging quality, or special require-  
 ment quality.  
 R is rerolling quality billets.

TABLE 22(a). (Continued)

OPEN-HEARTH ALLOY AND ELECTRIC FURNACE CARBON AND ALLOY STEELS (Blooms, Billets, Slabs, Bars, and Hot-Rolled Strip)									
A.I.S.I. No.	C	Mn	P Max*	S Max*	Si*	Ni	Cr	Mo	1942 S.A.E. No.
A 4134	0.32-0.37	0.40-0.60	0.040	0.040	0.20-0.35		0.80-1.10	0.15-0.25	
E 4135	0.33-0.38	0.70-0.90	0.025	0.025	0.20-0.35		0.80-1.10	0.18-0.25	
A 4137	0.35-0.40	0.70-0.90	0.040	0.040	0.20-0.35		0.80-1.10	0.15-0.25	4137
E 4137	0.35-0.40	0.70-0.90	0.025	0.025	0.20-0.35		0.80-1.10	0.18-0.25	
A 4140	0.38-0.43	0.75-1.00	0.040	0.040	0.20-0.35		0.80-1.10	0.15-0.25	4140
A 4141	0.38-0.43	0.75-1.00	0.040	0.040	0.20-0.35		0.80-1.10	0.14-0.19	
A 4142	0.40-0.45	0.75-1.00	0.040	0.040	0.20-0.35		0.80-1.10	0.15-0.25	
A 4143	0.40-0.45	0.75-1.00	0.040	0.040	0.20-0.35		0.80-1.10	0.30-0.40	
A 4145	0.43-0.48	0.75-1.00	0.040	0.040	0.20-0.35		0.80-1.10	0.15-0.25	4145
A 4147	0.45-0.52	0.75-1.00	0.040	0.040	0.20-0.35		0.80-1.10	0.15-0.25	
A 4150	0.46-0.53	0.75-1.00	0.040	0.040	0.20-0.35		0.80-1.10	0.15-0.25	4150
E 4150	0.48-0.53	0.70-0.90	0.025	0.025	0.20-0.35		0.80-1.10	0.20-0.27	
A 4317	0.15-0.20	0.45-0.65	0.040	0.040	0.20-0.35	1.65-2.00	0.40-0.60	0.20-0.30	
A 4320	0.17-0.22	0.45-0.65	0.040	0.040	0.20-0.35	1.65-2.00	0.40-0.60	0.20-0.30	4320
A 4337	0.35-0.40	0.60-0.80	0.040	0.040	0.20-0.35	1.65-2.00	0.60-0.80	0.30-0.40	
E 4337	0.35-0.40	0.60-0.80	0.025	0.025	0.20-0.35	1.65-2.00	0.70-0.90	0.23-0.30	
A 4340	0.38-0.43	0.60-0.80	0.040	0.040	0.20-0.35	1.65-2.00	0.70-0.90	0.20-0.30	X4340 4340
E 4342	0.40-0.45	0.60-0.80	0.025	0.025	0.20-0.35	1.65-2.00	0.70-0.90	0.23 0.30	
A 4608	0.06-0.11	0.40 max.	0.040	0.040	0.25 max.	1.40-1.75		0.15-0.25	
A 4615	0.13-0.18	0.45-0.65	0.040	0.040	0.20-0.35	1.65-2.00		0.20-0.30	4615
E 4617	0.15-0.20	0.45-0.65	0.025	0.025	0.20-0.35	1.65-2.00		0.20-0.27	
A 4620	0.17-0.22	0.45-0.65	0.040	0.040	0.20-0.35	1.65-2.00		0.20-0.30	4620
E 4620	0.17-0.22	0.45-0.60	0.025	0.025	0.20-0.35	1.65-2.00		0.20-0.27	
A 4621	0.18-0.23	0.70-0.90	0.040	0.040	0.20-0.35	1.65-2.00		0.20-0.30	
A 4640	0.38-0.43	0.60-0.80	0.040	0.040	0.20-0.35	1.65-2.00		0.20-0.30	4640
E 4640	0.38-0.43	0.60-0.80	0.025	0.025	0.20-0.35	1.65-2.00		0.20-0.27	
A 4645	0.43-0.48	0.60-0.80	0.040	0.040	0.20-0.35	1.65-2.00		0.20-0.30	
A 4816	0.13-0.18	0.40-0.60	0.040	0.040	0.20-0.35	3.25-3.75		0.20-0.30	4815
A 4820	0.18-0.23	0.50-0.70	0.040	0.040	0.20-0.35	3.25-3.75		0.20-0.30	4820
A 5120	0.17-0.22	0.70-0.90	0.040	0.040	0.20-0.35		0.70-0.90		5120
A 5130	0.28-0.33	0.70-0.90	0.040	0.040	0.20-0.35		0.80-1.10		
A 5140	0.38-0.43	0.70-0.90	0.040	0.040	0.20-0.35		0.70-0.90		5140
A 5145	0.43-0.48	0.70-0.90	0.040	0.040	0.20-0.35		0.70-0.90		
A 5150	0.48-0.55	0.70-0.90	0.040	0.040	0.20-0.35		0.70-0.90		5150
A 5152	0.45-0.55	0.70-0.90	0.040	0.040	0.20-0.35		0.90-1.20		
E 52095	0.95-1.10	0.25-0.45	0.025	0.025	0.20-0.35		0.40 0.60		
E 52098	0.95-1.10	0.25-0.45	0.025	0.025	0.20-0.35		0.90-1.15		
E 52100	0.95-1.10	0.25-0.45	0.025	0.025	0.20-0.35		1.20-1.50		
E 52101	0.95-1.10	0.25-0.45	0.025	0.025	0.20-0.35		1.30-1.60		
A 6120	0.17-0.22	0.70-0.90	0.040	0.040	0.20-0.35		0.70 0.90 0.10 min V		
A 6145	0.43-0.48	0.70-0.90	0.040	0.040	0.20-0.35		0.80-1.10 0.15 min V		
S.A.E. 6150	0.48-0.55	0.65-0.90	0.040	0.040	0.20-0.35		0.80-1.10 0.15 min V		6150
E 6151	0.47-0.53	0.70-0.90	0.025	0.025	0.20-0.35		0.80-1.10 0.15 min V		
A 6152	0.48-0.55	0.70-0.90	0.040	0.040	0.20-0.35		0.80-1.10 0.10 min V		
A 9255	0.50-0.60	0.70-0.95	0.040	0.040	1.80-2.20				
A 9260	0.55-0.65	0.75-1.00	0.040	0.040	1.80-2.20				
A 9262	0.55-0.65	0.75-1.00	0.040	0.040	1.80-2.20		0.20-0.40		

\* Lowest standard maximum phosphorus or sulfur content for acid open-hearth or acid electric furnace alloy steel is 0.05% each; silicon is 0.15% min.

NOTE (a): Sulfur range: 0.035 to 0.050%.

CODE: A is basic open-hearth alloy steel.  
B is acid bessemer carbon steel.  
C is basic open-hearth carbon steel.  
D is acid open-hearth carbon steel.

E is electric furnace steel.  
Q is forging quality, or special requirement quality.  
R is rerolling quality billets.

TABLE 22(a). (Continued)

BASIC OPEN-HEARTH AND ACID BESSEMER CARBON STEELS								1942
A.I.S.I. No.	Semi-finish	Bars	Wire Rods	C	Mn	P (b)	S (b)	S.A.E. No.
C 1005	—	—	✓	0.06 max	0.35 max	0.04	0.05	
C 1006*	Q, R	✓	✓	0.08 max	0.25-0.40	0.04	0.05	
C 1006*	Q, R	✓	✓	0.10 max	0.30-0.50	0.04	0.05	1008
CB 1008	—	✓	✓	0.10 max				
C 1009	Q	—	—	0.07-0.12	0.25-0.40	0.04	0.05	
C 1010*	Q, R	✓	✓	0.08-0.13	0.30-0.50	0.04	0.05	1010
C 1012	Q	✓	✓	0.10-0.15	0.30-0.50	0.04	0.05	
CB 1012	—	✓	—	0.15 max				
C 1013	—	—	✓	0.11-0.16	0.60-0.90	0.04	0.05	
C 1014	Q	✓	✓	0.13-0.18	0.40-0.60	0.04	0.05	
C 1015*	Q, R	✓	✓	0.13-0.18	0.30-0.50	0.04	0.05	1015
C 1016	Q	✓	✓	0.13-0.18	0.60-0.90	0.04	0.05	{X1015 1016
CB 1017	—	✓	—	0.10-0.25				
C 1017	Q	✓	✓	0.15-0.20	0.40-0.60	0.04	0.05	
C 1018	Q	✓	✓	0.15-0.20	0.60-0.90	0.04	0.05	
C 1019	Q	✓	✓	0.15-0.20	0.70-1.00	0.04	0.05	
C 1020*	Q, R	✓	✓	0.18-0.23	0.30-0.50	0.04	0.05	1020
C 1021	Q	✓	✓	0.18-0.23	0.40-0.60	0.04	0.05	
C 1022	Q	✓	✓	0.18-0.23	0.70-1.00	0.04	0.05	{X1020 1022
C 1023	Q	✓	✓	0.20-0.25	0.30-0.50	0.04	0.05	
C 1024	—	✓	—	0.20-0.26	1.35-1.65	0.04	0.05	1024
C 1025*	Q, R	✓	✓	0.22-0.28	0.30-0.50	0.04	0.05	1025
C 1026	Q	✓	✓	0.22-0.28	0.40-0.60	0.04	0.05	
C 1027	—	✓	✓	0.24-0.30	0.40-0.60	0.04	0.05	
C 1029	Q	✓	—	0.25-0.31	0.60-0.90	0.04	0.05	
C 1030	Q	✓	✓	0.28-0.34	0.60-0.90	0.04	0.05	1030
C 1031	Q	—	—	0.28-0.34	0.40-0.60	0.04	0.05	
CB 1032	R	✓	—	0.25-0.40				
C 1033	Q	✓	—	0.30-0.36	0.60-0.90	0.04	0.05	
C 1034	—	✓	—	0.32-0.38	0.50-0.70	0.04	0.05	
D 1034	—	—	✓	0.32-0.38	0.50-0.70	0.05	0.05	
C 1035	Q	✓	—	0.32-0.38	0.60-0.90	0.04	0.05	1035
C 1036	—	✓	—	0.32-0.39	1.20-1.50	0.04	0.05	1036
C 1037	C.r. strip	✓	—	0.32-0.38	0.40-0.60	0.04	0.05	
C 1038	Q	—	✓	0.35-0.42	0.60-0.90	0.04	0.05	
C 1039	C.r. strip	—	—	0.37-0.44	0.40-0.60	0.04	0.05	
C 1040	Q	✓	✓	0.37-0.44	0.60-0.90	0.04	0.05	1040
C 1041	—	—	✓	0.36-0.44	1.35-1.65	0.04	0.05	
C 1042	Q	✓	—	0.40-0.47	0.60-0.90	0.04	0.05	
C 1043	Q	✓	—	0.40-0.47	0.70-1.00	0.04	0.05	
C 1044	—	—	✓	0.43-0.50	0.50-0.70	0.04	0.05	
C 1045	Q	✓	—	0.43-0.50	0.60-0.90	0.04	0.05	1045
C 1046	Q	—	—	0.43-0.50	0.70-1.00	0.04	0.05	

NOTE 1. When silicon is specified in standard basic open-hearth steels, silicon may be ordered only as 0.10% maximum; 0.10 to 0.20%; or 0.15 to 0.30%. In the case of many grades of basic open-hearth steel, special practice is necessary in order to comply with a specification including silicon.

NOTE 2. Acid bessemer steel is not furnished with specified silicon content.

\* Compositions are given for forging quality; re-rolling quality differs slightly in analysis.

CODE: A is basic open-hearth alloy steel.  
 B is acid bessemer carbon steel.  
 C is basic open-hearth carbon steel.  
 D is acid open-hearth carbon steel.

E is electric furnace steel.  
 Q is forging quality, or special requirement quality.  
 R is rerolling quality billets.

TABLE 22(a). (Continued)

BASIC OPEN-HEARTH AND ACID BESSEMER CARBON STEELS								1942
A.I.S.I. No.	Semi- finish	Bars	Wire Rods	C	Mn	P (b)	S (b)	S.A.E. No.
C 1047	C.r. strip			0.43-0.50	0.40-0.60	0.04	0.05	
C 1049	C.r. strip			0.48-0.55	0.40-0.60	0.04	0.05	
D 1049	—	—	✓	0.43-0.50	0.50-0.70	0.05	0.05	
C 1050	Q	✓	—	0.48-0.55	0.60-0.90	0.04	0.05	1050
C 1051	—	—	✓	0.45-0.56	0.85-1.15	0.04	0.05	
C 1052	—	✓	—	0.47-0.55	1.20-1.50	0.04	0.05	1052
C 1054	—	—	✓	0.50-0.60	0.50-0.70	0.04	0.05	
D 1054	—	—	✓	0.50-0.60	0.50-0.70	0.05	0.05	
C 1055	Q	✓	—	0.50-0.60	0.60-0.90	0.04	0.05	1055
C 1056	C.r. strip			0.50-0.60	0.40-0.60	0.04	0.05	
C 1057	—	—	✓	0.50-0.61	0.85-1.15	0.04	0.05	
C 1058	C.r. strip			0.55-0.65	0.40-0.60	0.04	0.05	
C 1059	—	—	✓	0.55-0.65	0.50-0.70	0.04	0.05	
D 1059	—	—	✓	0.55-0.65	0.50-0.70	0.05	0.05	
C 1060	—	✓	✓	0.55-0.65	0.60-0.90	0.04	0.05	1060
C 1061	—	✓	—	0.54-0.65	0.75-1.05	0.04	0.05	
C 1062	—	—	✓	0.54-0.65	0.85-1.15	0.04	0.05	
C 1063	—	—	—	0.57-0.67	0.60-0.85	0.04	0.05	
C 1064	—	✓	✓	0.60-0.70	0.50-0.70	0.04	0.05	
D 1064	—	—	✓	0.60-0.70	0.50-0.70	0.05	0.05	
C 1065	Strip			0.60-0.70	0.60-0.90	0.04	0.05	
C 1066	—	✓	✓	0.60-0.71	0.80-1.10	0.04	0.05	{X1065 1066
C 1068	—	✓	—	0.65-0.75	0.50 max	0.04	0.05	
C 1069	—	—	✓	0.65-0.75	0.50-0.70	0.04	0.05	
D 1069	—	—	✓	0.65-0.75	0.40-0.60	0.05	0.05	
C 1070	—	✓	—	0.65-0.75	0.70-1.00	0.04	0.05	1070
C 1074	—	✓	✓	0.70-0.80	0.50-0.70	0.04	0.05	
D 1074	—	—	✓	0.70-0.80	0.40-0.60	0.05	0.05	
C 1075	—	—	✓	0.70-0.80	0.60-0.80	0.04	0.05	
C 1076	—	—	—	0.65-0.85	0.60-0.85	0.04	0.05	
C 1078	—	✓	✓	0.72-0.85	0.30-0.50	0.04	0.05	
D 1078	—	—	✓	0.70-0.85	0.30-0.50	0.05	0.05	
C 1080	—	✓	—	0.75-0.88	0.60-0.90	0.04	0.05	1080
D 1083	—	—	✓	0.80-0.95	0.30-0.50	0.05	0.05	
C 1084	—	—	✓	0.80-0.93	0.60-0.90	0.04	0.05	
C 1085	—	✓	—	0.80-0.93	0.70-1.10	0.04	0.05	1085
C 1086	—	✓	✓	0.82-0.95	0.30-0.50	0.04	0.05	
C 1090	Q	—	—	0.85-1.00	0.60-0.90	0.04	0.05	
C 1095	—	✓	✓	0.90-1.05	0.30-0.50	0.04	0.05	1095
D 1095	—	—	✓	0.90-1.05	0.30-0.50	0.05	0.05	
B 1006	—	—	✓	0.08 max	0.45 max	0.11 max	0.06 max	
B 1008	R	✓	—	0.10 max	0.30-0.50	0.11 max	0.06 max	
B 1011	—	✓	✓	0.13 max	0.50-0.70	0.11 max	0.06 max	

NOTE 1. When silicon is specified in standard basic open-hearth steels, silicon may be ordered only as 0.10% maximum; 0.10 to 0.20%; or 0.15 to 0.30%. In the case of many grades of basic open-hearth steel, special practice is necessary in order to comply with a specification including silicon.

NOTE 2. Acid bessemer steel is not furnished with specified silicon content.

CODE: A is basic open-hearth alloy steel.  
B is acid bessemer carbon steel.  
C is basic open-hearth carbon steel.  
D is acid open-hearth carbon steel.

E is electric furnace steel.  
Q is forging quality, or special requirement quality.  
R is rerolling quality billets.

TABLE 22(a). (Continued)

SULFURIZED OR PHOSPHORIZED CARBON STEELS								1942
A.I.S.I. No.	Semi- finish	Bars	Wire Rods	C	Mn	P (b)	S (b)	S.A.E. No.
B 1106	—	—	✓	0.09 max	0.50 max	0.11 max	0.04-0.09	
C 1108	—	—	✓	0.08-0.13	0.50-0.70	0.045 max	0.07-0.12	
C 1109	Q	✓	✓	0.08-0.13	0.60-0.90	0.045 max	0.08-0.13	
B 1110	—	✓	✓	0.13 max	0.60 max	0.11 max	0.045-0.075	
C 1110	—	✓	✓	0.08-0.13	0.60-0.90	0.045 max	0.10-0.15G	
B 1111	—	✓	✓	0.08-0.13	0.60-0.90	0.09-0.13	0.10-0.15	1111
C 1111	—	—	✓	0.08-0.13	0.60-0.90	0.045 max	0.16-0.23	
B 1112	—	✓	✓	0.08-0.13	0.60-0.90	0.09-0.13	0.16-0.23	1112
C 1112	—	✓	—	0.10-0.16	1.00-1.30	0.045 max	0.08-0.13	
B 1113	—	✓	✓	0.08-0.13	0.60-0.90	0.09-0.13	0.24-0.33	1113
C 1113	Q	✓	—	0.10-0.16	1.00-1.30	0.045 max	0.24-0.33	
C 1114	R	—	—	0.12-0.18	0.45-0.65	0.045 max	0.075-0.15	
C 1115	Q	✓	✓	0.13-0.18	0.70-1.00	0.045 max	0.10-0.15	1115
C 1116	Q	✓	✓	0.13-0.18	0.70-1.00	0.045 max	0.10-0.15	
C 1117	—	✓	✓	0.14-0.20	1.00-1.30	0.045 max	0.08-0.13	1117
C 1118	Q	✓	✓	0.14-0.20	1.30-1.60	0.045 max	0.08-0.13	1118
C 1119	—	—	✓	0.14-0.20	1.35-1.65	0.045 max	0.16-0.23	
C 1120*	Q, R	✓	✓	0.18-0.23	0.60-0.90	0.045 max	0.08-0.13	
C 1121	Q	✓	✓	0.18-0.23	0.70-1.00	0.045 max	0.08-0.13	
C 1122	Q	✓	✓	0.17-0.23	1.35-1.65	0.045 max	0.08-0.13	
C 1132	Q	✓	✓	0.27-0.34	1.35-1.65	0.045 max	0.08-0.13	1132
C 1137	Q	✓	✓	0.32-0.39	1.35-1.65	0.045 max	0.08-0.13	1137
C 1140†	Q	✓	—	0.37-0.44	0.60-0.90	0.045 max	0.04-0.07	
C 1141	—	✓	—	0.37-0.45	1.35-1.65	0.045 max	0.08-0.13	1141
C 1144	—	✓	—	0.40-0.48	1.35-1.65	0.045 max	0.24-0.33	
C 1145†	Q	✓	—	0.42-0.49	0.70-1.00	0.045 max	0.04-0.07	1145
C 1205	Q	—	✓	0.08 max	0.25-0.40	0.04-0.07	0.05 max	
C 1206	R	—	✓	0.08 max	0.25-0.40	0.04-0.07	0.05 max	
C 1209	R	—	✓	0.08-0.13	0.30-0.50	0.05-0.10	0.05 max	
C 1210	Q	—	✓	0.08-0.13	0.30-0.50	0.06-0.10	0.05 max	
C 1211	—	—	✓	0.08-0.13	0.60-0.90	0.09-0.13	0.10-0.15	
C 1217	—	✓	—	0.14-0.19	0.70-1.00	0.09-0.13	0.20-0.29	

(b): Phosphorus and sulfur are maximum for basic open-hearth and acid bessemer steels; sulfurized or phosphorized steels are not subject to check analysis for S or P.

NOTES: Acid bessemer steels (B series) are not furnished with specified silicon content.

\* Compositions given are for forging quality; rerolling quality differs slightly in analysis.

† Standard steels C 1140 and C 1145 may be ordered with silicon content either as 0.10% max, 0.10 to 0.20%, or 0.15 to 0.30%.

CODE: A is basic open-hearth alloy steel.  
B is acid bessemer carbon steel.  
C is basic open-hearth carbon steel.  
D is acid open-hearth carbon steel.

F is electric furnace steel.  
Q is forging quality, or special requirement quality.  
R is rerolling quality billets.

TABLE 22(a). (Continued)  
 NATIONAL EMERGENCY ALLOY STEELS  
 Revised August 15, 1943

OPEN-HEARTH ALLOY AND ELECTRIC FURNACE ALLOY STEELS (Blooms, Billets, Slabs, Bars and Hot Rolled Strip)									Hardenability (b)	
Designation	C	Mn	P Max (a)	S Max (a)	Si	Ni	Cr	Mo	Low	High
									Side	Side
Carbon-Manganese Steels										
NE 1330	0.28-0.33	1.60-1.90	0.040	0.040	0.20-0.35	(c)	(d)	(e)	1.42	3.72
NE 1335	0.33-0.38	1.60-1.90	0.040	0.040	0.20-0.35	(c)	(d)	(e)	1.57	4.00
NE 1340	0.38-0.43	1.60-1.90	0.040	0.040	0.20-0.35	(c)	(d)	(e)	1.68	4.22
NE 1345	0.43-0.48	1.60-1.90	0.040	0.040	0.20-0.35	(c)	(d)	(e)	1.78	4.49
NE 1350	0.48-0.53	1.60-1.90	0.040	0.040	0.20-0.35	(c)	(d)	(e)	1.89	4.71
Carbon-Chromium Steels										
NE 52100C	0.95-1.10	0.25-0.45	0.025†	0.025†	0.20-0.35	0.35 max	0.40-0.60	0.08 max	1.26	4.43
NE 52100B	0.95-1.10	0.25-0.45	0.025†	0.025†	0.20-0.35	0.35 max	0.90-1.15	0.08 max	1.53	6.70*
NE 52100A	0.95-1.10	0.25-0.45	0.025†	0.025†	0.20-0.35	0.35 max	1.30-1.60	0.08 max	1.72	*
Nickel-Chromium-Molybdenum Steels										
NE 8613	0.12-0.17	0.70-0.90	0.010	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	1.22	4.45
NE 8615	0.13-0.18	0.70-0.90	0.010	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	1.30	4.61
NE 8617	0.15-0.20	0.70-0.90	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	1.39	4.82
NE 8620	0.18-0.23	0.70-0.90	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	1.53	5.15
NE 8630	0.28-0.33	0.70-0.90	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	1.99	6.18
NE 8635	0.33-0.38	0.75-1.00	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	2.32	6.66
NE 8637	0.35-0.40	0.75-1.00	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	2.40	6.83
NE 8640	0.38-0.43	0.75-1.00	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	2.49	7.04
NE 8642	0.40-0.45	0.75-1.00	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	2.56	7.21
NE 8645	0.43-0.48	0.75-1.00	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	2.64	7.48
NE 8650	0.48-0.53	0.75-1.00	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.15-0.25	2.79	7.86
NE 8720	0.18-0.23	0.70-0.90	0.040	0.040	0.20-0.35	0.40-0.70	0.40-0.60	0.20-0.30	1.69	5.62
Silicon-Manganese and Silicon-Manganese-Chromium Steels										
NE 9255	0.50-0.60	0.70-0.95	0.040	0.040	1.80-2.20	(c)	(d)	(e)	1.51	3.73
NE 9260	0.55-0.65	0.75-1.00	0.040	0.040	1.80-2.20	(c)	(d)	(e)	1.64	4.07
NE 9261	0.55-0.65	0.75-1.00	0.040	0.040	1.80-2.20	(c)	0.10-0.25	(e)	1.78	5.27
NE 9262	0.55-0.65	0.75-1.00	0.040	0.040	1.80-2.20	(c)	0.25-0.40	(e)	2.30	6.01
Manganese-Silicon-Chromium-Nickel-Molybdenum Steels										
NE 9415	0.13-0.18	0.80-1.10	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	1.11	2.58
NE 9420	0.18-0.23	0.80-1.10	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	1.29	2.90
NE 9422	0.20-0.25	0.80-1.10	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	1.38	3.00
NE 9425	0.23-0.28	0.80-1.10	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	1.46	3.48
NE 9430	0.28-0.33	0.90-1.20	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	1.83	3.70
NE 9435	0.33-0.38	0.90-1.20	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	2.03	4.00
NE 9437	0.35-0.40	0.90-1.20	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	2.10	4.08
NE 9440	0.38-0.43	0.90-1.20	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	2.18	4.20
NE 9442	0.40-0.45	1.00-1.30	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	2.43	4.57
NE 9445	0.43-0.48	1.00-1.30	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	2.50	4.75
NE 9450	0.48-0.53	1.20-1.50	0.040	0.040	0.20-0.35	0.30-0.60	0.30-0.50	0.08-0.15	3.06	5.60
NE 9537†	0.35-0.40	1.20-1.50	0.040	0.040	0.40-0.60	0.40-0.70	0.40-0.60	0.15-0.25	3.88	11.40
NE 9540†	0.38-0.43	1.20-1.50	0.040	0.040	0.40-0.60	0.40-0.70	0.40-0.60	0.15-0.25	4.02	11.75
NE 9542†	0.40-0.45	1.20-1.50	0.040	0.040	0.40-0.60	0.40-0.70	0.40-0.60	0.15-0.25	4.13	12.01
NE 9545†	0.43-0.48	1.20-1.50	0.040	0.040	0.40-0.60	0.40-0.70	0.40-0.60	0.15-0.25	4.27	12.40
NE 9550†	0.48-0.53	1.20-1.50	0.040	0.040	0.40-0.60	0.40-0.70	0.40-0.60	0.15-0.25	4.50	13.10

\* Doubtful, from unknown effect of undissolved carbides.

† These limits are for electric furnace grades; if basic open-hearth the sulfur and phosphorus may be 0.04% max each.

‡ For large sections only.

(a) For basic open-hearth steel. The lowest standard maximum phosphorus or sulfur in acid open-hearth or electric alloy steel is 0.05% each. Not used in computing hardenability.

(b) Not part of the specification. Computed by Grossmann's methods.

(c) Supposedly none. Hardenability computations assume 0.10-0.25.

(d) Ditto. Assumed 0.05-0.10.

(e) Ditto. Assumed 0.00-0.08.



TABLE 22(b). STAINLESS STEEL STANDARD TYPE NUMBERS AND CORRESPONDING COMPOSITION RANGES\*

Type Number	Chromium	Nickel	Carbon	Other Elements
	%	%	%	%
301	16.00-18.00	7.00-9.00	0.09-0.20	Manganese 1.25 max
†302	18.00-20.00	8.00-10.00	Over 0.08-0.20	Manganese 1.25 max
†302B	18.00-20.00	8.00-10.00	Over 0.08	Silicon 2.00-3.00; manganese 1.25 max
†303	18.00-20.00	8.00-10.00	0.20 max	Sulfur or selenium 0.07 min.; molybdenum 0.60 max
304	18.00-20.00	8.00-10.00	0.08 max	Manganese 2.00 max
308	19.00-22.00	10.00-12.00	0.08 max	Manganese 2.00 max
309	22.00-26.00	12.00-14.00	0.20 max	
309S	22.00-26.00	12.00-14.00	0.08 max	
310	24.00-26.00	19.00-21.00	0.25 max	
311	19.00-21.00	24.00-26.00	0.25 max	
312	27.00-31.00	8.00-10.00	0.25 max	
315	17.00-19.00	7.00-9.50	0.15 max	{ Copper 1.00-1.50
316	16.00-18.00	14.00 max	0.10 max	{ Molybdenum 1.00-1.50
317	18.00-20.00	14.00 max	0.10 max	{ Molybdenum 2.00-3.00
321	17.00-20.00	7.00-10.00	0.10 max	{ Molybdenum 3.00-4.00
325	7.00-10.00	19.00-23.00	0.25 max	{ Titanium 4× carbon min
327	25.00-30.00	3.00-5.00	0.25 max	{ Copper 1.00-1.50
329	25.00-30.00	3.00-5.00	0.10 max	
330	14.00-16.00	33.00-36.00	0.25 max	Molybdenum 1.00-1.50
347	17.00-20.00	8.00-12.00	0.10 max	Columbium 10× carbon
349	17.00-18.50	10.00-11.00	0.08 max	Columbium 10× carbon
403	11.50-13.00		0.15 max	
405	11.50-13.50		0.08 max	Aluminum 0.10-0.20
406	12.00-14.00		0.15 max	Aluminum 4.00-4.50
410	10.00-13.50		0.15 max	
414	10.00-13.50	2.00 max	0.15 max	
416	12.00-14.00		0.15 max	Sulfur or selenium 0.07 min; molybdenum 0.60 max
418	12.00-14.00		0.15 max	Tungsten 2.50-3.50
420	12.00-14.00		Over 0.15	
420F	12.00-14.00		Over 0.15	Sulfur or selenium 0.07 min; molybdenum 0.60 max
430	14.00-18.00		0.12 max	
430F	14.00-18.00		0.12 max	Sulfur or selenium 0.07 min; molybdenum 0.60 max
431	14.00-18.00	2.00 max	0.15 max	
434A	14.00-18.00		0.12 max	{ Silicon 1.00
438	16.00-18.00		0.12 max	{ Copper 1.00
439	8.00		0.50-0.65	Tungsten 2.50-3.50
440	14.00-18.00		Over 0.12	Tungsten 8.00
441	14.00-18.00	2.00 max	Over 0.15	
442	18.00-23.00		0.35 max	
446	23.00-30.00		0.35 max	
501	4.00-6.00		Over 0.10	
502	4.00-6.00		0.10 max	

\* Courtesy of A.I.S.I. From Steel Products Manual, January, 1941.

† No specific composition limits within the above ranges may be placed on types 301, 302, 302B, and 303, except that carbon may be specified to a four-point range within the above limits.

TABLE 22(c). CORROSION- AND HEAT-RESISTING STEELS\*

Group A (Martensitic)	Group B (Ferritic)	Group C (Austenitic)
<p><i>Chemical Analysis</i> Chromium less than about 16%; carbon less than about 0.40%. May contain small percentages of tungsten, copper, nickel, silicon and more frequently molybdenum. Group is magnetic.</p> <p><i>Heat Treatment</i> Respond to hardening, tempering, and drawing. Resulting physical properties depend on chemical analysis (principally carbon content).</p> <p><i>Toughness</i> Are structurally dependable. After tempering are not brittle in notched sections or under impact.</p> <p><i>Grain Growth and Structural Changes at High Temperatures</i> Not subject to excessive grain growth. Thoroughly dependable for supporting any load or shock within their carrying capacity up to 1400°F. Brittleness in plain chromium steels when cooled after long heating is avoided by addition of molybdenum.</p>	<p>Chromium more than about 16%; carbon quite low, but can increase as chromium goes up. May contain small percentages of copper, nickel, silicon, molybdenum, tungsten, nitrogen. This group is magnetic.</p> <p>Do not respond. 18% chromium toughened by long anneal at more than 1400°F. and air cooling. Avoid decarburizing the skin. 25% chromium gets best strength and toughness by rapid cooling from 1650°.</p> <p>Laminated structure, from coarse ferrite in ingot, causes low impact values, but proper rolling and heating gives adequate toughness in rods, bars, and sheets. Structure is refined by nitrogen.</p> <p>The chromium-irons low in carbon and those high in silicon or aluminum (when cold worked) are subject to excessive grain growth, especially above 1900°F. Grain growth reduced by nitrogen. Long service at 800 to 950°F makes them brittle when cold, although they are not brittle at working temperatures.</p>	<p>Contains enough nickel to make steel austenitic and nonmagnetic. They usually contain twice as much chromium as nickel or vice versa; total alloy content at least 26%. Carbon is quite low.</p> <p>Do not respond to hardening by heat treatment. Must be rapidly cooled from soaking heat at 1800 to 2150°F to retain austenitic structure free of carbides. (Brinell 140 to 170.)</p> <p>Extremely tough at all temperatures down to liquid air. Dependable against shock except when corroded at grain boundaries (a preventable condition).</p> <p>Alloys near the austenite-martensite border line tend to precipitate carbides at grain boundaries during service at 800 to 1600°F, losing some toughness and becoming susceptible to intergranular attack. This is controlled by very low carbon, by titanium or columbium, by increasing the chromium and nickel, or by prior "stabilization."</p>

\* Arrangement by F. M. Palmer. Adapted from *The Book of Stainless Steels*, 2nd ed.

TABLE 22(c). (Continued)

Group A (Martensitic)	Group B (Ferritic)	Group C (Austenitic)
<p><i>Strength at Elevated Temperatures</i>                      Much better than straight carbon steel for temperatures up to 1000 or 1200°F. Retain tensile properties up to 750°F.</p>	<p>Heat-resisting varieties quite tough at temperatures up to 1600°F. Superior in ductility to Group C but not in creep resistance.</p>	<p>Have high creep strength up to 1200°F which is enhanced by tungsten or molybdenum. Toughness impaired in nonstabilized alloys by service at 800 to 1600°F.</p>
<p><i>Hot-Working Qualities</i>                      Readily forged, pierced, or rolled at 2000 to 1700°F. Preheat and soak stock at 1600°F. Plain chromium alloys air harden on cooling.</p>	<p>May be forged, rolled, or pierced. Should be heated quickly. Forge from 2200°F down to 1750°F. On last heat continue cold working to 1400°F to refine grain. Alloys do not air harden.</p>	<p>May be forged, rolled, or pierced. Preheat and soak at 1600°F, heat quickly to 2200°F, forge down to 1850°F. Hot short range: 1800 to 1300°F. Alloys do not air harden.</p>
<p><i>Cold-Working Qualities</i>                      Low-carbon varieties can be easily cold drawn into wire, cold rolled, bent, formed, upset, coined, and deep drawn.</p>	<p>Can be cold drawn into wire, cold rolled, bent, formed, upset, coined, and deep drawn, especially when warm (300 to 500°F).</p>	<p>Can be cold drawn into wire, cold rolled, bent, formed, upset, coined, and deep drawn. Work harden twice as rapidly as Groups A and B.</p>
<p><i>Machinability</i>                      Machine satisfactorily with properly designed tools when heat treated to 200 to 250 Brinell. Free-cutting grade contains zirconium sulfide.</p>	<p>Machine satisfactorily with properly designed tools. Cold working and high sulfur improve machinability.</p>	<p>Most difficult of all even with super high speed and carbide tools. Use sharp tools having greater top rake than usual, and cut continually. Free-cutting grade contains selenium and phosphorus.</p>
<p><i>Riveting</i>                      Make excellent cold rivets. Air hardening, plain steels not recommended for hot rivets driven above 1500°F.</p>	<p>Extra precautions required to avoid brittle rivets. Conical heads should be cold upset on ground bars; rivets driven at 1425°F into chamfered holes.</p>	<p>Excellent for either hot or cold rivets. Hot rivets may be driven at a high temperature (1900°F).</p>

TABLE 22(c). (Continued)

Group A (Martensitic)	Group B (Ferritic)	Group C (Austenitic)
<p><i>Welding Properties</i> Preheated parts can be welded with gas, electric arc, or resistance. Anneal immediately before weld air hardens. Little grain growth.</p> <p><i>Corrosion Resistance</i> Increases with chromium content. Resists weather, water, steam, and many organic and inorganic corrodents when chromium is 11.5% or more. If carbon is relatively high, metal must be hardened and tempered below 1000°F.</p> <p><i>Scale Resistance</i> Increases with chromium content. Generally useful for continuous temperatures up to 1200°F, and in some services up to 1500°F.</p>	<p>Can be welded. Anneal at 1450°F to reduce embrittlement alongside weld. Metals subject to grain growth are brittle adjacent to the weld. Metals not subject to grain growth yield satisfactory welds.</p> <p>Possess corrosion-resisting properties superior to Group A. Especially good for nitric and other oxidizing acids.</p>	<p>Can be welded with gas, electric arc, or resistance, if carburization is avoided. Weld does not air harden and is very tough. Only the relatively low carbon or "stabilized" metal should be welded if article must resist corroding media.</p> <p>Corrosion resistance depends largely upon total alloy content. Resists nearly all corrodents measurably better than Groups A and B; especially good for organic acids. Severe pitting may occur in stagnant chloride solutions under parities of foreign matter and along faying surfaces.</p>
	<p>Superior to Group A, especially when chromium is above 25%, then resist reducing atmospheres up to 2100°F, oxidizing up to melting points, and sulfur gases up to 1800°F.</p>	<p>Excellent where combination of high temperature and corrosion is to be met. High chromium alloys required to resist sulfurous gases.</p>

TABLE 22(d). CLASSIFICATION OF AMERICAN TOOL STEELS — I\*

General-Purpose Carbon Tool Steels					
(Water hardening; low wear resistance; high warpage; no red hardness; shallow hardening)					
<i>Carbon</i>	<i>Silicon</i>	<i>Manganese</i>	<i>Sulfur</i>	<i>Phosphorus</i>	<i>Vanadium</i>
0.60-1.25(a)	0.15-0.50	0.10-0.35	0.03 max	0.03 max	Note (b)
Common Uses					
Almost universal; note (c)					
(a) Usually subdivided by 0.10% steps; for instance 0.65-0.75%, 0.75-0.85%, etc.					
(b) Plain carbon steels have no vanadium; carbon-vanadium tool steels may have from 0.08 to 0.40% vanadium, depending on grade.					
(c) In lower carbon ranges the steels make shear blades, hammers, striking dies, rock drills. In medium ranges of carbon, the steels make chisels, smiths' tools, dies, and cutters for machine tools. In the higher ranges of carbon are small cutters, woodworkers' tools, and cutlery.					
Chromium-Vanadium or Low-Chromium Tool Steels (Substitutes for carbon tool steels)					
(Mostly water hardening; low wear resistance; high warpage; no red hardness; medium deep hardening)					
<i>Carbon</i>	<i>Silicon</i>	<i>Manganese</i>	<i>Chromium</i>	<i>Vanadium</i>	<i>Remarks</i>
0.50-1.40	0.15-0.50	0.10-0.35	0.10-0.25		Chromium corrects tendency toward soft spots.
0.50-1.40	0.15-0.50	0.10-0.35	0.25-0.50		More intense hardness.
0.50-1.40	0.15-0.40	0.10-0.35	0.60-1.20	0.10-0.20	Water hardening } Very tough in low carbon ranges.
0.50-1.40	0.15-0.40	0.40-0.60	0.60-1.20	0.10-0.20	Oil hardening }
High Carbon, Low Tungsten Tool and Die Steels (Finishing tools for hard steels or nonferrous alloys)					
(Oil hardening; medium wear resistance; medium toughness; low warpage; no red hardness; medium deep hardening)					
<i>Carbon</i>	<i>Silicon</i>	<i>Manganese</i>	<i>Chromium</i>	<i>Tungsten</i>	<i>Vanadium</i> (Optional)
0.90-1.10	0.20-0.40	0.15-0.30		1.00-1.50	
1.15-1.25	0.20-0.40	0.15-0.30		1.75-2.50	0.10-0.25
0.90-1.10	0.20-0.40	0.15-0.30		1.50-2.50	0.10-0.25
1.15-1.30	0.20-0.40	0.15-0.30	0.35-0.75	1.50-2.50	0.10-0.25
			0.35-0.75		Oil hardening } more dependable.

\* Adapted from J. P. Gill, *Metal Progress*, 1939 Reference Issue, Vol. 36, p. 440.

TABLE 22(d). (Continued)

Manganese Oil Hardening Die Steels ("Nondeforming"). (General-purpose tools and especially dies, punches, and broaches).						
(Oil hardening; low wear resistance; medium toughness; low warp; no red hardness; medium deep hardening)						
Carbon	Silicon	Manganese	Chromium	Tungsten	Molybdenum	Vanadium
Remarks						
0.85-0.95	0.20-0.40	1.50-1.75				0.10-0.25
0.85-1.00	0.20-0.40	1.15-1.45	0.30-0.60	0.30-0.60		0.10-0.25
0.85-1.00	0.20-0.40	1.35-1.65			0.20-0.35	0.10-0.25
0.90-1.00	0.20-0.40	0.90-1.15	0.50-0.90			
Tungsten Alloy Chisel and Punch Steels. (Oil hardening steels; shears and battering tools for cold metal; heading dies)						
(Medium wear resistance; high toughness; low warp; medium red hardness; medium deep hardening)						
Carbon	Tungsten	Chromium	Vanadium	Silicon		Remarks
0.45-0.60	0.75-1.25	0.75-1.25		1.00-1.50		Good wear resistance but somewhat brittle.
0.45-0.60	1.50-2.00	0.75-1.25		1.00-1.50		Higher tungsten improves wear resistance.
0.45-0.60	1.00-1.75	1.00-1.00				Low silicon increases toughness 25%.
0.40-0.55	1.75-2.25	0.75-1.25	0.10-0.30			} Most popular analyses, tough and fine grained.
0.55-0.65	1.75-2.25	0.75-1.25	0.10-0.30			
Tungsten Finishing Toolsteels and Drawing Dies. (Brittle but intensely hard and keen edges for cutting hard materials)						
(Water hardening; medium wear resistance; low toughness; high warp; no red hardness; deep hardening)						
Carbon	Tungsten	Chromium	Remarks			
1.20-1.40	5.00-6.00		Slightly better wear resistance than lower tungsten.	} High movement; best for drawing dies that must be rehardened after wear.		
1.20-1.40	3.00-5.00		Slightly tougher than higher tungsten.			
1.20-1.40	4.00-6.00	0.40-0.80	Chromium improves heat treatability and reduces volume change.			
1.20-1.40	4.00-6.00	1.00-1.50				
Silicon-Manganese Punch and Chisel Steels. (A water hardening and inexpensive steel for cold cutting)						
(Medium wear resistance; medium toughness; medium warp; medium hot hardness; medium deep hardening)						
Carbon	Silicon	Manganese	Chromium	Molybdenum	Vanadium	Remarks
0.50-0.60	1.80-2.20	0.60-0.90				Spring steel analysis; all high silicon steels liable to soft skin.
0.60-0.75	1.70-2.25	0.70-0.90				More carbon gives higher hardness.
0.50-0.60	1.75-2.25	0.70-0.90	0.20-0.35	0.15-0.30		Alloys increase hardenability and refine grain.
0.50-0.60	1.75-2.25	0.70-0.90	0.40-0.60			Molybdenum greatly increases hardenability.
0.50-0.60	0.75-1.25	0.35-0.60	0.20-0.40	0.40-0.60		Low silicon reduces brittleness and wear resistance.

TABLE 22(e). CLASSIFICATION OF AMERICAN TOOL STEELS — II\*

		High Carbon, High Chromium Punch and Die Steels (Durable rolls, mandrels, punches, dies and shears for cold work)		
Carbon	(High wear resistance; low toughness; low warpage; high hot hardness; deep hardening, difficultly machinable)	Vanadium	Molybdenum	Remarks
		Cobalt	Nickel	
2.25-2.45	12.00-14.00			
2.10-2.20	12.00-14.00	0.75-1.00		Somewhat tougher.
2.15-2.25	12.00-14.00		0.50-0.75	Slightly air hardening; most difficult to machine.
2.15-2.25	12.00-13.00	0.75-1.00	0.60-1.00	Slightly red hard.
1.40-1.50	12.00-13.00			<i>Air Hardening Types (Tougher Than Above; and Deform Less in Hardening)</i>
		0.50-0.60	3.00-4.00	Red hard properties. Good for cutting tools on nonferrous materials.
1.50-1.70	16.50-18.00			Liable to harden nonuniformly.
1.50-1.60	12.00-13.00	0.80-1.00		
1.50-1.60	12.00-13.00	0.80-1.00	0.40-0.60	Vanadium imparts greater toughness.
1.40-1.55	12.00-13.00	0.80-1.00	0.75-0.90	Most difficult to machine.
Chromium Die Steels for Hot Work (Cripper, bending and heading dies for light work up to 600°F)				
	(Air or oil hardening; medium wear resistance and toughness; low warpage; medium hot hardness; deep hardening)	Chromium	Molybdenum	Remarks
0.85-1.00		3.75-4.00		Usually quenched in light air blast.
0.85-1.00		3.25-3.75		Lower chromium reduces cracks during oil quenching.
0.65-0.75		3.75-4.25		Oil quenching (lower carbon) but not as rigid at 500°F.
0.85-1.00		3.75-4.25	0.40-0.60	Best air hardener.
Tungsten Die Steels for Hot Work (Blanking, forming, extrusion and casting dies to work up to 1100°F)				
	(Air or oil hardening; medium wear resistance; medium toughness; low warpage; high red hardness; deep hardening)	Tungsten	Chromium	Vanadium
0.25-0.35		8.00-10.00	2.50-3.50	0.30-0.60
0.35-0.45		8.00-10.00	2.50-3.50	0.30-0.60
0.40-0.50		9.00-12.00	1.25-1.75	

\*Adapted from J. P. Gill, *Metal Progress*, 1939 Reference Issue, Vol. 36, p. 441.

TABLE 22(e). (Continued)

		Tungsten Die Steels for Hot Work. Continued			Remarks	
		Chromium	Vanadium			
Carbon	Tungsten					
0.25-0.35	12.00-16.00	2.50-3.25	0.30-0.60			Increased tungsten raises serviceability to 1100°F. Hardenability and brittleness rises with carbon content. Low carbon, high speed steel.
0.35-0.50	12.00-16.00	2.50-3.25	0.30-0.60			
0.50-0.60	12.00-16.00	2.50-3.25	0.30-0.60			
0.50-0.60	17.00-19.00	3.00-4.50	0.60-1.20			
0.50-0.60	17.00-19.00	3.00-4.50	0.60-1.20			
Tungsten-Chromium Steels for Hot Work and Die Casting Dies						
(Air or oil hardening; medium wear resistance; good toughness; low warpage; high red hardness; deep hardening)						
Carbon	Tungsten	Chromium	Vanadium	Molybdenum	Silicon	Remarks
0.40-0.50	6.50-7.50	6.50-7.50	0.20-0.60		0.30-0.80	Maximum alloy for hottest services (1000°F).
0.35-0.45	5.50-6.50	5.00-6.00			0.30-0.80	Tougher.
0.30-0.40	0.75-1.25	4.50-5.00		1.00-1.50		Less expensive substitute.
0.35-0.40	0.75-1.25	4.50-5.00		1.00-1.50	0.80-1.00	Properties similar to steel above.
High Speed Steels						
(Cutting tools of all types; tools for severe hot work)						
(Air or oil hardening; high wear resistance; low toughness; low warpage; high red hardness; deep hardening)						
Carbon	Tungsten	Chromium	Vanadium	Molybdenum	Cobalt	Remarks
0.55-0.75	17.00-19.00	3.50-4.50	0.75-1.25			Most used; brittleness and cutting properties vary directly with carbon content. Better cutting ability but more brittle. Best cutting ability; excellent for finishing cuts. Roughing tools; somewhat erratic in hardening.
0.55-0.75	19.00-21.00	3.75-4.50	0.75-1.25			
0.75-0.85	17.00-19.00	3.50-4.50	1.75-2.25	0.40-0.90		
0.55-0.75	13.00-15.00	3.50-4.50	1.75-2.25			
Conventional Types						
Molybdenum High Speed Steel						
0.60-0.85	1.00-2.50	3.50-4.50	0.75-1.25	6.00-8.00		Less expensive; "strategic" alloying element used.
0.70-0.90		3.50-4.50	1.75-2.50	6.00-9.00		Improved by high vanadium content.
Cobalt High Speed Steel						
0.65-0.80	17.00-19.00	3.50-4.50	0.75-1.25	3.50-5.00		For cutting hard, gritty, or tough materials.
0.65-0.80	17.00-19.00	3.50-4.50	1.50-2.25	6.00-9.00		Cutting ability varies as total alloy content.
0.65-0.80	18.00-21.00	3.50-4.50	1.75-2.25	0.50-1.00	10.00-13.00	Maximum alloy to be forgeable.
0.65-0.80	12.00-15.00	3.50-4.50	1.75-2.25	5.00-8.00		Good service on special jobs.



TABLE 22(J). TOOL STEELS FOR HOT WORKING IRON AND STEEL\*

*Requirements for All Hot Work Tools*

1. Of sufficient toughness to resist working stresses.
2. Of such composition and in such heat-treated condition as to resist softening when in service.
3. To have adequate wear-resisting properties to assure normal, economical life.
4. Of such composition and heat-treated condition as to resist wholly or partially the tendency toward heat or fire checking.

*Influence of Design*

1. Wedge designs, sharp corners, and thin sections promote chances of breakage and require inherently tougher compositions, usually secured through lower total alloy content steels.
2. Designs including raised sections partially or wholly buried in hot metal require types of higher red hardness and may not require as high toughness characteristics as other wedge designs.

*Importance of Mechanical Set-Up*

1. All forging dies should be properly lined up.
2. Machines should be true to assure uniform application of pressure or impact.
3. Dies should be so adjusted in hand-fed and automatic forging machines as to prevent excessive pressure being developed on the faces of the dies, thus decreasing probability of fatigue failures.
4. Dies should not be mounted in worn or warped shoes or holders.

*Importance of Adequate Preheating*

1. Well-warmed dies and tools are less susceptible to cracking.
2. Minimum temperatures secured through use of buried unit

\*H. E. Replogle, *Metal Progress*, 1939, Vol. 36, p. 484.

heaters in certain types of drop-forging dies prolong service life and retard heat checking.

*Importance of Cooling*

1. Methods of cooling — air, oil, water. Retards localized heating which may exert a tempering and softening action.

(a) Air cooling least drastic — applicable to all types of tools. Also serves to blow away scale which, if present, will cause undue wear of dies.

(b) Oil cooling — somewhat more severe and rapid but rarely detrimental to any tool or die.

(c) Water cooling — most effective, but very drastic and often dangerous. When large dies attain high temperatures, water cooling tends to cause heat checking. Punches and small dies are often successfully cooled with an ample flow of water.

*Influence of Die and Tool Lubrication*

1. Heavy graphite bearing greases serve as lubricants and prevent sticking. Usually assures better wear.

*Quenching*

Among the data given below are recommendations as to the quenching medium; oil, air and "oil and air." The words "oil and air" signify an interrupted or timed quench. With this method, a tool or die is quenched in oil to a temperature of about 1000°F, or where all color disappears. When this state is reached, the tool or die is removed and allowed to cool naturally in still air until cool enough to be handled in the bare hands. It should then be drawn as directed.

TABLE 22(f). (Continued)  
Recommended Compositions, Heat Treatments, and Hardnesses

C	Mn	Si	Analyses, %				Heat Treatment, °F						Brinell Hardness		
			Ni	Cr	V	W	Mo	Preheat	High Heat	Quench	Draw				
0.55	0.25		1.25		0.18	2.75									400-450
0.55	0.35		4.00		1.00		0.50					1750	Oil	1200	400-450
0.30	0.30		3.25		0.25	9.00						1650	Air	1150	400-450
0.25	0.20		4.00		0.50	15.00						2150	Oil and air	1200	400-450
												2350	Oil and air	1200	400-450
0.40	0.30		1.75		0.18	11.00						2150	Air	1100	539-578
0.45	0.30		2.75		0.40	15.00						2200	Air	1150	539-578
0.55	0.25		1.25		0.18	2.75						1750	Oil	1100	450-500
0.55	0.30	0.40	4.00		1.00		0.50					1650	Air	800	450-500
0.30	0.30		3.25		0.25	9.00						2150	Air	1150	450-500
0.25	0.30	0.25	2.60		0.30	9.50						2150	Air	1150	450-500
0.40	0.35	1.00	5.00		0.50	1.50						1800	Air	1075	444-526
0.55	0.35		4.00		1.00	0.50						1625	Air	1000	444-526
0.30	0.45	0.95	4.25		1.25	1.65						1850	Air	1100	450-500
0.55	0.25		1.25		0.18	2.75						1800	Oil	1225	430-461
0.30	0.30		3.25		0.25	9.00						2150	Air	1175	430-461
0.30	0.45	0.95	4.25		1.25	1.25	1.65					1850	Air	1100	400-450
0.25	0.30	0.25	2.60		0.30	9.50						2150	Air	1200	400-450
0.55	0.25		1.25		0.18	2.75						1800	Oil	1250	388-429
0.40	0.30		2.25		0.40	12.00						1800	Air	900	388-429
0.30	0.30		3.25		0.25	9.00						2250	Oil and air	1175	425-450

*Insert Dies in Upsetters*

*Gripper Dies for Hand-Fed Machines*

*Gripper Dies for Automatic Machines*

*Header Dies for Hand-Fed Machines*

*Header Dies for Automatic Machines*

*Forging Punches*

The above data do not represent all of the types being used for the various applications listed, nor do they represent the only heat treatments or hardness values for these types. Neither do the above listings include flat, cut, and swaging dies used in beam, steam, or air hammers. However, the types and treatments listed represent the broadest general selections being used commercially today in the services noted.

TABLE 22(g). PHYSICAL PROPERTIES OF GRAPHITIC STEEL\*  
(Analysis: 1.51% C, 0.96% Si, 0.40% Mn, 0.015% P, 0.014% S)

Treatment	Combined Carbon	Yield Point	Ultimate Strength	Elong. in 2 in.	Red. of Area	Brinell	Izod Ft-lb
<i>Specimens Air Cooled from Respective Annealing Temperatures</i>							
1400°F	0.66	62,250	120,250	17.5	26.1	241	8.0
1500°F	0.69	65,500	138,500	13.5	20.3	255	7.0
1600°F	0.72	67,500	143,000	12.0	17.4	269	4.5
1700°F	0.75	70,750	147,000	10.5	15.2	285	4.0
<i>Specimens Furnace Cooled from Respective Annealing Temperatures</i>							
1400°F	0.59	47,250	97,000	23.5	38.6	197	18.5
1500°F	0.55	47,700	99,000	19.5	29.9	201	15.0
1600°F	0.48	50,000	100,000	18.0	22.0	201	10.0
1700°F	0.26	44,000	81,000	15.0	21.8	163	10.0
<i>Annealed Specimens Water Quenched from 1450°F and Tempered as Shown</i>							
900°F	0.86	158,000	201,500	8.5	18.1	388	
1100°F	0.79	116,000	154,000	14.0	30.0	302	

\* *Metal Progress*, 1937, Vol. 31, p. 412.

TABLE 22(h). COMMERCIAL MAGNETIC IRON-NICKEL BASE ALLOYS\*

Name	Per Cent Nickel	Sponsor
	<i>Alloys with Very High Permeability at Low Field Strengths</i>	
Permalloy	60-90 + special heat treatment and sometimes + Cr or Mo	Western Electric Co.
Mumetal	Approx. 76 + 6% Cu and 1.5% Cr	Telcont and Allegheny-Ludlum Steel Co.
Permaf	Approx. 80	Acieries de Firminy
1040 Alloy	72 + 14% Cu and 3% Mo	Siemens & Halske
	<i>High Permeability Alloys for Higher Field Strengths</i>	
45 Permalloy	45	Western Electric Co.
Megaperm 6510	65 + 10% Mn	Germany
Hipernik	50	Westinghouse E. & M. Co.
Hyperm	50	Krupp
Nicaloi	49	General Electric Co.
Audiolloy	48	Crucible Steel Co.
Permenorm	48	Heraeus-Vacuumschmelze
Allegheny electric metal	47	Allegheny-Ludlum Steel Co.
Anhyster C and D	45-50	Acieries d'Imphy
Radiometal	45-50	Telcont
2129	45-50	Telcont
Megaperm 4510	45 + 10% Mn	Germany
	<i>Moderately High Permeability Alloys of High Electrical Resistance</i>	
Rhometal	40-45 + 5% Cr and 3% Si	Telcont
Gamma	Approx. 35	Acieries d'Imphy
Anhyster A and B	Approx. 35	Acieries d'Imphy
	<i>Alloys with Constant Permeability Over a Range of Flux Densities</i>	
Perminvar	20-75 + 5-40% Co + special heat treatment and sometimes + Mo	Western Electric Co.
Conpernik	50 + special heat treatment	Westinghouse E. & M. Co.
Isoperm	40-55 + special treatment	Germany
Isoperm (precipitation types)	36-50 + 9-15% Cu 40-60 + 3-4% Al	Germany Germany
	<i>Alloys with Permeability Varying with Temperature</i>	
Temperature compensator alloy	30	Carpenter Steel Co.
Thermoperm	30	Krupp
N. M. H. G.	30	Acieries d'Imphy

\* A.S.M. Metals Handbook, p. 494.

† Telegraph Construction &amp; Maintenance Co., Ltd., London, England.

TABLE 22(i). MAGNETIC PROPERTIES OF VARIOUS ALLOYS\*

Material†	Initial Permeability	Maximum Permeability	Hysteresis Loss, ergs per cu cm per cycle‡	Residual Induction, gaussses	Coercive Force, oersted§	Saturation Value, gaussses**	Resistivity, microhm cm <sup>3</sup>
Armco iron	250	7,000	5,000	13,000	1.0	22,000	11
4% silicon-iron	600	6,000	3,500	12,000	0.5	20,000	50
78.5 Permalloy, quenched	10,000	105,000	200	6,000	0.05	10,700	16
45 Permalloy	2,700	23,000	1,200	8,000	0.3	16,000	45
3.8-78.5 Cr-Permalloy	12,000	62,000	200	4,500	0.05	8,000	65
3.8-78.5 Mo-Permalloy	20,000	75,000	200	5,000	0.05	8,500	55
45-25 Perminvar, baked	400	2,000	2,500	3,000	1.2	15,500	19
7-45-25 Mo-Perminvar, baked	550	3,700	2,600	4,300	0.65	10,300	80
70-7.5 Perminvar, annealed	750	3,500			0.8	12,000	16

\* A.S.M. Metals Handbook, p. 494.

† Single numbers preceding the word "Permalloy" signify the nickel content, and double numbers signify first the content of chromium or molybdenum, and second the nickel content, the balance being iron in each case. The two large numbers before "Perminvar" indicate the nickel and cobalt contents, respectively, and the small initial number indicates the molybdenum content.

‡ For saturation value of the flux density. \*\* Saturation value of the intrinsic induction.

TABLE 22(j). MAGNETIC PROPERTIES OF 50% NICKEL-IRON ALLOYS IN COMPARISON WITH OTHER ALLOYS\*

(In accordance with information obtained from the manufacturers)

Material	Initial Permeability	Maximum Permeability	Hysteresis Loss, ergs per cc. per cycle†	Residual Induction, gaussses‡	Coercive Force, oersted§	Saturation Value, gaussses	Resistivity, microhm-cm. <sup>3</sup>	Form of Sample	Specific Gravity
Armco iron (99.95% Fe)	100,000	150	9,000	0.05	21,600	10	7.9	Solid ring	7.6
4-4.5% Silicon Iron	500	800	6,000	0.3	19,500	55	7.6	0.014 in. sheet	8.3
Hipernik	4,500	100,000	100	0.03	16,000	45		0.014 in. sheet	
45 Permalloy	2,700	23,000	1,200‡	0.3‡	16,000	45			
Allegheny Electric Metal	5,000	32,500	718	0.1	16,000	45			

\* A.S.M. Metals Handbook, p. 495.

† For B = 10,000 except as noted. ‡ For B = 16,000.

TABLE 22(k). COMMERCIAL TYPES OF MAGNET STEELS\*

Type of Steel	Nominal Composition, † %				Nominal** Magnetic Properties B <sub>c</sub> gauss H <sub>c</sub> oersteds		Hardening Temp., °F	Quenching Medium	Manufacturer***
	C	Mn	Cr	W	Co	Mo			
C-Mn	0.60	0.80					1450	Water	1
Cr	0.60	0.40	0.90				1450	Oil	1, 2, 3, 4
	0.90	0.35	2.25				1500	Water, Oil	1, 2, 3, 4, 5, 3
Cr-Mo	0.95	0.20-0.60	3.00-4.00				1525	Oil	1, 3, 4, 6
	1.00	0.35	6.00				1550	Oil	1, 3, 4, 6
	1.00	0.35	4.00		0.35		1550	Oil	1, 4
W	0.70	0.30	0.20	5.50			1550	Water	1, 2, 3, 4, 5, 6
W-Cr	0.70	0.50	0.50	6.00	8.50		1525	Oil	3
Co	0.90	0.35	4.75	1.25			1650	Oil	1, 3, 6
	0.90	0.30-0.85	3.50-5.75	3.75-7.00	35.00-41.00		1700	Oil	2, 3, 4, 6
Co-Cr	0.95	0.30	9.00		16.00		†	Air	3, 6
Co-W	0.85	0.50	2.00-5.00	8.75	17.00		1750	Oil	2, 3, 4, 6

\* A.S.M. Metals Handbook, p. 502.

† Silicon limit usually 0.30 max, phosphorus and sulfur 0.03 max, nickel 0.50 max. \*\* Values for previously annealed materials usually 5-10% lower in H<sub>c</sub>.

‡ Triple heat treatment, 2100°F cool in air, 1150°F cool in air, 1850°F cool in air.

\*\*\* The above information is a composite from the following manufacturers:

1. Universal Steel Co.
2. Bethlehem Steel Co.
3. Halcomb Steel Co.
4. Carpenter Steel Co.
5. Ludlum Steel Co.
6. Simonds Saw and Steel Co.

Special compositions are also made to order but do not warrant listing in the table.

TABLE 22(l). PRECIPITATION HARDENING MAGNET ALLOYS\*†

Type of Alloy	Per Cent				Nominal Magnetic Properties— B <sub>c</sub> gauss H <sub>c</sub> oersteds	
	Ni	Al	Co	Ti	Mo	Fe
Fe-Ni-Al	24-30	9-13				Bal.
Fe-Ni-Al-Co	24-30	9-13	5-10			Bal.
Fe-Ni-Co-Ti	10-25		15-30	8-25	16	72
Fe-Co-Mo Oxide						Iron oxide, cobalt oxide

\* A.S.M. Metals Handbook, p. 503.

† The data so far reported on these materials vary rather widely both as to composition and properties. Standardization into a few recognized and useful types for commercial applications has not yet been accomplished and probably will not be until considerably more exploratory work has been done.

TABLE 22(m). BOLTING MATERIALS FOR SERVICE AT 750-1100°F\*

Symbol	C	Mn	Si	S	P	Ni	Cr	Mo	W	V	
B <sub>4</sub>	0.35-0.45	0.50-0.80	0.50 max	0.04 max	1.50-2.00	0.50-0.80	0.30-0.40				Ni-Cr-Mo
B <sub>5</sub>	0.35 max	0.30-0.50	0.03 max	0.03 max		4-6	0.45-0.65†	0.75-1.25†			5 Cr
B <sub>6</sub>	0.12 max	0.60 max	0.50†	0.14†		11.50-13					13 Cr (free mach.)
B <sub>7</sub>	0.35-0.45	0.60-0.90	0.15-0.25	0.04 max		0.80-1.10	0.15-0.25				Cr-Mo
B <sub>7a</sub>	0.35-0.45	0.60-0.90	0.15-0.25	0.04 max		0.80-1.10	0.45-0.65				Cr-High Mo
B <sub>11</sub>	0.40-0.60	0.20-0.40	0.15-0.30	0.04 max		1.00-1.50		1.70-2.30		0.20-0.30	W-Cr-V
B <sub>12</sub>	0.35-0.45	0.60-0.90	0.05 max	0.04 max		1.00-1.50	0.45-0.75	0.85-1.35			Ni-Cr
B <sub>13</sub>	0.30-0.40	0.60-0.90	0.15-0.30	0.04 max		7-10	0.45-0.75	0.40-0.65		0.20-0.30	W-Mo-Cr
B <sub>14</sub>	0.35-0.50	0.40-0.70	0.15-0.30	0.04 max			0.80-1.10	0.30-0.40			Cr-Mo-V
B <sub>15</sub>	0.40-0.50	0.40-0.70	0.05 max	0.03 max			1.00-1.50	0.40-0.60			Si-Cr-Mo
B <sub>8</sub>	0.07 max	0.20-0.70	0.75 max	0.14†			17-20				18-8 (free mach.)

\* A.S.T.M., No. A 193-37T.

† Either Mo or W may be used.

‡ When P is over 0.045, S shall not exceed 0.05. When S is over 0.05, P shall not exceed 0.045.

The ferritic steels are to be heat treated, including drawing back at least 100° above operating temperature. 18-8 to be reheated and rapidly cooled (2000°, water quenched, for example).

TABLE 22(n). ALLOY STEEL PIPE FOR SERVICE AT 750-1100°F\*

Ferritic steels are to be full annealed or normalized and drawn 200° above service temperature, except P<sub>6c</sub>, which is heated at 1350° for stabilization. Properties: tensile, 60,000, yield, normalized 30,000, full annealed 25,000, 30% elongation, 2 in. longitudinal, 25% transverse.

Steel	C	Mn	Si	S	P	Cr	Mo	W	Ti	Cb
P <sub>1a</sub>	0.15 max	0.40-0.60	0.45-0.75	0.05 max	0.04 max	1.50-2.00	0.60-0.80			
P <sub>2b</sub>	0.15 max	0.30-0.60	0.50 max	0.03 max	0.03 max	1.75-2.25	0.45-0.65			
P <sub>3a</sub>	0.15 or 0.20† max	0.50 max	0.50 max	0.03	0.03	4-6	0.45-0.65	0.75-1.25†		
P <sub>5b</sub>	0.15 max	0.30 max	1.00-2.00	0.03 max	0.03 max	4-6	0.45-0.65			
P <sub>6c</sub>	0.10 or 0.15† max	0.50 max	0.50 max	0.03 max	0.03 max	4-6	0.45-0.65			
P <sub>6</sub>	0.12 max	0.50 max	0.50 max	0.03 max	0.03 max	12-15	2.50-3.50			4 to 6 X C18 to 10 X C
P <sub>11</sub>	0.15 max	0.30-0.60	0.50-1.00	0.05 max	0.04 max	1-1.50	0.45-0.65			
P <sub>16</sub>	0.15 max	0.30 max	1.15-1.65	0.045	0.04		0.45-0.65			

\* A.S.T.M. No. A 158-37 T.

† As specified.

‡ Either Mo or W may be used.

TABLE 22(o). VALVES AND VALVE SEAT MATERIAL\*

No.	Chemical Composition							Rockwell Hardness		Brinell Hardness, Hot (g)		
	C	Si	Cr	Ni	W	Mo	Other	Natural	After 1475°F draw	At 930°F	At 1475°F	
1	0.40-0.50	3.0-3.5	8.0-9.0		<i>Martensitic or Pearlitic Steels</i>			C-32 to 35	C-20 to 29	169-179	16-20	
2	0.35-0.45	3.9-4.2	2.8-3.0			0.75		C-38	C-31	254	26	
3	0.50	1.5	8.0	1.0-2.0				C-55			38 at 1600°	
4	0.60-0.85	1.25-2.75	19-23	0.75-1.0		3.25-3.75	0.50-0.75	2.5-3.5 Co				
5	1.0-1.1	1.8-2.0	13-14	< 0.65		12-16	0.45-0.95					
6	1.27-1.43	< 0.65	11.5-14									
7	0.50-0.70	3.0-4.0	3.0-4.0	< 0.50								
8	1.0-1.2	< 0.50	12-14	1.5				0.5 Mn, 1.8 Al	C-40	C-19		28
9	0.5	0.2	11.0					0.6-0.8 Mn				
10	2.5-3.0	1.5-2.0	2.75-3.25									
11	1.0	1.0	25.0									
12	0.30-0.45	2.50-3.25	17.5-20.5	7.0-9.0	<i>Austenitic Steels and Nickel-Chromium-Iron Alloys</i>			C-26	C-24	142	45	
13	0.20-0.30	0.70-1.00	21-22	11-12				C-20 to 27	C-18 to 22	130-180	55-78	
14	0.20-0.30	2.5-3.0	21-22	11-12				C-24	C-20	166	71	
15	0.40-0.50	0.30-0.80	13-15	13-15	1.75-3.00	< 0.50		C-25	C-23	162	55	
16	0.40-0.50	2.75-3.25	13-15	13-15	1.75-3.00	< 0.50		C-30	C-22	165	53	
17	0.50	1.25	14	26	3.5			C-22	C-16	182	84	
18	0.40-0.50	0.30-0.80	24-26	13-15		2.0-3.0		B-94	B-94		76	
19	0.95-1.20	2.0-3.0	15-16	13-15				C-24	C-30		94	
20	0.50	1.0	20	32			1.0 Mn	C-21	C-19	174	80	
21	0.50-0.60	0.50	3.5	12			5.0 Mn	C-22	B-95	140	55	
22	0.10	0.30	14	80				B-83	B-83	107	54	
23	0.07	< 0.75	18	8				B-81	B-80	74	49	
24	0.25-0.35	2.0-3.0	12.0-13.5	7.0-7.75	<i>Transformation Hardening Steels</i>			C-42	C-41	244	98	
25	0.40-0.50	< 1.0	23.3-24.3	4.5-5.0		2.5-3.5		C-41	C-36	230	63	

\* S. D. Heron, O. E. Harder, and M. R. Nestor, *Metal Progress*, May, 1940, Vol. 37, p. 541.



TABLE 22(o). (Continued)

No.	Chemical Composition						Rockwell Hardness		Brinell Hardness, Hot (g)		
	C	Si	Cr	Ni	W	Mo	Other	Natural	After 1475°F draw	At 930°F	At 1475°F
26	1.25	2.7	27		4		Nonferrous Alloys 65 Co 54 Co 0.60 Fe 1.6 Fe 0.5 Fe 4-6 Fe			217 at 1200°F	132 at 1600°F
27	2.0	0.9	30		12					314 at 1200°F	185 at 1600°F
28	0.20	0.30	21	Balance		0.90 Mn					
29	0.16	0.02	30.3 Cu	66.9		0.90 Mn					
30			Bal. Cu			0.16 Al					
31			Bal. Cu			9.5 Al					
32			Bal. Cu	4.0-6.0		10.5-11.5 Al					
				< 99.0							
No.	Sealing Loss (a)		Corrosion Resistance in Exhaust Condensate	Relative Attack by Lead Compounds (b)			Utility and Remarks				
	Oxidizing atmosphere	Reducing atmosphere		PbO at 1800°F	PbO at 1550°F	2PbO·3PbSO <sub>4</sub> at 1800°F					
1	50	140	Poor	41	100	200	Martensitic or Pearlitic Steels Most widely used exhaust valve material. Cheaper variety; inferior as to burning and rusting. Unsatisfactory substitute for No. 1. Rapidly replacing No. 1. Limited use replacing No. 6. Superseded No. 7 for aircraft use in early 1920's. High speed tool steel; adopted in U.S. in 1911; much used in War; first valve with good hot strength. Cutlery stainless (modified); used in Europe for 1916-1918 aircraft. Reputation for unreliability in automobiles. Cast exhaust valve seats for passenger cars and trucks. In experimental use.				
2	160	360	Very bad	41	106	258					
3	10,000	12,000	Very bad								
4	40	75	Complete	1	104	8					
5	5,000	2,200	Very bad	16	136	6					
6			Very bad								
7			Very bad								
8	19,000 (c)	19,000 (c)	Very bad	56	64	3					
9			(d)	26	113	5					
10	18,000	17,000		36	240	520					
11	60	100	Complete	2	14	1					

(a) Loss in mg on 3/8 X 2 in. rod after 300 40-min cycles between 1800 and 650°F. Fuel is a special kerosene with antiknock additions, burned with 15 1/2 lb air per lb for oxidizing atmosphere and 12 1/2 lb for reducing. Low results may be misleading. (b) Calingart test. Relative loss after 6 min in molten compound. (c) After 250 cycles. (d) Probably very bad. (e) Complete if not nitrided; poor when nitrided. (f) Maximum temperature on heating cycles: 1600°F. (g) By mutual indentation.

TABLE 22(c). (Continued)

No.	Sealing Loss (g) Oxidizing atmos- phere	Resistance Reducing at- mos- phere	Corrosion Resistance in Exhaust Condensate	Relative Attack by			Utility and Remarks
				PbO-PbBr <sub>2</sub> at 1550°F	PbO at 1800°F	2PbO-3PbSO <sub>4</sub> at 1800°F	
<i>Austenitic Steels and Nickel-Chromium-Iron Alloys</i>							
12	90	70	Complete	63	57	46	Wide use in automobiles for its hot strength.
13	30	60	Complete	37	43	2	Wide use in bus and truck engines.
14	50	90	Complete	48	48	17	Higher silicon than No. 13 does not improve resistance to burning.
15	2,600	1,600	Complete (e)	20	126	26	U. S. aircraft exhaust valves; internally cooled and seat faced.
16	100	150	Complete	25	92	184	Too hard to drill; seat inserts in aluminum cylinders.
17	840	370	Complete	28	73	228	European aircraft exhaust valves.
18	50	40	Complete (e)	12	47	0.3	Recently introduced to replace No. 15; about same in severe service; no intergranular attack by sodium.
19	140	160	Complete				Castings for both intake and exhaust valves on Ford motors.
20	60	40	Complete				Limited use, as cast, in auto, bus, and truck valves.
21	11,000	11,000	Complete (g)				Exhaust valve seats in European aircraft. High thermal expansion requires threaded design to remain tight.
22	60	50	Complete	40	42	254	Not used, despite interesting properties.
23	2,400	1,700	Complete	25	112	2	Not used, despite interesting properties.
<i>Transformation Hardening Steels</i>							
24	2,800	2,300	Very good	49	84	24	Had limited use in autos and wide use in aircraft.
25	40	50	Complete	2	35	1	Better wear and scuffing resistance than austenitic steels; embrittled by many cycles between 1400 and 1600°F.
<i>Nonferrous Alloys</i>							
26	20	15	Complete	0.5	4	0.5	Stellite No. 6; almost universal in U. S. for welded-on seat facings in aircraft engines.
27	50	15	Complete	72	6	1	Valve seat inserts for bus and trucks, with higher hot hardness and wear resistance than No. 26.
28	45	15 gain	Complete	71	52	197	Brightray; used in Europe for welded-on seat facings.
29	13,000	30	Very good				Monel; used in Europe for some exhaust valve seat inserts.
30	1,000(f)		Good	100	244	243	Formerly much used as extruded valve seat inserts in aluminum cylinders.
31			Good				Cast and heat-treated substitute for No. 30. Neither good for leaded fuels.
32	250	70	Complete	3	340	504	Commercially pure nickel; has unusually high hot corrosion resistance.

(a) Loss in mg on  $\frac{3}{8} \times 2$  in. rod after 300 40-min cycles between 1800 and 650°F. Fuel is a special kerosene with antiknock additions, burned with 15- $\frac{1}{2}$  lb air per lb for oxidizing atmosphere and 12 $\frac{1}{2}$  lb for reducing. Low results may be misleading. (b) Callingaert test. Relative loss after 6 min in molten compound. (c) After 250 cycles. (d) Probably very bad. (e) Complete if not nitrided; poor when nitrided. (f) Maximum temperature on heating cycles: 1600°F. (g) By mutual indentation.

TABLE 22(p). NICKEL-IRON ALLOYS\*  
(Lohr and Hopkins)

Composition, %			Inflection† Temp., °C	Average Coefficient of Expansion to Inflection, Temp. × 10 <sup>-6</sup>
Mn	Si	Ni		
0.11	0.02	30.14	155	9.2
0.15	0.33	35.65	215	1.54
0.12	0.07	38.70	340	2.50
0.24	0.03	41.88	375	4.85
		42.31	380	5.07
		43.01	410	5.71
		45.16	425	7.25
0.35		45.22	425	6.75
0.24	0.11	46.00	465	7.61
		47.37	465	8.04
0.09	0.03	48.10	497	8.79
0.75	0.00	49.90	500	8.84
		50.00	515	9.18
0.25	0.20	50.05	527	9.46
0.01	0.18	51.70	545	9.61
0.03	0.16	52.10	550	10.28
0.35	0.04	52.25	550	10.09
0.05	0.03	53.40	580	10.63
0.12	0.07	55.20	590	11.36
0.25	0.05	57.81		12.24
0.22	0.07	60.60		12.78
0.18	0.04	64.87		13.62
0.00	0.05	67.98		14.37

\* A.S.M. Metals Handbook, 1939, p. 469.

† Note that in alloys with higher than 55% nickel, the inflection temperature is not in evidence.

TABLE 22(q). TENSILE RESULTS

Authority	Material	Treatment, °F	Test Temp., °F
			<i>Carbon</i>
			Room
			- 4
Colbeck MacGillivray Manning	Armco C 0.035%	As rec'd	- 58
			- 94
			-148
			-184
			-292
Hadfield	Swedish charcoal iron C 0.03%, Mn 0.04%	As forged	Room
			-296
			-423
Colbeck, etc.	C 0.13%	As rec'd	Room
			- 85
			-292
Hadfield	Carbon steel C 0.14%, Mn 0.07%	Annealed 1472	Room
			-296
			-423
Sands	C 0.21%	As rec'd	Room
			-114
Bull	Rolled bar C 0.21%, Mn 0.60%		Room
			-114
Bull	Carbon casting C 0.21%, Mn 0.70%		Room
			-114
Bull	Carbon forging C 0.26%, Mn 0.46%		Room
			-114
Kinzel Krafts Egan	S.A.E. 1035	Normalized	+ 25
			- 25
			- 60
			-190
Hadfield	Carbon steel C 0.37%, Mn 0.20%	Annealed 1472	Room
			-296
			-423
Strauss	C 0.40%	Annealed	Room
			Liq. air
Strauss	C 0.40%	Treated	Room
			Liq. air
Bull	Carbon forging C 0.40%, Mn 0.52%		Room
			-114
Hadfield	Carbon steel C 0.78%, Mn 0.10%	Annealed 1472	Room
			-296
			-423

## ON STEELS AT LOW TEMPERATURES\*

Tensile Strength, psi	Yield Point, psi	Elong., % in 2 in.	Red. Area, %	Brinell
<i>Steels</i>				
45,700		27.9	73.2	
53,750	30,700	42.0	75.0	
59,400	42,200	43.0	74.0	
61,700	43,400	37.5	72.0	
66,800	57,200	27.5	70.0	
77,000	66,700	17.0	68.0	
112,000		Nil	Nil	
52,500	41,700	25	81.0	104
116,500		Nil		230
117,000	117,000	Nil	Nil	232
66,300	54,700	29.7	71.8	
80,700	67,700	33.6	70.3	
121,300		26.5	55.0	
45,700	42,700	27.5	77.5	114
137,000		7.5		281
155,000	155,000	0.3	2.5	326
62,000	39,800	35.5	53.0	
69,000	47,780	35.5	56.8	
62,600	39,800	35.5	53.0	
68,995	47,780	35.5	56.8	
71,840	32,195	34.8	55.3	
77,585	39,540	33.3	52.5	
57,300	38,940	34.0	54.7	
72,840	50,325	36.0	53.2	
85,000	50,000	29.0	52.0	
95,000	60,000	27.0	48.0	
102,000	76,000	30.0	48.0	
144,000	143,000	5.0	5.0	
76,200		20.0	63.0	157
148,000		17.0	39.0	294
151,000	151,000	Nil	Nil	316
79,400	45,800	30.8	49.0	
139,400	114,100	7.3	7.1	
104,400	76,900	25.0	61.3	
160,400	150,200	9.8	9.4	
77,440	44,670	29.0	45.3	
83,310	47,075	30.8	44.9	
99,000	95,000	12.0	35.0	194
154,700		Nil		325
123,000	123,000	0.2	Nil	244

\* A.S.M. Metals Handbook, 1939, pp. 87 and 88.

TABLE 22(q).

Authority	Material	Treatment °F	Test Temp., °F
			<i>Alloy</i>
Hurtgen	C 0.53%	1500 oil	+100
	Cr 0.97%	1120 tempered	0
	Mo 0.22%		-100
			Room
Colbeck, etc.	C 0.33%	1560 oil 1185 tempered	- 6
	Cr 0.67%		- 76
	Ni 2.45%		- 90
	Mo 0.64%		-141
			-292
Hadfield	C 0.35%	Oil quench, 1200 tempered	Room
	Cr 0.71%		-423
	Ni 3.34%		
Strauss	Ni 3%	Annealed	Room
		Treated	Liq. air
			Room
Strauss	Cr 14%	Treated	Liq. air
			Room
Strauss	Cr 16%	Annealed	Liq. air
			Room
Strauss	Cr 20%	Treated	Liq. air
			Room
Nickel Steel Topics	C 1.27%		-296
	Mn 12.69%		-423
Hadfield	Cr 18%		Room
	Ni 8%		-423
Russell	Cr 8%	Annealed	Room
	Ni 21%		Liq. air
Colbeck, etc.	C 0.11%	Water quenched 2010	-292
	Ni 10.5 %		
	Cr 15.6 %		
Colbeck, etc.	C 0.06%, Cr 13.45%	As above	Room
	Ni 10.05%, Mn 4.07%		-292
Hadfield	C 0.41%		Liq. air
	Ni 20.0 %		
Nickel Steel Topics	C 0.56%		Room
	Ni 24.6 %		-112
Russell	Ni 26%	Annealed	Room
			Liq. air
Russell	C 0.56%		64
	Ni 24.6 %		-112
	Mn 1.18%		

(Continued)

Tensile Strength, psi	Yield Point, psi	Elong., % in 2 in.	Red. Area, %
<i>Steels</i>			
135,000	90,000	21.0	62
138,000	97,500	21.5	59
150,000	107,500	22.0	55
152,000	137,700	14.0	65.0
154,500	141,000	15.6	64.0
164,000	143,300	14.0	63.0
163,000	145,500	15.6	62.0
170,000	149,000	16.4	61.0
201,500	183,500	17.0	63.0
146,000	133,000	13.5	59.5
243,000	243,000	4.5	48.5
79,400	57,000	31.5	57.2
116,600	111,000	6.8	6.7
98,800	76,400	27.3	65.9
148,700	132,900	15.5	17.6
225,800	212,200	9.8	37.3
259,700	210,800	2.8	3.5
75,100	42,800	34.0	70.8
145,700	123,200	14.0	14.3
91,900	51,900	24.0	59.3
99,200	99,200	0.0	0.0
148,000	77,300	44.5	39.0
137,000		2.5	
146,000	146,000	Nil	Nil
117,000		56.0	54.0
268,000		25.0	31.0
107,600	48,300	44.3	60.1
180,200	102,800	25.3	21.5
232,000	77,000	30.5	45.0
80,400	38,500	59.5	75.5
197,500	89,500	47.0	60.0
353,000		15.0	
120,500		20.4	
160,000		14.1	
99,800	52,900	38.3	52.1
205,000	157,800	11.5	9.7
120,500	71,200	20.4	67.4
160,000	105,000	14.1	64.0

### CARBURIZING AND CASE HARDENING

Carburizing was known many centuries ago as *cementation*. Wrought iron was packed in charcoal, heated to about 1700–1800°F for carbon absorption and blister steel of high carbon was obtained.

Today it is the practice to carburize low carbon and alloy steels, primarily for high surface hardness and resistance to abrasion. A case of high carbon content varying in thickness from a few thousandths to about 0.030 in. is produced which is later hardened and tempered. Heavy sections may be carburized to a case depth of 0.060 in. and even higher.

Case hardening is the combined process of carburizing an iron-base alloy so the carbon content of its outside portion or case is increased; this is followed by quenching and tempering so its case is hardened while its core is relatively soft and tough. In recent years, however, case hardening has been extended to include cyaniding and nitriding.

#### Carburizing Methods

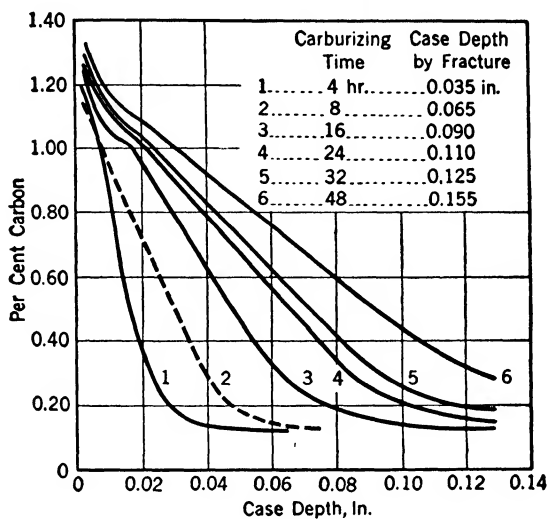
There are three commercial methods for carburizing: (1) pack carburizing, (2) gas carburizing, and (3) liquid carburizing. The proper choice of a particular method for certain work depends on many economic factors such as design of part, type and depth of case, permissible distortion, production volume, initial investment, and operating costs.

**Pack Carburizing.** The pack carburizing or pack hardening method is the oldest and is most extensively employed in smaller shops. The method is frequently called *box carburizing*. The parts are packed in one of many commercial carburizing compounds composed of hardwood charcoal 40–65%, barium carbonate 5–16%, calcium carbonate 2–7%, sodium carbonate 3–12%, moisture 3–5%, and coke about 20%. Another type is composed of charred bone 70–80%, hardwood charcoal 10–15%, carbonates 3–15%. The carbonates are called energizers and should be above about 8%. The container boxes or pots are usually of iron-nickel-chromium heat-resisting alloys and the parts are surrounded with carburizing compound of a fineness about pea size. A cover is luted on with fireclay, common salt, water, asbestos fiber, etc., and the pots charged to batch type or continuous furnaces. The boxes are usually heated to about 1700°F and held at temperature for sufficient time to produce the proper depth of case. Case depth is usually measured in inches from the outside of the part through the diffusion zone to the first location having the original carbon content of the core, about 0.15–0.20% carbon.

The higher the carburizing temperature the greater the depth of case, because of increased diffusion, and the higher will be its carbon content



because of increased solubility. At 1700°F the carbon content of the austenite will be about 1.20% on the extreme outside of case and will gradually diffuse from this *hypereutectoid zone* to the eutectoid zone and



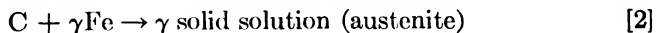
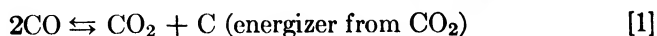
*Courtesy A.S.M. Handbook*

FIG. 99. Carbon gradient curves for S.A.E. steel 3115. Carburized at 1700°F in hardwood charcoal, coke, sodium carbonate compound.

then into the hypoeutectoid zone and the original carbon content of the core.

Fig. 99 shows the relation between carbon content, case depth, and time of carburizing for S.A.E. 3115.

**Mechanism of Carburizing.** In reality box carburizing is gas carburizing because the mechanism is governed by the following chemical reactions and carbon monoxide is the active carburizing agent.



Several hours of carburizing with charcoal alone at 1700°F will produce almost no case if the box is evacuated to about 5 mm of mercury, indicating the necessity for the presence of oxygen in the carburizing reaction.

Box carburizing is usually considered the most fool-proof method and the safest without trained supervision. The solid carburizing compound gives good support for pieces tending to warp. Disadvantages are in the long time of carburizing because of low heat transfer through the compound, high labor cost for packing and unpacking, and the presence of much dust. If one wishes to harden directly from the

carburizing heat there is more difficulty than with other carburizing processes.

A modified pack method uses a rotary retort. When parts can withstand rough treatment by slow tumbling, the carburizing is faster for a given depth of case and the method is the most economical because of low labor cost and bulk handling.

**Gas Carburizing.** This process is used mostly where a large volume of work is to be handled by skilled operators. The first cost is high and the controls are complicated but the process is extremely flexible in regard to temperature, case depth, carbon content of the outer case, and carbon gradient. Case depths between 0.005 and 0.035 in. are easily and accurately controlled in large production.

The gases used are classified as follows:

<u>Carburizing Gases</u>	<u>Decarburizing Gases</u>	<u>Neutral Gases</u>
Carbon monoxide, CO	Carbon dioxide, CO <sub>2</sub>	Nitrogen, N <sub>2</sub>
Methane, CH <sub>4</sub>	Water vapor, H <sub>2</sub> O	
Ethane, C <sub>2</sub> H <sub>6</sub>	(Oxygen reacts to form above gases in retort.)	
Propane, C <sub>3</sub> H <sub>8</sub>	Hydrogen*	
Butane, C <sub>4</sub> H <sub>10</sub>		

\*Small amounts of methane will neutralize the decarburizing tendency of hydrogen.

Carbon monoxide as a commercial carburizing gas is limited to the skin case hardening of medium-carbon steels. It is an excellent gas for diluting the heavier hydrocarbon gases such as methane and ethane of natural gas, propane, and butane. Commercial propane is available in tanks or steel cylinders as a liquid in a rather pure state and is quite satisfactory as a carburizing gas.

It is the practice in many plants to dilute a carburizing gas with a decarburizing gas by partial combustion either in a separate furnace retort or in a gas generator. Water vapor is usually condensed out or absorbed because of its strongly decarburizing action.

**Protection Against Carburization.** In order to prevent carburizing on certain areas of a particular part, the whole part is copper plated and later machined off at surfaces where carburizing is desired such as on the faces of cams on an ordinary cam shaft. Copper paints and clay packs are also used.

Fig. 100 shows the box-cooled structure from case to core of carburized ingot iron at 75 $\times$ . The micrograph of the case at  $\times 1000$  shows that the structure is slightly *abnormal*; this means that the proeutectoid carbide in the hypereutectoid zone is not completely in a uniform network but has occasional large patches of massive carbide and ferrite.

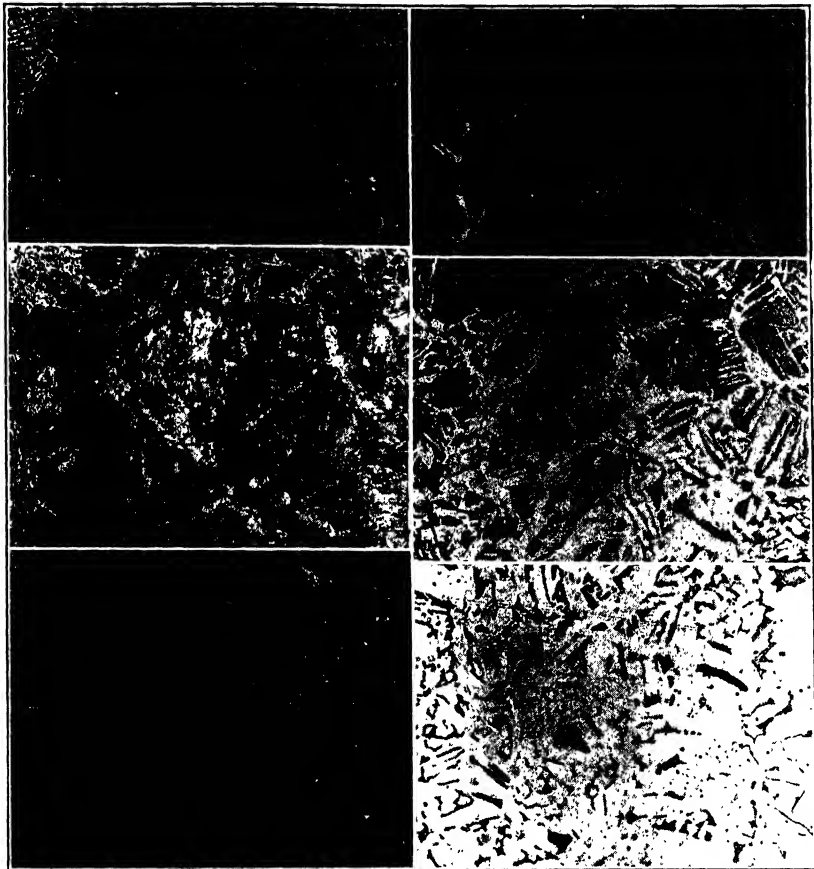


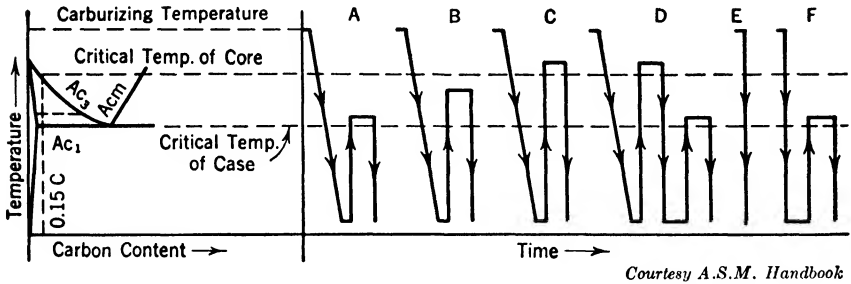
FIG. 100A. Structure of carburized ingot iron from case to core. Abnormal. Cooled in box to form pearlitic structure.  $\times 75$ .

**Heat Treatment after Carburizing.** Fig. 101 shows a diagrammatic representation of the various heat treatments for carburized steels, together with the case and core properties and recommendations dependent on grain size. The figure is self-explanatory. The sloping lines under *A*, *B*, *C*, and *D* indicate box cooling; the vertical lines either heating or quenching according to the direction of the arrow; and the horizontal lines holding, at the temperatures shown. Network cementite forms in the hypereutectoid zone on box cooling and if not eliminated by a later solution treatment will cause extreme brittleness in the case. Tempering after quenching is not always carried out because there is less internal stress and less breakage with case-hardened parts than with



FIG. 100B. Same as 100A. *Top*, hypereutectoid zone of case; *middle*, eutectoid zone between case and core; *bottom*, hypoeutectoid zone of core.  $\times 1000$ .

untempered tool steels. Tempering at 350–500°F, however, is recommended for important parts.



Courtesy A.S.M. Handbook

TREATMENT	CASE	CORE
<i>A</i> Best adapted to fine-grained steels.	Refined; excess carbide not dissolved.	Unrefined; soft and machinable.
<i>B</i> Best adapted to fine-grained steels.	Slightly coarsened; some solution of excess carbide.	Partially refined; stronger and tougher than <i>A</i> .
<i>C</i> Best adapted to fine-grained steels.	Somewhat coarsened; solution of excess carbide favored; austenite retention promoted in highly alloy steels.	Refined; maximum core strength and hardness; better combination of strength and ductility than <i>B</i> .
<i>D</i> Best treatment for coarse-grained steels.	Refined; solution of excess carbide favored; austenite retention minimized.	Refined; soft and machinable; maximum toughness and resistance to impact.
<i>E</i> Adapted to fine-grained steels only.	Unrefined with excess carbide dissolved; austenite retained; distortion minimized; file proof when carbon is high.	Unrefined but hardened.
<i>F</i> Adapted to fine-grained steels only.	Refined; solution of excess carbide favored; austenite retention minimized.	Unrefined; fair toughness.

FIG. 101. Various heat treatments for carburized steels.

**Liquid Carburizing and Cyaniding.** In liquid carburizing it is customary to use molten baths composed of about 60–70% of calcium and sodium chlorides and 30–40% of sodium cyanide (NaCN). The bath is ordinarily operated between 1500 and 1650°F and the ordinary carburizing steels S.A.E. 1010, 1020, 1120, etc., are cased to a depth of about 0.010 in.

This early process of liquid carburizing was known as *cyaniding* and, if it is carried out at lower temperatures, considerable nitrogen dissolves in the outer portion of the case in addition to carbon. The inner portion of the case frequently shows needles of iron nitride but most of the case is quite structureless. A cyanide bath decomposes during operation mainly by oxidation so it is customary to add 96–98% NaCN to main-

tain its strength of about 30% NaCN for production work. With considerable "drag out" from the parts being quenched it is customary to add only 30% NaCN. Cyaniding is widely used in industry to produce a thin case at a low cost.

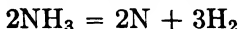
In recent years there has been a tendency to deviate from the harder, more brittle and shallower cases caused by nitriding in the cyaniding process and to obtain deeper and less brittle cases which are more carburized than nitrided. This has led to the so-called "activated baths" utilizing calcium cyanamide,  $\text{CaCN}_2$ , polymerized hydrocyanic acid, or sodium cyanide with controlling chemicals to govern the decomposition of the cyanides.

The case obtained with activated baths is generally between 0.010–0.030 in. and as a rule contains from 50 to 75 per cent less nitrides than cases obtained by cyaniding. Above 0.030 in. it is more economical to carburize by the pack or gas methods. The salts are usually purchased in the fused state in lumps and are added to the pots when necessary. Heat-resisting alloy pots are most satisfactory but many pressed mild steel pots are in service.

Cyanided work is usually hardened in water. Oil quenching, however, gives less brittleness and distortion and is advocated where more toughness and slightly less hardness are desired. Parts of small size are handled by submerged baskets. Ventilated hoods should be provided to carry off fumes. Fig. 102 shows a comparison of case depths with time for the two types of baths.

**Nitriding.** The case-hardening process whereby steels containing 0.20–0.45% C, 0.90–1.50% Al, 0.0–1.80% Cr, 0.15–1.00% Mo, and 0.0–3.75% Ni are subjected to atomic nitrogen to form a surface layer high in nitrogen is called nitriding.

The steels are quenched and tempered to a sorbitic structure before nitriding. They are nitrided in a retort. Ordinarily anhydrous ammonia gas is drawn off from a cylinder and is bled into a retort at a low positive pressure. The rate of flow of  $\text{NH}_3$  gas is regulated so as to have a dissociation of about 30 per cent according to the reaction



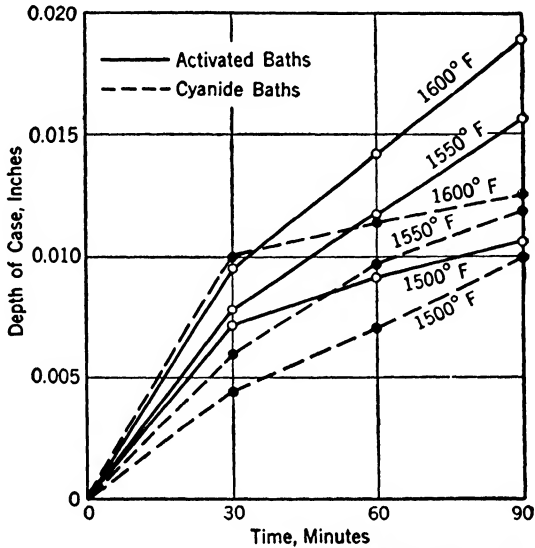
The nascent nitrogen dissolves in the special steels, forming solid solutions and complex nitrides having high hardness.

A case depth of about 0.020 in. may be obtained in about 50 hours with its outer hardness about 1000 Vickers. A carburized case is ordinarily about 850 Vickers.

In order to protect against nitriding at certain areas of a particular part, a lead-tin solder coating of 80% Pb–20% Sn is customary although

it is molten at nitriding temperatures. Tin plating of 0.007 in. in thickness, nickel plating of 0.0005 in., or special paints are also used.

After nitriding the work is cooled to below scaling temperature before opening the retort and removing the basket containing the work. The hardness in the slow-cooled state is about 1000 diamond Brinell and it is not necessary to quench in order to obtain full hardness.



*Courtesy Beckwith, A.S.M.*

FIG. 102. Case depths for activated baths and cyanide baths.

Advantages of the process are: there is almost no distortion of work; high hardness and excellent wear resistance are obtained; extremely large sections can be surface hardened.

Several disadvantages are: the case is more brittle, especially under impact; the cost is about three times that of carburizing; the steels required are more expensive; and a long time cycle is necessary.

### CAST IRON AND MALLEABLE CAST IRON

Cast irons are very useful and important iron-base alloys with carbon usually between 1.7 and 4.5% and containing various amounts of silicon, manganese, phosphorus, and sulfur. The last two are considered impurities but may, under special conditions, contribute useful properties. These alloys are further complicated by nickel, chromium, molybdenum, etc., and referred to as alloy cast irons. In cast alloys there is no appreciable malleability at any temperature because of high-carbon content.

It should be remembered that about 1.7% carbon represents the maximum solubility of carbon in austenite and that cast irons are generally hypoeutectic alloys. The network of eutectic structure, ledeburite ( $\gamma$  solid solution and cementite), together with graphite flakes, is responsible for the absence of plasticity.

### **Pig Iron**

Pig iron is made by reducing iron ore with coke and melting in a blast furnace. It is used with various proportions of gray iron scrap and steel scrap to produce cast iron.

Silicon is ordinarily present in pig iron and is considered the pyrometer of the blast furnace, as the higher the operating temperature the more the silicon is reduced from  $\text{SiO}_2$  which enters the pig iron. Foundry pig iron compositions contain 1.5–3.00% Si, 0.02–0.06% S, 0.25–1.00% P, 0.50–1.00% Mn, and 3.50–4.25% T.C. (total carbon). Silicon is classed as a graphitizer and when present in large amounts expels graphite as the liquid iron cools, forming graphite flakes (kish) which leave the iron.

### **Gray Cast Iron**

Gray cast iron is an alloy of iron with carbon from about 2.8–3.5% and silicon from about 1.25–3.00%, which has a gray fracture in the "as cast" condition. It sometimes contains nickel, chromium, copper, and molybdenum to enhance certain properties. The principal micro-constituent is pearlite; the gray fracture results from the presence of graphite flakes. A small amount of free ferrite is usually also present. Free cementite is avoided if good machinability is desired. The flake graphite of gray iron forms mostly on solidification (Fig. 103).

Gray iron is usually made in an ordinary foundry cupola furnace by melting pig iron, scrap iron and steel, with coke as a fuel, at a comparatively low melting cost. Table 23 gives some typical compositions of plain cast iron with common applications.

The degree of graphitization is controlled by the cooling rate and silicon content. In order to make cast iron machinable for a certain size of section of a casting, it is necessary to regulate closely its silicon content. Heavy sections of about two inches will have a silicon content of about 1.25%, whereas light sections, such as piston rings, will require about 2.90% silicon to resist chill in casting and graphitize sufficiently to be machinable.

A summary of the structural effects of alloys on cast iron is shown in Table 24.

**Effect of Phosphorus.** Phosphorus increases the castability of cast iron by lowering its freezing point; the phosphorus may be up to 1% for



thin sections. Up to 0.90% P there is little effect on the tensile strength of the ordinary cast iron in the range of tensile strength of 40,000 psi. In high percentages it is detrimental to strength. Most of the phos-

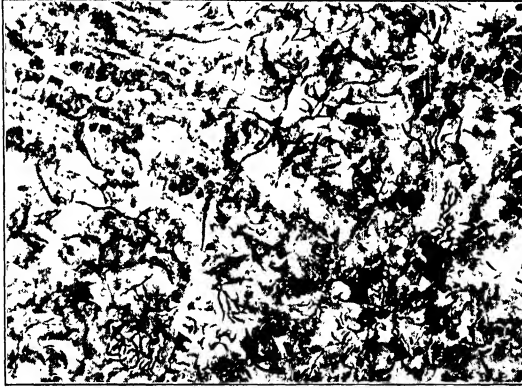


FIG. 103. Gray cast iron. Light gray dendrites are pearlite which was  $\gamma$  solid solution before transformation to pearlite. White structure around dendrites is eutectic constituent, ledeburite (Geist, University of Minnesota).  $\times 100$ .

phorus is present in the microconstituent Steadite appearing as white, fine, dotted eutectic. Steadite is a eutectic of austenite, saturated with



FIG. 104. Steadite in gray cast iron. Composition: T.C. 2.60%, Si 2.90%, Mn 0.65%, S 0.086%, P 0.39%. Structure: pearlite, graphite flakes, and steadite (Nagler, University of Minnesota).  $\times 1000$ .

phosphorus, and iron phosphide ( $\text{Fe}_3\text{P}$ ). It contains about 10.2% P and has a melting point of about 1800°F. Its structure is shown in Fig. 104.

TABLE 23. TYPICAL ANALYSES OF SOME COMMERCIAL GRAY IRON CASTINGS\*  
(Not intended for specifications)

Casting	Per Cent							
	Total C	Si	Mn	P	S	Ni	Cr	Mo
Auto cylinder, plain iron	3.25	2.25	0.65	0.15	0.10			
Auto cylinder, Ni-Cr iron	3.25	2.25	0.65	0.15	0.10	0.75	0.30	
Auto cylinder, Ni-Cr iron, heavy duty	3.25	1.90	0.65	0.15	0.10	1.75	0.45	
Auto cylinder, Ni iron	3.25	1.80	0.65	0.15	0.10	1.25		
Auto pistons, plain iron	3.35	2.25	0.65	0.15	0.10			
Auto pistons, Mo iron	3.35	2.25	0.65	0.15	0.10			0.50
General castings (auto), soft iron	3.40	2.60	0.65	0.30	0.10			
Piston rings (auto), individually cast	3.50	2.90	0.65	0.50	0.06			
Brake drums (auto)	3.30	1.90	0.65	0.15	0.08	1.25	0.50	
Brake drums (auto)	2.75	2.25	0.70	0.15	0.08			0.50
Cams	3.10	1.50	0.65	0.15	0.10	2.00	0.60	
Machinery iron:								
Light service or thin section	3.25	2.25	0.50	0.35	0.10			
Medium service or heavy section	3.25	1.75	0.50	0.35	0.10			
Heavy service with heavy section	3.25	1.25	0.50	0.35	0.10			
Water pipe, sand cast:								
Light and medium	3.60	1.75	0.50	0.80	0.08			
Heavy	3.40	1.40	0.50	0.80	0.08			
Chilled plow shares	3.60	1.25	0.55	0.40	0.10			
High strength iron, plain	2.75	2.25	0.80	0.10	0.09			
High strength iron, nickel	2.75	2.25	0.80	0.10	0.09	1.00		
High strength iron, Mo	2.75	2.25	0.80	0.10	0.09			0.35
Heat-resistant iron, fire pots, and kettles	3.50	1.15	0.80	0.10	0.07			
Caustic pots, Ni-Cr	3.30	0.70	0.50	0.10	0.08	1.50	0.60	
Caustic pots, plain	3.60	1.00	0.75	0.20	0.07			
Ingot molds	3.50	1.00	0.90	0.20	0.07			
Car wheels	3.35	0.65	0.60	0.35	0.12			
Air cylinders, ammonia cylin- ders, plain iron	3.25	1.25	0.65	0.20	0.10			
Heavy compressor cylinders, nickel iron	3.00	1.10	0.80	0.20	0.10	2.00		
Light compressor cylinders, Ni-Cr	3.30	2.10	0.55	0.25	0.10	1.25	0.45	
Light forming and stamping or forging dies, Ni-Cr iron	3.30	1.50	0.60	0.20	0.10	2.00	0.60	
Heavy forming and stamping or forging dies, Ni-Cr iron	3.00	1.25	0.60	0.20	0.10	2.75	0.80	
Light forging dies, Mo iron	3.30	2.00	0.60	0.20	0.10			1.00
Heavy forging dies, Mo iron	3.10	1.50	0.60	0.20	0.08			1.00
Valves and fittings (medium)	3.30	2.00	0.50	0.35	0.10			

\* A.S.M. Metals Handbook, 1939, p. 630.

TABLE 24. SUMMARY OF STRUCTURAL EFFECTS OF ALLOYS ON CAST IRON\*

	Percentages Used in Pearlitic Irons	"Chill"	Effect on Carbides (at high temps.)	Effect on Graphite Structure	Effect on Combined Carbon in Pearlite	Effect on Matrix
Chill-inducing elements						
Chromium	0.15-1.0	Increases**	Strongly stabilizes	Mildly refines	Increases	Refines pearlite and hardens
Vanadium	0.15-0.50	Increases	Strongly stabilizes	Refines	Increases	Refines pearlite and hardens
Mildly chill-inducing						
Manganese	0.30-1.25	Mildly increases	Stabilizes	Mildly refines	Increases	Refines pearlite and hardens
Molybdenum	0.30-1.00	Mildly increases	About neutral	Strongly refines	Mildly increases	Refines pearlite and strengthens
Mildly chill-restraining						
Copper	0.50-2.0	Mildly restrains	About neutral	About neutral	Mildly decreases	Hardens
Chill-restraining						
Carbon		Strongly restrains	Decreases stability	Coarsens	Strongly decreases	Produces ferrite and softens
Silicon		Strongly restrains	Decreases stability	Coarsens	Strongly decreases	Produces ferrite and softens
Aluminum		Strongly restrains	Decreases stability	Coarsens	Strongly decreases	Produces ferrite and softens
Nickel	0.10-3.0	Restrains†	Mildly decreases stability	Mildly refines	Mildly decreases and stabilizes at eutectoid	Refines pearlite and hardens
Titanium	0.05-0.1	Restrains	Decreases stability	Strongly refines†	Decreases	Produces ferrite and softens
Zirconium	0.10-0.3	Restrains	Decreases stability	About neutral		Produces ferrite and softens

\* Alloy Cast Irons, American Foundrymen's Association, 1939. Table 2, p. 34.

\*\* Chill-inducing effect about balances chill-restraining effect of 1½ parts Si or 2½ of Ni.

† Chill-restraining effect about one-half that of silicon.

‡ When added in small amounts and particularly when oxygen also is present.

**Effect of Sulfur and Manganese on Cast Iron.** Sulfur does not seem to be harmful up to about 0.18% and exists as MnS if sufficient manganese is present. A manganese content of 0.60–0.80% is sufficient to form MnS because most American cast irons are under 0.12% sulfur and the ratio of Mn to S in MnS is 55 to 32. The source of sulfur in cast iron is mostly from the coke made from high-sulfur coal.

The tensile strength of gray irons may be increased from 40,000 psi to 70,000 psi by lowering the carbon to about 2.60% and alloying with about 2.15% silicon and 1.10% nickel so there will be less graphitic carbon in flakes with more pearlite in the matrix (pearlitic iron). With special cupola practice the same strength may be obtained with about 0.35% molybdenum instead of the nickel.

Electric furnace irons with carbon of 3.00%, Si 2.35, S 0.09, P 0.13, Mn 0.80, Cr 0.37, Mo 0.58, and N 0.44% can be obtained with about 55,000 psi and 241 Brinell hardness from a bar 1.20 in. diameter.

These high-strength cast irons are not so readily machinable as the low-strength irons. In high-strength irons the matrix is harder and contains less graphite with a better distribution and a smaller size of flake. They may be made in many ways with many combinations of alloy additions. High-strength irons can be made by adding calcium silicide, silicon carbide, etc., to the molten metal for the purpose of controlling graphitization and reducing grain size.

**Growth of Cast Iron.** When ordinary cast irons are heated for prolonged times at temperatures above 800°F they “grow” or increase in size in all directions because of graphitization and absorption of gases. To prevent graphite formation, special irons having stable carbides are made with chromium additions. A 6–8% silicon iron does not grow because it has no carbides to dissociate to ferrite and graphite which occupy more space and are responsible for most of the growth. An austenitic cast iron of about 14% nickel, 5% copper, and 1–4% chromium is also quite stable as regards growth tendencies, corrosion, and scaling.

Gray irons are classified by A.S.T.M. according to strength and transverse properties, and specifications are given for specific uses such as cast iron pipe, chilled car wheels, etc. These specifications are revised and published every three years in the *A.S.T.M. Book of Standards* and should be consulted for cast iron and also for other metal specifications.

Recently A.F.A. and A.S.T.M. published a chart on graphite flake classification in gray cast iron which fulfills an important objective because the mechanical properties of cast iron are directly related to the length, type, and distribution of graphite flakes. The micrographs are at 100× and the chart has eight sizes numbered from 1 to 8 having, respectively, graphite flakes of more than 4 in. to less than  $\frac{1}{16}$  in. in length.

The parts of the chart are lettered *A*, *B*, *C*, *D*, and *E*, and are labeled respectively as: uniform distribution, random orientation; rosette groupings, random orientation; superimposed flake sizes, random orientation; interdendritic segregation, random orientation; and interdendritic segregation, preferred orientation.

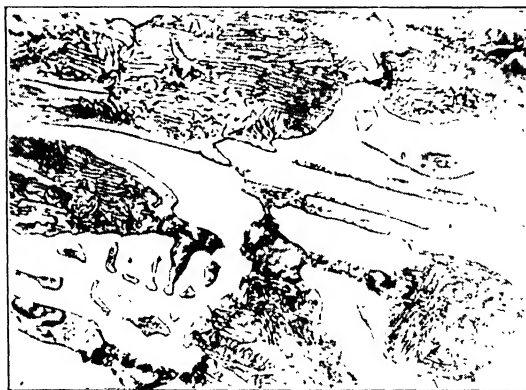


FIG. 105. Typical white cast iron, showing pearlite and cementite.  $\times 1000$ .



FIG. 106. Special hypereutectic cast iron, showing primary cementite and ledeburite eutectic. Carbon about 4.5%. Not a typical white cast iron because it contains an excess of carbon as  $\text{Fe}_3\text{C}$ .  $\times 100$ .

### White Cast Iron

White cast iron or white iron has a white fracture and contains almost no graphite in its microstructure, as shown in Fig. 105. Fig. 106 shows the structure of the eutectic of white iron. This iron contains about 4.5% carbon and shows primary cementite surrounded by ledeburite. It was saturated with carbon and cooled quickly in a chilled iron mold.

Most white cast irons contain carbon from 1.7 to 3.00%, with silicon 0.8–1.25%; nearly all the carbon is combined as  $\text{Fe}_3\text{C}$ . Chromium may be added as a carbide stabilizer.

White cast iron is extremely hard and brittle, having low tensile strength because of excessive brittleness. It is useful in applications requiring high resistance to abrasion; however, it is seldom used where the whole part is white iron. More frequently only a part of the section is white iron and the remainder mottled or gray iron (Fig. 107). In this



FIG. 107. Mottled cast iron. Location between white iron structure at chilled portion and gray iron toward the center of the casting. Showing dendrites of pearlite (formerly  $\gamma$ ) as gray constituent; eutectic of ledeburite as white; graphite nodules as dark constituent. No graphite flakes (Geist, University of Minnesota).  
 $\times 100$ .

case the term *chilled iron* is used and the depth of chill may be governed in two ways: (1) by composition adjustment and (2) by casting against metal pieces called "chills." Large sections will show less chill than small sections of the same composition. Dry-sand molding practice gives less chill than green-sand practice for these castings.

Some of the many applications of chilled iron are: chilled car wheels, rolling mill rolls, plow shares, etc., where high resistance to abrasion is important.

### Malleable Iron

Malleable cast iron is a special white cast iron, annealed so as to impart ductility to the finished casting. The first step in making malleable iron is to obtain a casting of white iron having a composition as shown in Table 25, which is brittle and hard. The second step consists in graphitizing the white iron by a special annealing treatment which decomposes the  $\text{Fe}_3\text{C}$  to iron and graphite in the form of nodules called temper

carbon. The graphite has the same x-ray crystal structure as the flake graphite of gray iron and lampblack. The graphite in malleable iron after the "malleablizing anneal" is shown in Fig. 108 to be in large nodules, not continuous, embedded in ferrite.

Air or electric furnaces may be used for melting, or a duplex process consisting of melting at a fast rate in a cupola with steel scrap to keep the carbon down and then transferring to an electric to adjust composition and refine. Triplexing is melting in a cupola, transferring to a Bessemer converter to remove excess carbon, and then refining in an electric furnace. The plain cupola practice is used for lower-strength malleable for use as pipe fittings, etc., which are more free machining and have pressure tightness. It is easier to obtain soundness with higher

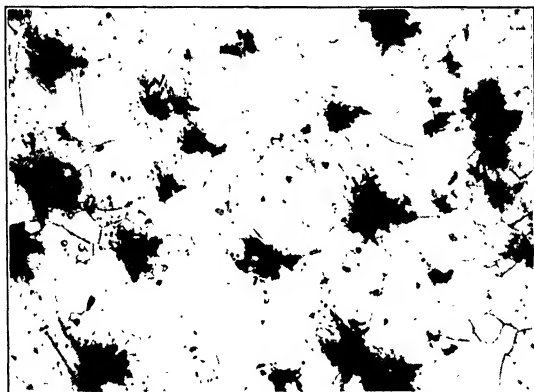


FIG. 108. Malleable iron after annealing. Etched in picral. Showing matrix of ferrite with grain boundaries. Dark gray nodules are graphite.  $\times 100$ .

carbon in thin sections because the lower-carbon irons have less fluidity and a higher degree of shrinkage, approaching that of steel. It is possible to anneal white iron castings with carbon as high as 3.50%. Flake graphite in the original casting is to be avoided so that when high-strength castings are to be made the carbon is usually below 2.35% and the silicon about 1.00%. The higher the silicon the easier it is to anneal but the greater the chance of obtaining flake graphite in the original casting.

Annealing is now carried out in continuous automatically controlled furnaces of the car type. A cycle for a batch type furnace is as follows:

Time of heating to 1500°F	45 hr
Time of holding 1500°F to max. 1650°F	50 hr
Time of cooling	60 hr
	<hr/>
Total	155 hr

TABLE 25. COMPOSITION AND PROPERTIES OF MALLEABLE IRON\*

	For Classes of Iron to Meet—			
	A.S.T.M. Specification A47-33, Grade 35018		A.S.T.M. Specification A47-33, Grade 32510	
	Range	Most probable value	Range	Most probable value
<i>Chemical Composition† — White Iron</i>				
Carbon, %	1.75-2.30		2.25-2.70	
Silicon, %	0.85-1.20		0.80-1.10	
Manganese, %	less than 0.40		less than 0.40	
Phosphorus, %	less than 0.20		less than 0.20	
Sulfur, %	less than 0.12		0.07-0.15	
<i>Chemical Composition — Finished Product</i>				
Temper carbon, %	less than 1.80		less than 2.20	
Silicon, %	less than 1.20		less than 1.10	
Manganese, %	less than 0.40		less than 0.40	
Phosphorus, %	less than 0.20		less than 0.20	
Sulfur, %	less than 0.12		less than 0.13	
<i>Physical Properties</i>				
Specific gravity	7.20-7.45		7.34-7.25	
Shrinkage allowance, in. per ft		3/16		3/16
Coefficient of thermal expansion, per °C		0.000012		0.000012
per °F		0.0000066		0.0000066
Specific heat, cal. per g. per °C average between 20 and 100°C		0.122		0.122
<i>Mechanical Properties</i>				
Tensile strength, psi	53,000-60,000	57,000	50,000-52,000	50,000
Yield point, psi	35,000-40,000	37,500	32,500-35,000	32,500
Elongation in 2 in., %	18-25	22	10-18	14
Modulus of elasticity in tension, psi		25,000,000		25,000,000
Poisson's ratio		0.17		0.17
Ultimate shearing strength, psi		48,000		48,000
Yield point in shear, psi		23,000		23,000
Modulus of elasticity, psi		12,500,000		12,500,000
Modulus of rupture in torsion, psi		58,000		58,000
Brinell Hardness Number		110-145	110-135	
Charpy impact value, ft-lb, "key hole" notch 0.04-in. radius at bottom, 0.394 in. square bar				7
V-notch — 0.197 in. depth of notch			10-14	12
Izod impact value, ft-lb (using V-notch 0.394 in. square bar, 0.079 in. depth of notch)		16	10-14	12
Fatigue endurance limit, psi	22,000-30,500	27,000	25,000-26,500	25,500
Endurance ratio (endurance limit/ultimate strength)‡	0.43-0.54	0.50		0.50
Resistivity, micro-ohms per cu cm		30		32

\* From *Cast Metals Handbook*, American Foundrymen's Association, 1940, p. 222.

† These chemical compositions are not to be taken as specifications, because the specifications for mechanical properties can be met by a number of compositions, depending on foundry practice and conditions.

‡ The longer range of values for grade 35018 material is in part due to more frequent investigations.



The castings are usually packed in boxes with sand, cinders, or mill scale to support and keep them from warping at the high heat. The long annealing cycle of 120–160 hr is necessary for castings having properties shown in Table 25.

During malleablizing  $\text{Fe}_3\text{C}$  dissociates and the graphite precipitates in nodules as temper carbon. Elements which accelerate graphitization during annealing are silicon, aluminum, titanium, and, to a lesser extent, copper, nickel, and phosphorus. Retarding elements are chromium, manganese, vanadium, and, to some extent, molybdenum and sulfur.

In black-heart malleable practice the annealing cycle cannot be hastened much in production without the possibility of pearlite formation in the finished product; this seriously affects the ductility.

**Uses.** Some of the important uses of malleable iron are for purposes for which ordinary cast iron is too brittle and fair ductility and good machinability are desirable. Many applications are for parts for plows, tractors, freight car hardware, tools, automobiles, stoves, pipe fittings, etc.

**Pearlitic Malleable.** In some cases where a ductility of only a few per cent is permissible, it is desirable to have a “short cycle” malleable which has a high strength. This is accomplished by altering the composition with the elements which retard graphitization; i.e., as adding manganese up to 1% and higher chromium 0.10–0.50%, molybdenum 0.20–1.00%, and some additional accelerators as well.

The malleablizing anneal for the short cycle is to graphitize as much as possible above the critical and then cool at faster rates of  $10^\circ$  to  $100^\circ\text{F}$  per hour so as to form a matrix of pearlite, either laminated or spheroidal, as desired. This type of material has found application for brake bands in the automotive field. One automotive company uses a “cast alloy steel” crankshaft containing about 1.35–1.60% C, 0.60–0.80% Mn, 0.85–1.10% Si, 1.50–2.00% Cu, and 0.40–0.50% Cr, which in reality is a pearlitic malleable, graphitized partially but later treated like steel. The treatment consists in holding at  $1650^\circ\text{F}$  for 20 minutes; normalizing in air to maximum of  $1200^\circ\text{F}$ ; reheating to  $1400^\circ\text{F}$  for one hour; cooling in furnace to  $1000^\circ\text{F}$  in one hour. It is claimed that the properties are: tensile strength 107,500 psi, yield point 92,000 psi, elongation 1.75%, reduction in area 2.5%, and Brinell hardness 269. There are many possibilities of similar irons for special service where ductility is not an important consideration.

## CHAPTER X

### NONFERROUS METALS AND ALLOYS

Approximately forty of the metallic elements are used commercially in the pure or the alloyed form. Of these, iron is employed by far the most widely because of its low cost and its many useful properties. Over a period of many years the world production of iron has amounted to ten to twenty-five times the combined tonnage of all other metals. Up to the opening of World War II, copper, lead, and zinc were the important nonferrous metals, accounting for almost nine-tenths of the total nonferrous metal tonnage, but under war-time conditions the production of aluminum and magnesium was expanded very rapidly to bring these two metals into the same class. Tin and nickel are also used in large quantities and neither is produced in this country in appreciable amounts.

Each of the metals possesses a unique combination of properties upon which its usefulness depends. Such characteristics as resistance to corrosion or oxidation, pleasing appearance, ease of fabrication, light weight, high thermal conductivity, special electrical or magnetic properties, as well as suitable mechanical properties, may make a given metal or alloy especially useful for a particular application.

Many of the metals are used widely in the commercially pure unalloyed form. The mechanical properties of various commercial grades of the more important of these are given in Table 26. The physical constants of metals of high purity can be found in Table 1. Many of the metals which are not used extensively in the commercially pure form are used in the production of alloys. The more important of these are manganese, chromium, molybdenum, cobalt, vanadium, titanium, columbium, antimony, arsenic, bismuth, beryllium, calcium, rhodium, osmium, and iridium.

#### COPPER AND COPPER-BASE ALLOYS

Copper and its alloys have been in use since the early stages of the development of our civilization and they still maintain their position among the most useful of our metals and alloys. A major portion of the copper produced today is used in the unalloyed form, particularly for conductors of electricity in the form of rod and wire, and for plumbing,



TABLE 26. (Continued)

	Tensile Str. $\frac{\text{psi}}{1000}$	Yield 0.2% set $\frac{\text{psi}}{1000}$	Elong. % in 2'	Reduction of Area %	Brinell Hardness Number	Endurance Limit $\frac{\text{psi}}{1000}$	Young's Modulus $\times 10^{-6}$	Ave. Price 1929-38 \$/lb avdp
Magnesium, cast	13	3	6		30		6.25	0.428
Magnesium, wrought, annealed	25	9	5		33		6.25	0.225 (1942)
Magnesium, wrought, hard rolled	26	9.5	4		40			
Magnesium, wrought, extruded	33	1.2		33	41	7.8	50	2.75 (1942)
Molybdenum, annealed wire	88		11		147			
Molybdenum, hard wire	285		25	40	220			
Nickel, 97% cast	63	21	22		100		30	0.35
Nickel, 99.4 (Ni + Co) hot rolled	73	24	50	65		31		
Nickel, 99.4, wrought, annealed, 650°C	33	20	48		90	29	28	
Nickel, 99.4, wrought, hard rolled	123	110	4		240	50		
Palladium, wrought, annealed	17		24		47		12	374
Palladium, wrought, hard rolled	47		1		109		14.5	
Platinum, 99.99, wrought, annealed	16		41		42		18	633
Platinum, 99.99, wrought, hard rolled	44		1		97		21.5	
Silver, cast	15		41	38	30		11.2	6.37
Silver, wire, annealed 650°C	23	8	54		28		10.4	
Silver, wire, hard drawn	53	44	3		70		11	
Tantalum, hard drawn, wire	42-132		46		75-125		27	65.00 (1942)
Tin, cast	3.8		35		6		4	0.408
Tin, rolled	3.8	0.2			5		6	
Tungsten, swaged	214		4	28				2.68 (1942)
Tungsten, hard drawn, wire	430			65	290		58.5	
Zinc, cast	5.4	4.7	0		39		13.7	0.046
Zinc, 99.9+, rolled	18	9	33		64		16	
Zinc, 99.9+, rolled, annealed 150°C		10.7	38	40	43		12	
Zirconium, annealed, 925°F, 3 hr	56		12				10.7	7.00 (1942)

roofing, and chemical engineering equipment in the form of sheet and tubing. The most useful properties of copper are: very high electrical and thermal conductivities, good corrosion resistance, good mechanical properties, and ease of fabrication.

### Commercial Grades of Copper

*Electrolytic and low resistivity lake copper*, both of which contain at least 99.90% copper and silver, are used for electrical conductors and for wrought alloys.

*High resistance lake or arsenical*, 99.90% minimum copper, silver, and arsenic (usually 0.25 to 0.50% As), is used mainly for service at higher temperatures where its high recrystallization temperature is advantageous.

*Fire refined other than lake*, 99.70% copper and silver minimum, 0.1% arsenic maximum, is used for rolling into sheets and shapes used for mechanical purposes.

*Oxygen-free or deoxidized copper* possesses exceptional plasticity, good welding properties, and is not subject to embrittlement caused by exposure to hot hydrogen gas. Some grades have high electrical conductivity (OFHC).

The name "tough pitch" is sometimes applied to copper with a controlled oxygen content of 0.03 to 0.07%. This small amount of oxygen gives improved casting properties and good mechanical properties, but induces susceptibility to hydrogen embrittlement.

Pure copper can be formed very readily by either cold or hot working. It can be hardened only by cold work and in the work-hardened state its high electrical conductivity is reduced but slightly. A myth which has persisted for many centuries credits the ancients with the so-called "lost art of hardening or tempering copper." All specimens of ancient copper tools which have been studied by scientific methods have been found to owe their hardness to cold working or to alloy contents. In most cases the alloying elements were natural impurities occurring in the copper ores. No specimens have ever been tested which approach in hardness the values that can be obtained with modern heat-treated copper-beryllium alloys.

## COPPER-BASE ALLOYS

### Nomenclature

Alloys of copper with zinc are usually called brasses; of copper with tin, bronzes, tin bronzes, or phosphor bronzes; of copper and aluminum, aluminum bronzes; of copper and silicon, copper silicon or silicon bronze;

of copper and beryllium, beryllium copper or beryllium bronze. A number of copper-zinc alloys are sold under the nobler name of bronze and these designations might be regarded as misnomers: "commercial bronze" is a wrought red brass; "manganese bronze," a high-zinc brass; and several proprietary brasses are sold under trade names that include the word bronze.

Copper-base alloys possess to a high degree some of the valuable properties of pure copper, particularly good corrosion resistance and

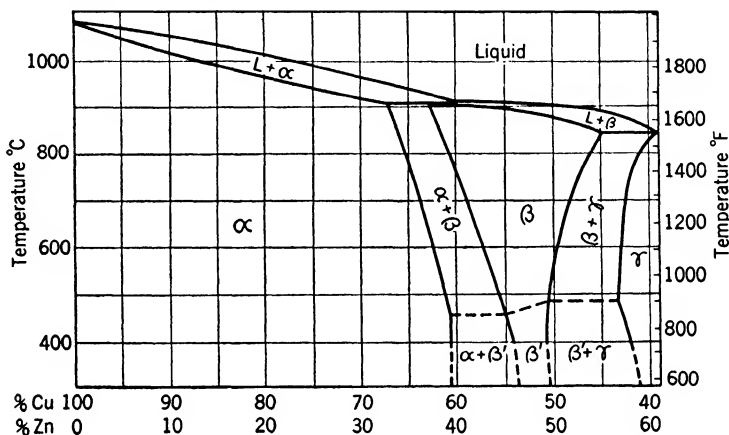


FIG. 109. Copper-zinc constitution diagram.

relatively high conductivity of heat and electricity. For any given application, the choice between brass and the various bronzes depends upon the combination of properties desired and also upon the cost of the alloy as well as the cost of fabricating it into the finished product.

Brasses are the cheapest and the most widely used of the copper-base alloys. They can be worked more readily by most cold-working processes than other alloys and their mechanical properties are good.

Tin bronzes are more expensive, possess better corrosion resistance in general, have a more pleasing golden color, are harder, and are more resistant to abrasion. Their working properties are definitely inferior.

Aluminum bronzes are characterized by good corrosion resistance and high tensile properties. Silicon bronzes possess high corrosion resistance toward many corroding agents, with good mechanical properties, and some grades also have good working properties. Beryllium bronzes can be hardened by heat treatment to a degree not approached by any other copper-base alloy. They are the most expensive of the copper-base alloys but possess the highest strength, and some of the alloys have high electrical conductivity.

## BRASSES

The constitution diagram of copper-rich alloys of copper and zinc is given in Fig. 109. Wrought brasses containing over approximately 62% copper consist of only one phase, the  $\alpha$  solid solution, which is very ductile and has the face-centered cubic type of crystal structure. Brasses containing 54 to 62% Cu are made up of two phases,  $\alpha$  and  $\beta$ . The  $\beta$  phase is body-centered cubic and undergoes a transformation on

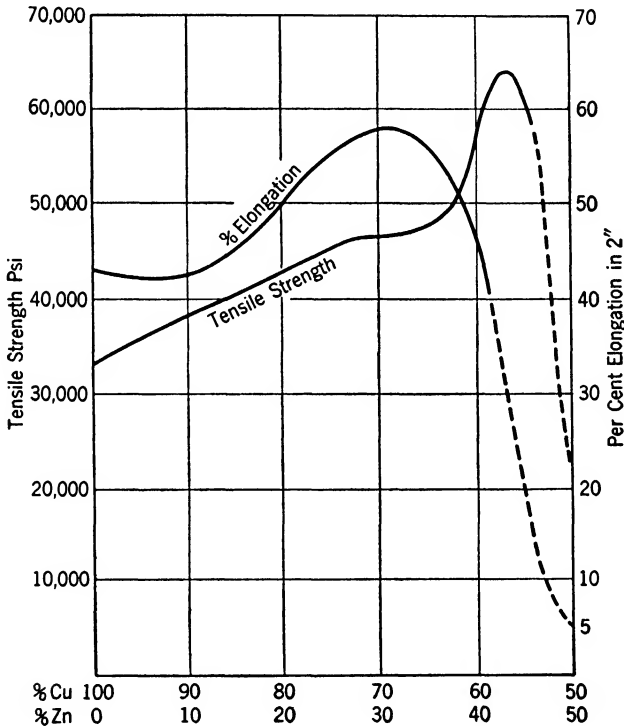


FIG. 110. Tensile strength and elongation of annealed wrought brasses. Compiled from various sources.

cooling at approximately 470–453°C, which apparently involves the formation of an ordered solid solution designated as  $\beta'$ . This phase is rather brittle at room temperature but has good hot-working properties.

The color of the  $\alpha$  solid solution varies according to the copper content from a copper red for high-copper alloys to a yellow color at about 62% copper. The  $\beta$  phase is slightly more reddish than the saturated  $\alpha$  solid solution, so the lightest yellow color is attained in brasses of about 62% Cu.

TABLE 27. WROUGHT COPPER-BASE ALLOYS

	Composition Cu Zn Sn Pb	Form	Tensile psi 1000	Yield psi 1000	Elong. in 2" An- nealed	BHN An- nealed	Rockwell B An- nealed	Characteristics and Uses
Red Brasses "Commercial Bronze"	90 10	Sheet	37	11	43	50	1	High corrosion-resistant. Red color. (Worked cold or hot. Worked cold, better ductility.
Red Brasses Low brass	85 15 80 20	Sheet Sheet	41 43	17 15	45 52	52 53	10 11	
Yellow Alpha Brasses Cartridge brass High brass Free-cutting rod	70 30 66 34 62 35	Sheet Sheet Rod	45 46 47	15 15 32	60 60 60	53 52 54	15 15 16	
Alpha-Beta Brasses Muntz metal Extrusion brass	60 40 58 39	Sheet Shapes	56 50	15 15	46 20	80	42 24	Worked hot or cold. Extrusions, forgings, free machining.
Tin Brasses Admiralty Naval brass	70 29 1 60 39.2 0.75	Sheet Rod	45 54	95 62	60 45	55	15 55	
Phosphor-bronze (wrought) Grade A (A.S.T.M.)	95.5 (P 0.15)	Sheet	45	100	50	82	25	Springs, diaphragms, High strength. Corrosion resistant.
Grade C (A.S.T.M.)	92 (P 0.15)	Sheet	62	115	55	90	45	
Aluminum-Bronze (wrought) 88-9-3	95 (Al 5) 88 (Al 9, Fe 3)		50 70	65 85	40 40	50 45	60 120	High strength; corrosion resistant. Marine machinery, etc.
Copper-Silicon (Silicon-Bronze) Type A Type C	Cu 95 (Si 3.25; Mn, Zn or Fe) Cu 90 + (Si 3.25; Zn 4; Mn, Fe or Sn)	Sheet Sheet Sheet	50 50 42	110 110 77	48 48 65	100 45	40 40 20	
Type B	Cu 97 + (Si 1.25; Sn or Zn)	Sheet	70	118	45	110	96	Best forming properties. Springs, gears, diaphragms. Good electrical conductivity. Highest hardness, strength.
Beryllium-Copper (Beryllium-Bronze) Cu 97 + Same, heat treated		Sheet	175	193	6	340	83	



Brasses possess relatively good corrosion resistance and exceptionally good working properties. They are used both in the wrought form and as castings, the casting alloys differing from the wrought alloys in composition.

The properties of wrought copper-base alloys are given in Table 27.

### Wrought Brasses

The best working properties are obtained with simple binary copper-zinc alloys. Other alloying elements harm the cold-working properties, but a small amount of lead or tellurium is occasionally added to improve

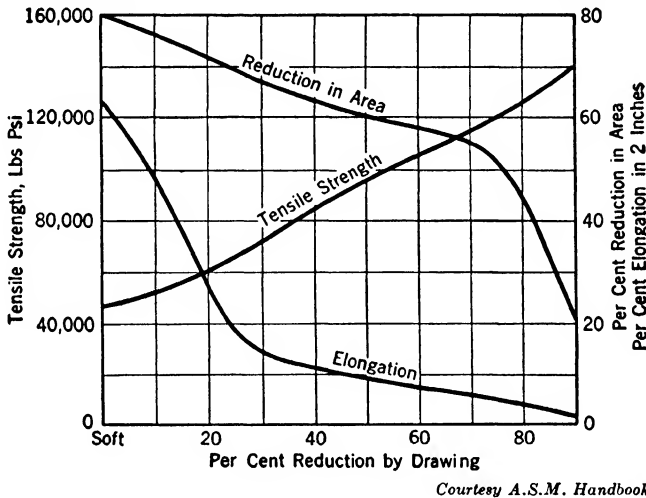


FIG. 111. Effect of cold working on the mechanical properties of high brass.

machinability (0.5 to 3%); small additions of tin, antimony, phosphorus (.03%) or arsenic are used in several alloys, mainly to improve the corrosion resistance toward certain media and inhibit dezincification of condenser tubes.

The approximate tensile properties of wrought copper-zinc alloys of various compositions are given in Fig. 110. The maximum ductility is reached at approximately 67 to 70% copper, and maximum tensile strength at slightly below 60% copper.

Most of the commercial alloys can be classified into three main groups. The most important are: (1) the *yellow  $\alpha$  brasses*, high brass (66-34) and cartridge brass (70-30) being the most widely used compositions in this group; (2) the *red brasses*, usually of the 85-15 or the 90-10 composition; and (3) the  *$\alpha$ - $\beta$  brasses*, which usually fall near the 60-40 (Muntz Metal) composition.

**Yellow a Brasses.** These are the most ductile of all brasses and they are especially suited for the most severe cold-forming operations such as deep drawing, stamping, and spinning. They are almost always cold rolled and cold formed, although some hot working is possible if the alloys are made of high-purity copper and zinc.

The effect of cold working upon the mechanical properties of high brass is given in Fig. 111. Cold-rolled sheet and strip can be obtained com-

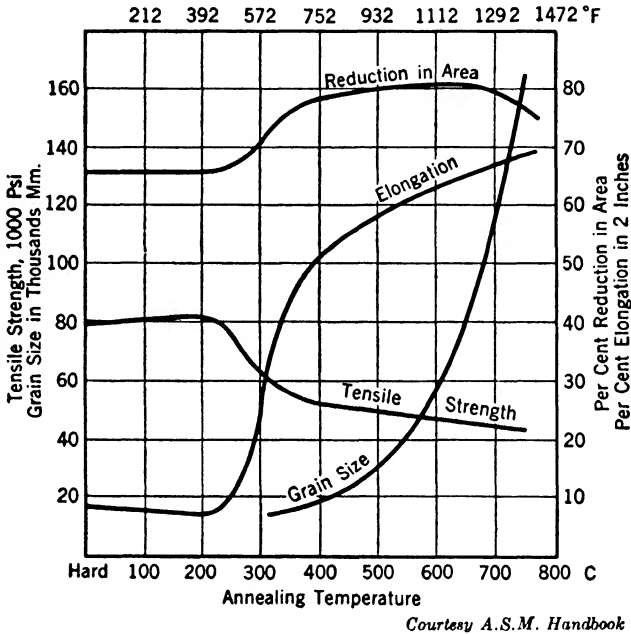


FIG. 112. Effect of annealing temperatures on the properties of high brass.

mercially in seven different "tempers," representing different degrees of cold rolling ranging from "quarter hard" (10.9% reduction) to "extra spring" (68.7% reduction).

The effect of annealing at various temperatures upon the mechanical properties of three-quarter hard high brass is given in Fig. 112. The degree of annealing is commonly designated in terms of resultant grain size. The largest grain size is specified for the most severe cold-forming operations but for less severe cold forming the finer grain sizes are preferred because they give a smoother surface finish.

After severe cold-forming operations, all yellow brasses should be annealed to avoid "season cracking." This annealing may be performed at a temperature as low as 570°F (300°C), if it is desired to pre-

vent loss of strength and hardness. Season cracking is a gradual, intergranular disintegration caused by the combined effect of internal stresses and corrosion; the time required to bring it about varies with the severity of the corrosion conditions. Atmospheric corrosion may develop this condition in a few months whereas under conditions of interior exposure it may appear after several years of service. Certain chemicals, particularly ammonia or mercury compounds, may cause failure in a very short time. Arsenical brasses seem to be the most susceptible to intergranular corrosion. To test for susceptibility to season cracking the finished part can be immersed in a solution containing 100 g of  $\text{HgNO}_3$  and 13 ml  $\text{HNO}_3$  per liter for 15 min. No cracks should develop during this test if the brass has been annealed properly.

In general, yellow brasses are slightly less resistant to corrosion than red brasses. There is one type of pitting corrosion, often called "dezincification," which is encountered almost exclusively in yellow brasses. It is characterized by a reddish, porous deposit of copper at the corrosion pits. It may be caused by contact with acids or with impure and salt-bearing waters. The resistance to salt water corrosion can be improved by the addition of approximately 1% of tin. Admiralty Metal (70 Cu, 29 Zn, 1 Sn) is widely used for condenser tubes.

The mechanical properties of some typical wrought brasses are given in Table 27, together with compositions, characteristics, and uses.

**Red Brasses.** Three commercial wrought brasses fall definitely into this group: the 85-15 "red brass" or "rich low brass," the 90-10 "commercial bronze," and the 95-5 "commercial bronze" or "gilding metal." A fourth alloy, the 80-20 "low brass" could be classed with these, but its properties are to some extent intermediate between those of the other red brasses and those of the yellow  $\alpha$  brasses.

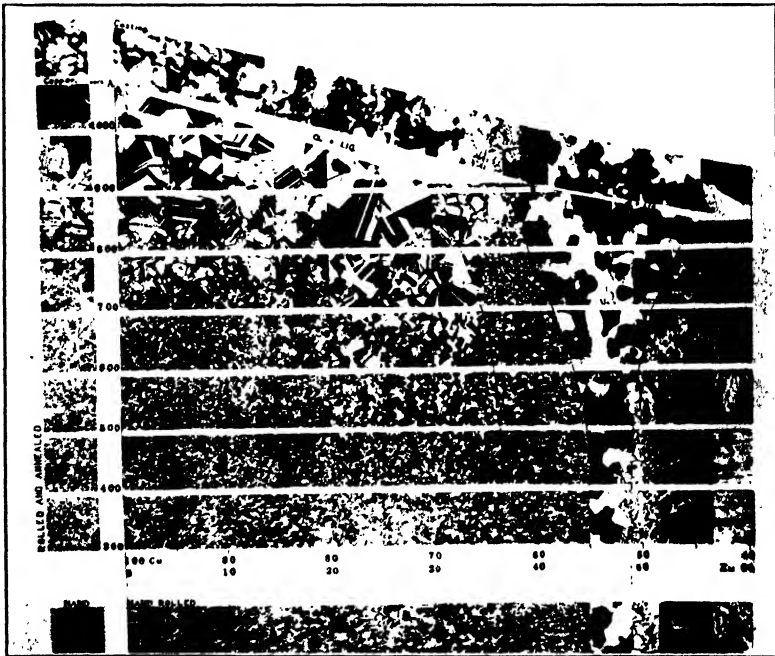
The red brasses as a group are characterized by a slightly better resistance to most types of corrosion, as compared with yellow brasses, with practically no susceptibility to dezincification or season cracking. In hot-working properties they are superior to the yellow  $\alpha$  brasses and in cold working they are more plastic the lower the zinc content; consequently they are preferred for cold heading and upsetting applications. They are more expensive and are used mainly for applications where their bronze color or corrosion resistance are advantages, particularly for hardware, screws, rivets, forgings, radiator cores, detonator fuse caps and primer caps (95-5), plumbing pipe (85-15), bellows and flexible hose (80-20), and all sorts of cold-formed parts. Leaded red brasses (1.5% Pb) are used for automatic screw machine work.

**Alpha-Beta Brasses; Muntz Metal.** These two-phase alloys, usually of approximately the 60-40 composition, are yellow in color and are

characterized by high strength and good hot-working properties. With respect to general corrosion resistance they are usually ranked as slightly better than the yellow  $\alpha$  brasses, and they are also subject to dezincification and season cracking. Their resistance to certain media, such as salt water, is improved by small additions of tin (naval brass). Leaded alloys are used for forgings and extrusions when good machinability is desired.

**Microstructures of Brasses**

Fig. 113 illustrates the microstructures of copper-zinc alloys of various compositions. The top row of micrographs shows structure of castings of various compositions as shown on the composition scale at the foot of



*Courtesy W. H. Bassett and C. H. Davis, American Brass Co.*

**FIG. 113.** Microstructures of brasses.

the page. The remainder of the page illustrates the microstructures of wrought brasses of various compositions which have been annealed after severe cold rolling. The annealing temperatures are given in centigrade on the vertical scale at the left-hand edge of the page.

Referring to the constitution diagram and discussion of phases in

copper-zinc alloys, the microstructures of wrought brasses between 100% copper and approximately 62% copper consist of homogeneous  $\alpha$  solid solution, varying in grain size with annealing temperature. Fig. 113 shows clearly that the low-copper  $\alpha$  brasses show more grain growth and recrystallization at lower temperatures than do the high copper alloys. Annealing twins occur in all wrought  $\alpha$  brasses in profusion.

Wrought brasses containing between 62 and 54% copper contain two phases,  $\alpha$  and  $\beta$ , and Fig. 113 illustrates how the presence of two phases interferes with grain growth on annealing. Even after annealing at relatively high temperatures, these alloys are fine grained. The  $\beta$  brasses (54 to 50% copper) are coarse grained and are too brittle for practically all industrial applications.

### Cast Brasses

The top row of micrographs in Fig. 113 shows the structures of cast brasses of various compositions. The cast alloys from approximately 75 to 100% copper show the typical dendritic or "cored"  $\alpha$  solid solution structure. According to the copper-zinc diagram (Fig. 109), the first solid to form during the freezing of these alloys is rich in copper whereas the last melt to freeze is rich in zinc.

In cast alloys below 75% copper a second phase appears, the  $\beta$ , since the last melt to freeze for these alloys reaches the  $\alpha + \beta$  or the  $\beta$  range of composition. Alloys of the Muntz Metal composition (60-40) freeze as all  $\beta$ , but the solubility of copper in the  $\beta$  phase drops at lower temperatures and, on slow cooling, the  $\alpha$  phase begins to separate out at slightly below 750°C. Alloys of the  $\alpha$ - $\beta$  range of compositions in the form of castings or of forgings which have been slowly cooled from a high temperature show a very typical segregate structure, illustrated in Fig. 114. The precipitated  $\alpha$  phase is arranged along certain crystallographic planes of the matrix of  $\beta$ , resulting in a Widmanstätten structure.

### Commercial Casting Alloys

Whereas wrought brasses are usually simple binary alloys of copper and zinc, the casting alloys almost always contain very appreciable amounts of other alloying elements. The range of compositions is as follows: zinc up to a little over 40%, tin 1-6%, lead 1-10%; some high-strength brasses also contain iron, manganese, nickel, and aluminum. The A.S.T.M. classification of cast brasses includes four main groups: *red brass*, 2-8% Zn; *semi-red brass*, 8-17% Zn; *yellow brass*, over 17% Zn but under 2% total Al, Mn, Ni, and Fe; and *high-strength yellow brass*

(often called "manganese bronze"), over 17% Zn with over 2% total Al, Mn, Si, Ni, and Fe.

**Red Casting Brasses.** Commercial alloys of this group are usually high in lead and tin; in fact, tin is the most important alloying element in these alloys since the hardening effect of tin is approximately twice as great as that of zinc. Consequently, these alloys are also known as *valve bronzes* and they are characterized by a reddish-bronze color, good corrosion resistance, machinability, and pressure tightness. They are more expensive than the yellow or semi-red brasses.

Table 28 gives the compositions and properties of various commercial casting brasses. The alloy 85-5-5-5 is probably the best known of the



FIG. 114. Brass. Muntz Metal, 60% Cu-40% Zn, as cast. Etchant: Rosenhain's reagent. Showing Widmanstätten structure resulting from  $\alpha$  (light) separating from  $\beta$  along certain crystallographic planes. Final structure is  $\alpha$  light +  $\beta'$  (dark).  $\times 100$ .

red brass group. Alloys of higher lead content machine very readily, make pressure-tight castings, but possess lower strength at elevated temperatures.

**Semi-Red Brasses.** Alloys of this group might be regarded as a compromise between *red brass* and *yellow brass*, particularly with respect to cost, corrosion resistance, and appearance. Their casting properties and machinability are very good. They are used extensively for low-pressure valves and fittings and for plumbing fixtures.

**Yellow Brasses.** These are the cheapest casting brasses, high in zinc content (usually 20 to 35%), with only small percentages of tin and lead. The alloys near the upper limit for zinc are more difficult to cast than lower zinc brasses, and their corrosion resistance in general is also lower except when used in contact with gasoline or fuel oils which contain sulfur. They are widely used for miscellaneous ornamental castings, plumbers' fittings, and small machine parts.

TABLE 28. CASTING ALLOYS OF COPPER; CASTING BRASSES AND BRONZES\*

Designations A.F.A. A.S.T.M. S.A.E. B 30-42T	Cu	Zn	Composition Sn Pb	Tensile psi 1000	Yield psi 1000	Elong. in 2%	Hard- ness BHN	Characteristics
<b>Leaded Red Brasses (Valve Brasses)</b>								
2 4A	85	5	5	30-38	14-20	20-30	55-65	Good corrosion resistance; machinability. Standard valve bronze. Used up to 400°F. Good pressure tightness. Used up to 300°F. For high pressures. Used up to 500°F.
3	77	6	10 (Ni 2)	25-30	12-18	15-25	50-60	
1 2A	88	4	1.5	34-42	16-22	22-30	60-70	
<b>Leaded Semi-Red Brasses</b>								
1 4B	83	7	4	30-36	15-20	20-30	55-65	Moderate casting properties and machinability. Moderate corrosion resistance and cost. Used extensively for low-pressure valves, fittings, and high-grade plumbing fixtures. Weaker than valve bronze at high temperatures.
2 5A	80+	9.5	3	15-20	15-20	15-25	55-65	
3	77	10	3	20-30	12-17	10-20	50-60	
	76	15	6	30-40	12-20	15-30	50-65	
<b>Leaded Yellow Brasses</b>								
1 6A	71	24+	1.5	30-35	15-20	25-35	50-60	Low cost casting brasses. Slightly lower corrosion resistance, except for gasoline and high sulfur oils.
2	62	35	2	35-45	18-25	15-25	55-65	
6B 41	65	31+	7	20-38	11-15	15-35	40-60	
6C	60	37.5	1	35-45	14-20	15-25	50-75	
<b>High Strength Yellow Brasses (Manganese Brasses)</b>								
1 8A	43	55-62	Bal 0-1.5 (Mn 2-3.5) (Fe 0-2) (Al 3-1.5)	65-85	25-50	20-35	90-120	High strength casting brasses. Marine castings, pump and machine parts. Good resistance to salt water corrosion.
2	430	62	26.5 (Mn 3.5, Fe 3, Al 5)	90-120	30-90	8-20	170-250	
<b>Tin Brasses (Phosphor Brasses)</b>								
1 1A	62	88	2	30-45	16-23	15-40	50-85	Government bronze, gun metal, zinc bronze.
2 1B	65	88	4	38 min	16 min	22 min	60-80	
				33-45	19-26	7-15		Gear bronze. Good wear and corrosion resistance.
<b>High Lead-Tin Brasses (Bearing Brasses)</b>								
1 3A	64	80	10	27-39	15-21	6-14	55-70	Standard alloy.
2 3B-C	66	Bal	1-4	22-38	11-21	8-18	45-60	
3 3D	67	78	0-3	22-38	12-18	9-18	50-60	High lead alloys more plastic.
4 3E	67	70	5	20-28	8-14	3-16	40-55	
<b>Aluminum Brasses</b>								
1 9A-1	68A	88	(Al 9, Fe 3)	65-75	25-35	20-40	70-125	High strength retained at elevated temperatures. Good corrosion resistance. This alloy can be heat treated. Quench 1500-1600°F. Temper 700-1100°F.
2 9B	68B	89	(Al 10, Fe 1)	65-75	25-30	15-25	100-140	
3 9B	68B		Heat treated	80-90	40-60	4-14	140-225	
<b>Silicon Brasses</b>								
1	95-		(Si 4, Mn 1.1)	40-58	18-25	20-30	80-100	Good corrosion resistance. High toughness and strength.
2	95-		(Si 4, Fe 1.5)					
3	95		(Si 4, Zn 1.0)					

\* A.F.A. Cast Metals Handbook, 1940; A.S.T.M. Metals Handbook, 1939; A.S.T.M. Standards, 1942; S.A.E. Handbook, 1943.

**High-Strength Yellow Brass; "Manganese Bronze."** A rather wide variety of compositions is used, most of them falling in the range of compositions given in Table 28. They are essentially  $\alpha + \beta$  brasses containing several of the following addition elements: Mn, Fe, Al, Sn, and Ni. Lead is kept below 0.4%. These alloys are much stronger, harder, and tougher (Izod 20–40 ft-lb) than other casting brasses, but more difficult to cast and machine. They possess good corrosion resistance toward certain media, particularly to sea water, but castings that

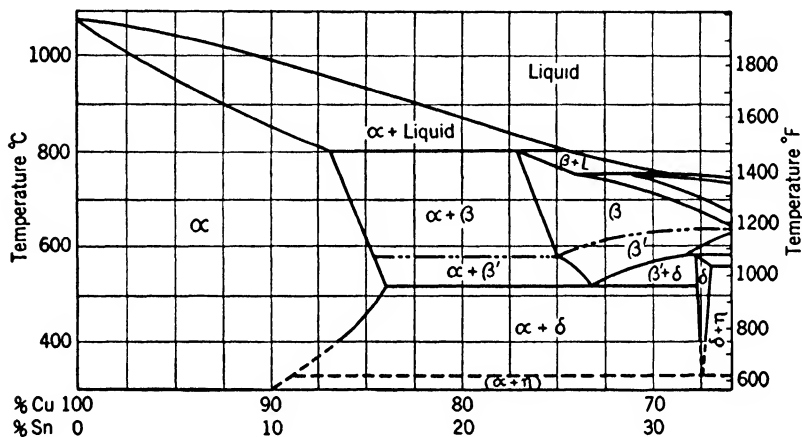


FIG. 115. Copper-tin constitution diagram.

have been stressed beyond the yield point may be subject to season cracking. They are used for propellers, hydraulic machinery, part of marine engine pumps, valves, engine frames, and gears.

### TIN BRONZES

The constitution diagram for copper-tin alloys is given in Fig. 115. The maximum solid solubility of tin in copper is somewhere between 13 and 16%, depending on the annealing temperature. Commercial wrought alloys of less than approximately 13% tin contain only one phase, the alpha ( $\alpha$ ) solid solution. This range of composition includes most of the commercial alloys of copper and tin.

The beta ( $\beta$ ) phase is stable only at elevated temperatures and on cooling slowly it undergoes a eutectoid transformation at 520°C. This portion of the diagram has been constructed differently by various investigators and the diagram shown here has been chosen for its close correlation with the microstructures of commercial alloys. Another version



of this diagram, covering the entire range of composition from zero to 100% copper, can be found in Plate V.

The broken line at 580°C represents a heat effect on the cooling curves which is sometimes considered to be due to a phase change ( $\beta \rightarrow \gamma$ ), but in Fig. 115 it is regarded as a simple case of atomic rearrangement within the  $\beta$  solid solution phase,  $\beta'$  being an "ordered" solid solution.

The product of the transformation at 520°C is the  $\alpha + \delta$  eutectoid (Figs. 116 and 117). The  $\delta$  phase is hard and brittle, and has a bluish gray color. Under all ordinary conditions it is stable at room tempera-



FIG. 116. Bronzite. Eutectoid structure of Cu-Sn system. Cast alloy having composition Cu 73%-Sn 27%. Reaction is  $\beta - \alpha + \delta$ .  $\alpha$  (light) is the matrix with  $\delta$  (dark) in relief. This structure is called bronzite because it strongly resembles lamellar pearlite in Fe-Fe<sub>3</sub>C system.  $\times 1000$ .

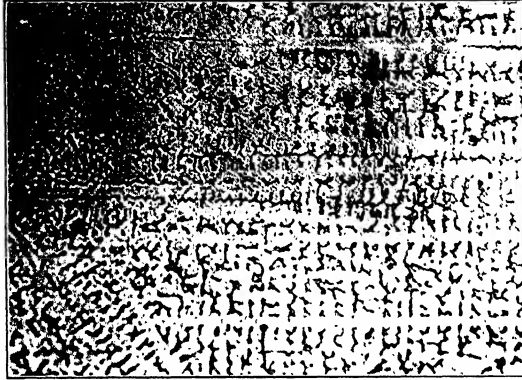
ture. Alloys that have been severely cold worked and annealed for very long periods below approximately 330°C (below the normal recrystallizing temperature) have been shown by means of x-ray studies to undergo another phase change as indicated by the dotted lines at the bottom of the diagram. The  $\delta$  phase disappears with the formation of eta ( $\eta$ ), and the same studies indicate a sharp drop in the solid solubility of tin in the  $\alpha$  solid solution at low temperatures. These changes are never encountered in commercial alloys, and cannot be checked by means of microscopic examination.

The solid lines in Fig. 115 agree closely with the microstructures of wrought bronzes. The structure of cast bronzes depends largely upon the degree of equilibrium attained during the cooling of the casting. Castings which have been cooled slowly contain only the  $\alpha$  phase if the tin content is below approximately 7%. This phase in castings shows the characteristic cored or dendritic structure. There is some  $\alpha + \delta$

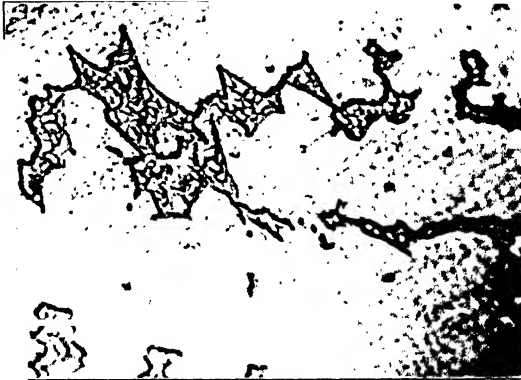
eutectoid in most castings containing over 7% tin and in chill cast alloys of over 5% tin (Fig. 117).

### Effect of Third Alloying Elements

**Effect of Phosphorus.** Phosphorus in the form of phosphor-copper or phosphor-tin is commonly used to deoxidize molten bronze before



× 100



× 1000

FIG. 117. Bronze. Composition: Cu 85%, Sn 15%. Slowly cooled after casting.

casting. It promotes soundness in the castings and fluidity in the molten alloy. Very often the amount of phosphorus added is just sufficient to deoxidize the melt and only a trace, if any, remains in the metal. When greater amounts of phosphorus are added, there results a definite improvement of mechanical and chemical properties: higher tensile strength, especially at elevated temperatures; greater toughness, hardness, and corrosion resistance. The degree of improvement is a function of the phosphorus content, but there is no standardized amount

used and it may run anywhere from a few hundredths of one per cent to as much as one per cent. Higher percentages cause brittleness and impair surface appearance.

The term phosphor-bronze, as used in the industry, means very little since it is at times applied to all tin-bronzes whether or not they contain any phosphorus. In the present A.S.T.M. and A.F.A. systems of classification of cast bronzes the term is avoided altogether. The Non-ferrous Ingot Metal Institute suggests that the name be reserved for tin-bronzes containing over 0.05% phosphorus.

**Effect of Zinc.** Zinc is a common addition element in tin bronzes, being used to replace a part of the tin, usually in the proportion of 2% zinc for each per cent of tin replaced. A 2% zinc addition will improve casting properties and toughness with little effect on wear resistance. Higher proportions of zinc are often added to lower the cost of the alloy but when the amount exceeds about 5% it is usually regarded as an adulterant. High-zinc bronzes have an inferior brassy color and the corrosion resistance toward some media is lowered.

**Effect of Lead.** Lead is often added to casting bronzes to improve the machinability, pressure tightness, and wear resistance. It lowers impact toughness and strength at elevated temperatures. Some specifications for high-strength casting bronzes place a very low limit on lead (S.A.E. No. 62, Pb 0.20% max) but published data indicate that amounts up to 0.5% and possibly as high as 1.5% have very little effect upon mechanical properties except for a slight reduction in hardness. An addition of 0.5% lead produces a marked improvement in the machinability of bronze and slightly greater improvement can be obtained with more lead. In valve bronzes the lead content varies from 1.5 to 10%, the lower value being for valves which are to be used at high temperatures (400–500°F). Most bearing bronzes contain from 5 to 25% lead.

**Effect of Nickel.** Moderate improvements in mechanical properties have been reported with additions of approximately 1% nickel, particularly in gear bronzes. In high-lead bearing bronzes, nickel helps to promote uniform distribution of the lead.

Commercial copper-tin alloys usually contain one or more of the elements phosphorus, zinc, lead, or nickel. The casting alloys are used more widely than wrought bronzes and will be discussed first. Compositions, properties, and characteristics of casting bronzes are summarized in Table 28.

### Casting Bronzes

**Gear Bronzes and Phosphor Gear Bronze.** Alloys containing approximately 10–12% tin and 0–1% phosphorus are used for gears and machine parts which require a bearing surface. They develop a polished surface

with excellent wear resistance and low tendency to gall or seize when operating against a hardened steel surface. Two typical alloys of this type are S.A.E. No. 65 phosphor gear bronze (11% Sn, 0.2% P) and S.A.E. No. 640 nickel phosphor bronze (11% Sn, 1% Ni, 0.2% P, 1% Pb).

**Zinc Bronze or Gun Metal.** Because of superior casting properties these alloys are widely used where the combination of strength, toughness, bearing properties, and resistance to corrosion are desired, particularly in marine work. The two most common compositions are the 88-10-2 and the 88-8-4 and they are also known as Government Bronze, G Bronze, or Admiralty Gun Metal. The 88-8-4 alloy has two advantages over the original gun metal composition (88-10-2): it is cheaper and in large castings it is less likely to give trouble in machining resulting from segregation and hard spots. Phosphorus, although used as a deoxidizer, is not recommended as an alloying element. Lead, if added to improve machinability, is usually not over 0.5%. This alloy has to a large extent replaced the straight copper-tin gear bronze.

**Valve Bronzes.** These alloys of Cu-Sn-Zn-Pb are also known as *leaded red brasses* and are discussed under that heading. The mechanical properties of commercial cast bronzes are summarized in Table 28.

**Statuary Bronze or Art Bronze.** Art bronze has not been standardized and the compositions used vary through the range: Cu, 72 to 95; Sn, 2 to 10; Zn, 1 to 25; Pb, 0 to 2.5. Usually the zinc content exceeds the tin since good casting properties and ability to be worked with a file or chisel are important requirements. An average composition would be about Cu 79, Zn 15, Sn 4, and Pb 1.5.

### **Wrought Bronze**

Wrought phosphor-bronze is used to some extent for springs and diaphragms where corrosion resistance is required. These alloys have good wear resistance, high yield strength, and resistance to fatigue. Alloys containing up to 10% tin are now being produced commercially and are available in the form of sheet and wire and in several tempers ranging from the annealed to the severely cold-worked (extra spring temper) condition. The range of mechanical properties for the two most common grades is given in Table 27.

For coining operations, alloys containing small amounts of tin and zinc are sometimes used.

### **ALUMINUM BRONZE**

The copper-aluminum constitution diagram is given in Plate II.\* The maximum solubility of aluminum in the copper-rich  $\alpha$  solid solution is

\* Plates will be found in the Appendix.

approximately 9.5% at 570°C (1058°F), and at the solidus temperature, 1031°C (1886°F), the solubility is 7.4%. The  $\alpha$  phase is face-centered cubic.

The  $\beta$  phase is stable only at elevated temperatures and cannot be retained by quenching. It undergoes a eutectoid inversion at 570°C and the composition at the eutectoid point is approximately 11.8% aluminum. In slow cooling the product of this transformation is a eutectoid mixture of  $\alpha$  and  $\gamma'$  phases. The  $\gamma'$  phase (formerly called  $\delta$ ) is hard and brittle, being analogous to the  $\gamma$  phase in copper-zinc alloys.

Aluminum bronzes which contain the  $\beta$  phase are interesting because of their response to heat treatment and because of certain similarities to steels. The eutectoid structure formed on slow cooling often resembles the lamellar pearlite structure of annealed steels. On quenching from above the eutectoid temperature, an acicular structure resembling martensite can be produced. Two transition phases,  $\beta_1$  and  $\beta'$ , have been found in quenched alloys by means of x-ray diffraction studies. Certain commercial aluminum bronzes are being heat treated by quenching from 815–870°C (1500–1600°F) followed by tempering at 370–590°C (700–1100°F) to increase the strength and hardness at the expense of reduced ductility.

Commercial aluminum-bronzes usually contain between 4 and 13.5% aluminum, up to 4.5% iron, and occasionally some nickel and manganese. They are characterized by good corrosion resistance toward many media, high strength, ductility, resistance to fatigue and shock, and fairly high hardness which is maintained well at elevated temperatures. Their color resembles 10-karat gold. In casting properties they are definitely inferior to the brasses and they are much more difficult to machine.

Commercial casting alloys range from 8 to 13.5% aluminum and 1 to 4.5% iron. Aluminum has a greater hardening effect than iron, but iron has the beneficial effect of refining the grain size and improving ductility. The 88–9–3 alloy is used without heat treatment whereas the 89–10–1 composition is widely used in the heat-treated condition. Mechanical properties for these two alloys are listed in Table 28.

Alloys of this type are used for gears, gun mounts, propellers, pump parts, bearings and bushings requiring exceptionally high strength, fans, acid equipment, and general machine parts. Aluminum bronzes of higher alloy content are harder (up to 340 Brinell) and more brittle. They are used for nonsparking tools, drawing and forming dies, and for bushings, liners, and guides operating against hardened steels.

Some use is made of aluminum bronzes in the wrought form for valve stems, propeller-blade bolts, condenser bolts, air pumps, diaphragms, and

slide liners. The alloys used most frequently are the 88-9-3 composition for rods, bars, shapes, and forgings, and the 95-5 alloy for plates, sheet, and strip. Mechanical properties of these wrought alloys are given in Table 27.

These alloys can be worked hot or cold, but if the aluminum content exceeds about 11% a marked tendency toward brittleness becomes evident, particularly if appreciable amounts of other alloying elements are present.

#### SILICON-BRONZE

The copper-silicon alloys are better known under their trade names, Everdur, Herculoy, Duronze, Olympic, PMG, etc. They combine very good corrosion resistance, particularly toward certain media, with good mechanical properties. The constitution diagram for these alloys is given in Plate V. The solubility of silicon in the  $\alpha$  solid solution varies with temperature from 6.8 to 4%. Most of the commercial alloys fall in the  $\alpha$  solid solution range and are used both for castings and in the wrought form. Those with low alloy content (Type B) have good working properties whereas the other grades have high strength and hardness and satisfactory ductility. The properties of wrought and cast alloys are given in Tables 27 and 28, respectively.

The silicon content of commercial alloys usually ranges from 0.7 to about 4% and one or more of the following elements are always present: Mn, 0-1.2; Zn, 0-4; Sn, 0-2; Fe, 0-2; and, in free machining grades, Pb up to 0.5%.

Copper-rich silicon alloys can be cast, rolled, spun, stamped, forged, and welded. They are available in the form of sheet, strip, wire, rods, tubes, forgings, and castings. They resist the corrosion of many substances to a satisfactory degree, including sea water, sulfuric and hydrochloric acids, many of the salts of these acids, alkalies, many alkali salts, and many organic compounds.

#### BERYLLIUM BRONZES

Copper-beryllium alloys have been made commercially only a short time and are still more expensive than other copper-base alloys but are finding increasingly wide application in many fields where corrosion-resistant alloys of high hardness and strength are required. Beryllium-bronzes are the hardest and strongest of the copper-base alloys and their mechanical properties can be changed by heat treatment.

The constitution diagram for copper-beryllium alloys is given in Plate III. The important feature of this diagram is the change in solubility of Be in Cu with temperature, which is responsible for the

susceptibility of these alloys to precipitation hardening. At 864°C (1590°F) this solubility is 2.4% whereas at 400°C (752°F) it is 0.6%.

The most common commercial alloy contains from 1.75 to 2.25% Be. It is available in the form of sheet, rod, and wire, and can be worked hot or cold but not so readily as some other copper-base alloys. It work hardens very rapidly and requires frequent annealing during cold-working operations. Alloys containing less Be are preferred for the more severe cold-forming operations, as in the production of tubing.

Other commercial alloys contain, in addition to copper and beryllium: cobalt to promote uniformity after heat treatment, nickel for grain refinement, or chromium for conductivity.

Castings are being made of alloys containing about 0.5% Be with Co, Ni, or Cr which possess good electrical conductivity (up to 55% of the conductivity of copper) and also have moderately high mechanical properties.

**Heat Treatment.** Beryllium-copper alloys respond to the precipitation hardening type of heat treatment. Hot-worked alloys are first given a solution treatment consisting of soaking at 1427–1472°F (775–800°C) followed by water quenching. The alloys are then in the softest and most workable condition which is often designated as the “annealed” state. The hardening or “precipitation” heat treatment is carried out at 250–325°C (482–617°F) and follows the solution treatment in the case of hot-worked alloys. Cold-worked alloys respond to the precipitation heat treatment without any solution treatment and, when treated in this manner, give slightly higher tensile properties and lower ductility than if the solution treatment were applied first. The effect of heat treatment upon the mechanical properties of the standard alloy is summarized in Table 27.

At present the most important uses of copper-beryllium alloys are found in the electrical and aircraft industries, mainly for springs, diaphragms, gears, bearings, electrodes, and other applications where electrical conductivity, corrosion resistance, nonmagnetic properties, hardness and wear resistance, high tensile properties, and good resistance to fatigue are required. A rather full line of nonsparking tools is being made of beryllium-bronze for the petroleum and explosive industries.

## LIGHT METAL ALLOYS

Aluminum and magnesium are the only metals of low specific gravity which are available at a moderate cost and possess suitable mechanical properties with sufficient chemical stability to be useful in the production of light metal alloys. Steels, brasses, and many other common alloys are approximately three times as heavy as aluminum and four and one-

TABLE 29. WROUGHT

Alcoa Number	Form	Tensile Str., 1000 psi		Yield 1000 psi		Elongation, % in 2"		BHN	Shear Str.	Fatigue Limit	Relative Cold Bending Properties	Corrosion Resistance NaCl
		Typical	Min	Typ.	Min	Typ.	Min					
2SO	1/4" sheet	13	(15.5 max)	5		35	30	23	9.5	5	A	B
2S 1/2H	1/4" sheet	17	16	14		9	7	32	11		B	B
2SH	1/4" sheet	24	22	21		5	4	44	13	8.5	F	B
3SO	1/4" sheet	16	(10 max)	5		30	25	28	11	6	A	B
3S 1/2H	1/4" sheet	21	16	18		8	7	40	14	9	C	B
3SH	1/4" sheet	29	27	25		4	4	55	16	10	G	B
52SO	1/4" sheet	29	(31 max)	14		25	20	45	18	17	A	B
52S 1/2H	1/4" sheet	37	34	29		10	7	67	21	19	D	B
52SH	1/4" sheet	41	39	36		7	4	85	24	20.5	G	B
17SO	1/4" sheet	26	(35 max)	10		20	12	45	18	11	B	E
17ST	1/4" sheet	60	55	37	32	20	18	100	36	15	H	D
17SRT	1/4" sheet	65	55	47	42	13	12	110	38		J	J
Alclad 17ST		56	50	33	28	18	16		32		I	A
17ST	Forgings	55	55	30	30	16	16	100	36	15		D
A17S	1/2" rod	43		24		24		70	26	13.5	F	D
24SO	1/4" sheet	26	(35 max)	10		20	12	42	18	12	B	E
24ST	1/4" sheet	68	62	44	40	19	17	105	41	18	J	D
24SRT	1/4" sheet	70	65	55	50	13	12	116	42		K	D
Alclad 24ST	1/4" sheet	62	56	41	37	18	16		40		J	A
61SW	1/4" sheet	35		21		22		65	24	12.5	F	C
61ST	1/4" sheet	45		39		12		95	30	12.5	G	C
53SW	1/4" sheet	33	28	20	16	22	17	65	20	10	F	B
53ST	1/4" sheet	39	35	33	28	14	10	80	24	11	G	B
A51ST	Forging	44		34		14		90	32	10.5		C
25ST	Forging	55		30		16		100	35	15		E
14ST	Forging	65		50		10		130	45	16		D
70ST	Forging	50		40		16		85	37	19		F
18ST	Forging	55		35		10		100	35			E
32ST	Forging	52		40		5		115	38	14		C
11ST3	1/2" rod	44		42		14		100	30	12.5		E

Heat Treatments: O = Annealed; T = Heat Treated; W = As Quenched;

half times as heavy as magnesium. The alloys of these two metals, therefore, are particularly useful in applications where low specific gravity is of primary importance, as in the construction of aircraft. Beryllium, with a specific gravity of 1.85, has been mentioned as a possible competitor in the light alloy field, but up to the present time attempts to produce this metal at a reasonable cost and to develop useful beryllium-base alloys have met with very little success.

Although both aluminum and magnesium are among the most abun-



ALLOYS OF ALUMINUM

Alcoa Number	Composition					Characteristics and Uses
	Cu	Si	Mn	Mg	Misc.	
2S					Al 99%	Best forming properties, weldability. Good corrosion resistance; low yield. Cooking utensils, sheet, tubing.
3S		Trace	1.2			Similar to 2S in properties and uses. Slightly higher strength, low ductility. Cooking utensils, sheet metal work.
52S				2.5	Cr 0.25	Strongest work-hardening alloy. Good corrosion resistance, fatigue strength. High strength sheet metal work.
17S	4.0	Tr.	0.5	0.5		Duralumin. Most common heat-treated alloy. Used in all standard wrought forms. Structural applications. Alclad sheet used for best corrosion resistance.
A17S	2.5	Tr.		0.3		Better forming properties. Rivets.
24S	4.6	Tr.	0.6	1.5		High strength alloy for rolled products. Used widely in aircraft construction. Yield strength raised by cold rolling.
61S	0.25	0.35		0.95	Cr 0.25	Good forming properties. High yield strength. Good corrosion resistance. Requires artificial aging.
53S		0.7		1.3	Cr 0.25	Best corrosion resistance of heat-treated alloys. Architectural uses. All wrought forms.
A51S		1.0		0.6	Cr 0.25	Good forgeability. Intricate forgings.
25S	4.5	0.8	0.8			Good forgeability. Lower cost.
14S	4.4	0.8	0.8	0.4		Forging alloy. High yield strength.
70S	1		0.7	0.4	Zn 10	Low cost forging alloy.
18S	4.0			0.5	Ni 2	High temperature strength. Forged pistons.
32S	0.8	12.0		1.0	Ni 0.8	Forged aircraft pistons.
11ST3	5.5		(Bi 0.5)	Pb 0.5		Free cutting (automatic) screw machine products.

H = Hard Rolled; R = Rolled after Heat Treatment.

dant elements in the earth's crust, their production on a commercial scale has been developed rather recently. Most of the other important metals have been in use for hundreds or thousands of years, but the commercial production of aluminum began around 1888 and that of magnesium in 1909. The production of both of these metals has expanded very rapidly and aluminum now ranks fifth among the metals in commercial importance.

Commercial aluminum of an average purity of approximately 99% Al

TABLE 30. SAND-CASTING

Alcoa Number	Condition	Tensile 1000 psi		Yield 1000 psi Typical	Elongation, % in 2"		Brinell Hardness 500 kg	Shear 1000 psi	Endurance Limit 5 × 10 <sup>6</sup> cycles	Modified Charpy Impact
		Typ.	Min		Typ.	Min				
12	As cast	22	18	14	2		50-70	20	7.5	0.7
212	As cast	22	18.5	14	2		50-70	20	7.5	0.6
112	As cast	22	18.5	14	1.5		55-80	20	8.0	0.6
195T4	Soln. H.T.	31	28.5	16	8	5.5	55-75	24	6	2.8
195T6	Soln. H.T.	36	31.5	22	4	2.5	70-90	30	6.5	1.8
195T62	H.T.	40	35.5	31	2		80-100	31	7	1.3
43	As cast	19	16.5	9	6	2.5	35-50	14	6.5	1
47	" Modified "	26	23.5	11	8	4.5	45-60	18	6	3
108	As cast	21	19	17	2	1.5	60	20	8.5	
A334	As cast	26	22	20	1.5		65	24		0.7
355T4	Soln H.T.	30	26.5	20	5	3.5	50-65	28		1.8
355T6	H.T.	35	31.5	25	3.5	1.5	65-85	30		1.1
355T61	H.T.	38	35	33	1	0.5	80-95			0.8
355T51	H.T.	28	24.5	23	1.5		50-70	22	6.5	
A355T51	H.T.	28	25	24	1.5		65	21	8	
A355T59	H.T.	25	23	21	2.0		60	20	8	
356T4	Soln. H.T	28	25.5	16	6	4.5	50-70	18		1.7
356T6	H.T.	32	29.5	22	4	2.5	60-80	22	8	1.0
214	As cast	25	21.5	12	9	5.5	40-60	19	5.5	3.8
220T4	Soln. T	44	42	25	12	12	70-85	33	7	4.5
109	As cast	24	19	18	1.5		75	20	10	
122	As cast		18.5							
122T2	Soln. H.T.	25	23	21	1		75	22.5	9.5	0.7
122T61	H.T.	36	30	30	1		100	29.5		0.68
142	As cast	28	23	24	1		85	24	8	0.6
142T61	H.T.	37	31.5		0.5		100	32	8	
142T571	H.T.	30	29	28	0.5		85	27	8	
645	As cast	29	25	22	4	2.5	70	22.5	7.5	1
L5	As cast	27		17	7	1	68			

is produced by electrolysis of a fused bath of alumina and cryolite. The commercial grade can be further refined to give metal of 99.95 to 99.99% purity. The impurities in the ordinary 99% grade are chiefly iron, silicon, and copper, and this small amount of impurities materially alters the tensile properties. The physical constants for aluminum of high purity are given in Table 1 (page 2) and the mechanical properties of commercial grades are listed in Table 29 and under the alloy No. 2S in Table 30.

The most useful properties of aluminum are: light weight, good corrosion resistance, high thermal and electrical conductivity, high reflectivity of radiant energy, and ease of fabrication.

ALLOYS OF ALUMINUM

Alcoa Number	A.S.T.M. B26-42T	S.A.E. No.	Composition						Relative Casting Properties	Characteristics and Uses											
			Cu	Si	Mg	Fe	Zn	Ni													
212	CS21	36	8	1.2		1.0				B	Most common casting alloy.										
112	CS22	33	7.5			1.2	1.5				General castings — not heat treated.										
195T4	C1	HT1	38	4						C	High strength heat-treated castings.										
195T6		HT2									Aircraft and marine engine parts; crankcases.										
196T62		HT3																			
43	S2	35		5						A	Intricate pressure-tight castings; good corrosion resistance.										
47	S3	37	12.5 (Trace Na)								A	Alpac, silumin, high strength, needs no H.T.									
108				4	3						A	Good casting properties.									
A334	SC21	HT1	322-1	3	4	0.30				A	Intricate castings.										
355T4											HT2	322-2	1.25	5	0.5				A	Liquid-cooled cylinder heads.	
355T6																					
355T61											HT3	322-3								A	Water jackets, cylinder blocks, water cooled.
355T51										Exhausts manifolds; good corrosion resistance											
A355T51			1.4	5	0.5 (Mn 0.75)	0.75															Crankcases and cylinder heads for diesel and liquid-cooled aircraft engines. Good cast. pr.
A355T59																					
356T4	SG9	HT1	31	7	0.3					A	H.T. castings of intricate design.										
356T6		HT2									Good corrosion resistance; pressure tight.										
214	G1	320			3.75						C	Good corrosion and tarnish resistance, tough.									
220T4		324			10						C	Toughest Al casting alloy. Special found. tech									
109		32	12								C	High hardness, poor shock resistance.									
122																					
122T2	CG1			10	0.2	1.2				C	More frequently cast in permanent molds.										
122T61																				Piston alloy. Good wear resistance, high temp. str.	
142	CN21	30	4		1.5				2	B	Good strength at elev. temp. and stability of dimensions with temp. changes.										
142T61												Usually cast in permanent molds.									
142T571																				General casting alloys.	
645											31	2.8		1.2	11	11					Used extensively in Europe.
L5																					

The corrosion resistance of aluminum is due to a thin, firmly adherent oxide film which tends to protect the surface against further corrosion. Under ordinary atmospheric exposure most of the alloys of aluminum show very little deterioration of mechanical properties, although the resistance to tarnish is not the same for the various alloys. In general, the best corrosion resistance toward most media can be obtained with high-purity aluminum. Commercial aluminum (99%) and alloys containing manganese, magnesium, or chromium are usually more resistant than other alloys of aluminum. The alloys with silicon are only slightly less resistant than commercial aluminum, and the alloys containing copper, nickel, iron, and zinc are the least resistant toward most media.

Another advantage of aluminum alloys under corrosive conditions is the colorless, tasteless, and nontoxic character of most of the corrosion products.

A uniform and adherent oxide film can be produced on aluminum alloys by anodic oxidation in an electrolyte of 10%  $H_2SO_4$ . This film serves as an excellent base for other protective coatings such as paints and lacquers. The oxide coating can also be dyed to give a brilliantly colored finish.

The electrical conductivity of an aluminum wire of a given weight is twice the conductivity of a copper wire of the same weight. An aluminum wire cable with a strong steel core is used extensively for the transmission of electric power. High-voltage lines with extremely long spans between supports are thus made possible, but this advantage is very much less important in climates where the danger of heavy sleet loading makes necessary the closer spacing of supports.

The high reflectivity of aluminum makes possible its use in the form of foil as a thermal insulator, and in the flake form as a pigment in paints which are particularly useful in keeping down absorption and radiation of radiant heat.

Commercial aluminum and many of the aluminum alloys can be readily formed by all sorts of cold-forming operations including rolling, drawing, stamping, cupping, spinning, and bending. The hot-working properties of many of the alloys are excellent and commercial shapes are often produced by the extrusion process. Machining aluminum and aluminum alloys is more difficult than might be expected and a special technique is required for best results.

**Welding.** Aluminum alloys can be welded by the gas, arc, or resistance welding processes. A flux is necessary for torch and arc welding and, in arc welding, a coated filler rod can be used to advantage. Welding lowers the strength of work-hardened and precipitation-hardened alloys, and in most cases the corrosion resistance is also lowered at the weld.

There are many solders on the market which will produce a satisfactory joint in aluminum structures, but in practically all cases the composition of the solder is widely different from that of the alloy and the danger of electrolytic corrosion is very great. Recently some aluminum-base solders have been developed which are claimed to be superior in this respect.

## ALUMINUM ALLOYS

Aluminum alloys are made in a wide variety of compositions and each of these alloys possesses a different combination of useful properties

and characteristics such as forming properties, casting properties, response to heat treatment, degree of corrosion resistance, different combinations of strength and ductility.

The most common alloying elements used in commercial alloys of aluminum are: copper up to 10%, silicon up to 14% (occasionally up to 23%), magnesium to 10%, manganese to 2%, zinc to 20%, nickel to 4%, and iron to 1.5%. Occasionally small amounts of other elements are also added, particularly chromium, bismuth, lead, titanium, cadmium, tin, sodium, and vanadium.

### **Wrought-Aluminum Alloys**

Aluminum alloys can be classified into two main groups: the wrought alloys and the casting alloys. Very few of the alloys are used in both the cast and wrought forms. Of the wrought alloys some are susceptible to hardening by heat treatment (precipitation hardening or age hardening), whereas others can be hardened only by cold working (strain hardening).

The commercial grade of aluminum (99% Al) is used extensively in wrought form and is a strain-hardening alloy. In this grade, which is designated as alloy No. 2S by the principal producer, the alloying elements are the impurities iron, silicon, and copper. Other important strain-hardening alloys are 3S and 52S. These alloys are available in several "tempers" or degrees of hardness, determined by the amount of cold rolling after the last annealing treatment, and designated as quarter-hard ( $\frac{1}{4}$  H), half-hard ( $\frac{1}{2}$  H), etc. The composition and mechanical properties of these alloys in several tempers are given in Table 29. Alloy 2S has the best forming properties but 52S has the highest strength of the strain-hardening alloys. The fatigue limit of 52SH is higher than that of any other aluminum alloy produced in this country. The corrosion resistance of the strain-hardening alloys is better than that of any of the precipitation-hardening groups.

The original precipitation-hardening alloy is duralumin (17S). Its response to heat treatment is due principally to the change in solid solubility of copper in aluminum with changes in temperature. According to the aluminum-copper constitution diagram given in Plate II of the Appendix, this solubility increases from 0.5% at 200°C (392°F) to 5.5% at 548°C (1022°F). Duralumin contains approximately 4% copper and is heat treated by heating to a temperature above the solubility line until the aluminum-copper compound is dissolved completely (about 25 minutes), whereupon the alloy is quenched. The first step in the heat treatment, sometimes called the solution heat treatment, produces a supersaturated solid solution which tends to break down into the phases stable at room temperature. This change takes place, or is initiated,

during the second step in the heat treatment which is called the aging or the precipitation heat treatment, and is accompanied by a remarkable increase in the hardness and strength of the alloy. In the original duralumin alloy (17S), maximum hardness can be obtained by simply aging the quenched alloy at room temperature for about four days. Some modifications of this alloy (61S, 53S, 25S) do not age-harden at room temperature, but must be given artificial aging or precipitation heat treatment at slightly higher temperatures (315–355°F for 8 to 18 hours). Alloys heated to higher temperatures or for longer periods than required to develop maximum hardness become “overaged”; such a condition is characterized by lower mechanical properties and reduced resistance to corrosion, particularly at the grain boundaries.

The exact stage of the precipitation reaction which has been reached at the instant when maximum hardness is attained is a controversial matter since at that stage almost all the precipitated particles are much too small to be resolved under a microscope. In fact it is very likely that they are smaller in diameter than a hundredth of the size of the smallest resolvable particle. Various published estimates of this so-called “critical size” of the precipitated particles range from some ten atom diameters down to sizes so small that the nuclei may still be in the process of formation. The latter condition has been referred to as a “pre-precipitation” phenomenon and considered by some metallurgists to be the condition attained during the aging of duralumin at room temperature. This might also apply to the early stages of the aging reaction of many other age-hardening alloys.

The mechanism of age hardening as explained by the various theories that have been proposed is essentially the same; the hardening is supposedly due to an increased resistance to slippage along the glide planes of the parent solid solution crystals. This increased resistance may be due to the keying effect of a large number of precipitated particles of a second phase along the glide planes or to a similar keying effect caused by distortion of the space lattice about points where nuclei of the second phase are beginning to form. The keying action along the glide planes has been likened to the effect of placing grains of sand between two cakes of ice. By means of this simple theory, all known changes in properties during the aging of duralumin can now be explained.

The precipitating phases in duralumin aged at room temperature are the  $\theta'$  form of  $\text{CuAl}_2$  and other compounds which contribute to the age-hardening reaction. Other precipitation-hardening alloys of aluminum are modifications of the original duralumin composition, some of which contain no magnesium and some little or no copper but more magnesium and silicon.

The compositions, properties, and characteristics of the various alloys

are given in Table 29. Each alloy has some unique characteristics which make it especially useful for certain applications. Alloys 24S and 14S are stronger than 17S; alloys 61S, 25S, A51S, and A17S possess superior working properties; 11ST3 is a free-machining alloy; but 18S and 32S retain their strength better at elevated temperatures than other alloys of this group. The proper heat-treating temperatures vary slightly with composition and the manufacturer's recommendations in this respect should be followed closely.

The corrosion resistance of alloys 53S and 61S is said to approach that of the strain-hardening alloys 2S, 3S, and 52S. For applications where still greater corrosion resistance is required, as in seaplane construction, a composite sheet product known as Alclad is available. It consists of a duralumin sheet covered with a thin layer of high-purity aluminum on both sides.

### Casting Alloys of Aluminum

Casting alloys of aluminum can be classified according to the method of casting: sand castings, permanent mold, and die castings. Most of the common sand-casting alloys used in this country are listed in Table 30, which also gives their characteristics and mechanical properties. Modifications of the 8% copper alloy (S.A.E. 30, 33, and 36) are used most widely and possess a favorable combination of casting properties, machinability, and low cost with fair mechanical properties. They are used for a wide variety of miscellaneous castings which are not subjected to high stresses: automotive castings such as crankcases, oil pans, transmission housings; parts for washing machines, vacuum cleaners, typewriters; and other similar applications.

In Europe another alloy, containing 10–14% zinc and 2–3% copper is used extensively for general casting purposes. S.A.E. No. 31 is the American modification of this composition and it is used to a limited extent in this country. Its mechanical properties are superior to those of the 8% copper alloy but it loses ductility upon aging at room temperature and it is inferior with respect to corrosion resistance and strength at elevated temperatures.

Alloys of aluminum and silicon are becoming increasingly popular because of their superior casting properties, corrosion resistance, and weldability. They can be readily cast into thin or complex sections, are relatively free from hot shortness, and readily produce castings which will withstand fluid pressures without leakage. The 5% silicon alloy (S.A.E. 35) is very ductile and resistant to shock, but possesses rather low yield strength and hardness. It is used for marine castings, manifolds, water jackets, architectural and ornamental castings.

Castings made of high-silicon alloys of aluminum (S.A.E. 37) are normally coarse grained and brittle unless they are chill cast or "modified" by treatment of the molten alloy with an alkali fluoride flux or with 0.05% of metallic sodium. When properly modified, this alloy has a very fine-grained structure and its mechanical properties are superior to those of most other aluminum alloys which have not been heat treated. This alloy is used extensively in Europe, under the names of Silumin and Alpac, for highly stressed castings.

Precipitation hardening alloys are commonly used in this country for applications requiring maximum strength. The most widely used alloy of this group is S.A.E. 38 (Alcoa 195T), containing 4% copper. Heat treatment No. 1 (195T4) consists of the solution heat treatment alone and gives the best ductility but only moderate tensile and yield strengths. Partial artificial aging is included in heat treatment No. 2 (195T6), the effect upon mechanical properties being similar to that of several months' aging at room temperature. Maximum strength is obtained by the full artificial aging heat treatment, No. 3 (195T62), which also reduces the ductility to rather low values.

The 4% copper alloy is not suitable for the production of intricate castings; these are usually made of more complex alloys which generally contain from 4 to 7% silicon (S.A.E. 322, A.S.T.M. alloys N or M, Alcoa A334, 355, A355, and 356). The alloys which retain their strength well at elevated temperatures include S.A.E. 39 and 322, A.S.T.M. alloys H, F, and N, Alcoa 122, 142, 355, and A355.

Alloys of aluminum with 3.75 to 10% magnesium have been developed in recent years for applications requiring maximum corrosion resistance. The 3.75% magnesium alloy (S.A.E. 320, A.S.T.M. alloy L, Alcoa 214) is used without heat treatment and has good ductility and toughness. Alloys containing 6 to 10% magnesium require special foundry technique because of the high magnesium content. The 10% magnesium alloy (S.A.E. 324, Alcoa 220T), when heat treated, develops the highest tensile strength as well as the highest ductility and toughness that can be obtained with any commercial casting alloy of aluminum.

The procedure followed in the heat treatment of casting alloys is similar to that of duralumin with the exception that a very long time, 18 hours or more, is required for the solution heat treatment of cast alloys. The actual temperatures for the solution heat treatment and the precipitation heat treatment vary with composition.

### **Permanent-Mold and Die-Casting Alloys**

When a large number of duplicate castings are produced, certain advantages can be gained by using permanent metal molds into which the molten alloy can be poured by gravity (permanent mold castings)



or under pressure (die castings). The high initial cost of the mold may be more than offset by lower labor costs, particularly in the machining and finishing of the castings. The use of permanent molds permits much closer dimensional tolerances and gives a very smooth surface finish.

Some of the alloys used for sand castings are also used for permanent mold castings. Owing to the more rapid solidification in a metal mold a structure of finer grain is obtained and the strength of the chill-cast alloys is slightly higher.

Of the alloys listed in Table 30, the following are used for permanent mold castings as well as for sand castings: F, H, C, J, N, and L.<sup>1</sup>

In general, the high-copper alloys are cheaper and have a tendency toward hot shortness. Silicon is a major alloying element in most of these alloys and small amounts of magnesium are present in many of the alloys which are susceptible to heat treatment. Some chill-cast alloys respond to the artificial aging heat treatment alone, without a previous solution heat treatment. The mechanical properties of permanent mold and die castings fall within the following ranges: tensile strength 20-48,000 psi, yield strength 8-42,000 psi, elongation 0-8%, Brinell hardness 40-110.

### MAGNESIUM ALLOYS

The use of magnesium alloys has expanded during the past two decades at an extremely rapid rate in spite of many handicaps which had to be overcome by industry, and the selling price has been reduced progressively to less than 25 cents per pound. The problem of corrosion has been solved to some extent by the development of new alloys and by rigid control of impurities. Difficulties in foundry practice have been overcome by the development of special technique. Fabrication processes have been worked out in spite of relatively poor cold-working properties, and the welding of magnesium alloys is carried on successfully today although their extreme tendency toward oxidation had delayed this development for many years.

The chief advantage of magnesium alloys is their light weight; with a specific gravity of about 1.85 as compared with 2.8 for aluminum alloys, they are the lightest alloys available commercially and have a high strength-to-weight ratio. Another advantage is excellent machinability. Of the disadvantages mentioned previously, relatively poor corrosion resistance is probably the most serious. Unprotected surfaces will resist ordinary atmospheric exposure only if adequate provision is made for

<sup>1</sup> For compositions and properties of other permanent-mold and die-casting alloys see the *A.S.T.M. Book of Standards* and *Alcoa Aluminum and Its Alloys* by the Aluminum Company of America

free drainage and good ventilation for all surfaces. In assemblies, contacting surfaces should be sealed to exclude moisture. In humid, and particularly in salt-laden atmospheres, some sort of protective coating is necessary. A number of special chemical surface treatments have been developed to inhibit corrosion and provide an excellent base for paints and other protective coatings. Severe electrolytic corrosion is likely to occur when magnesium alloys are used in contact with other metals if moisture is present.

Magnesium alloys work harden rapidly when worked cold and only a limited amount of cold forming can be accomplished without intermediate annealing treatments. Hot forming is generally more satisfactory, the best range of working temperatures being 500–750°F. Wrought parts are usually made in a forging press, but special alloys are available which can be forged under a hammer. Extrusion is the most satisfactory method of working magnesium alloys and is used to produce bars, rods, structural shapes, and tubing.

The most important alloying elements in commercial alloys of magnesium are aluminum, zinc, and manganese; many alloys contain all three. The aluminum content is usually 4 to 10%, zinc 0–3%, and manganese about 0.2%. Occasionally silicon, cadmium, or tin are also added. The impurities, iron and nickel, are kept below 0.005% each in several alloys for improved resistance to salt water corrosion. Manganese in small amounts improves corrosion resistance.

The constitution diagrams for the magnesium-aluminum and magnesium-zinc systems are given in Plates II and III of the Appendix. They show that the solid solubility of aluminum in magnesium varies from 3% at room temperature to 12% at 436°C (817°F), and the solubility of zinc from 1.8 to 8.4% (340°C, 644°F). Hence these alloys are susceptible to precipitation-hardening. The solution heat treatment requires prolonged soaking for both cast and wrought alloys at a temperature, varying with composition, from 630–810°F. The solution heat treatment is often used alone without a subsequent precipitation heat treatment to improve tensile strength and ductility. The precipitation heat treatment at about 350°F usually reduces ductility to a rather low value without materially increasing tensile strength, but the hardness and yield strength, which are affected only slightly by the solution treatment, are increased very substantially by the precipitation heat treatment. Extruded alloys are susceptible to the precipitation heat treatment without a previous solution heat treatment.

Table 31 gives the compositions, properties, and characteristics of the more important commercial alloys used in this country. The ranges of mechanical properties obtainable with various alloys are approximately:

tensile strength 12-50,000 psi, yield strength 4-38,000 psi, elongation in 2 in. 0-19%, Brinell hardness 33-85, endurance limit up to 18,000 psi.

### DIE CASTINGS

Die castings are made in metal molds, the molten alloy being forced into the dies under pressure. The trend in modern die-casting machines is toward high-pressure machines of the plunger type. The cost of the mold is usually high, several hundred to several thousand dollars, but when a number of duplicate castings is required the cost per casting may be considerably less than for sand-cast and machined parts. The smooth surface finish of die castings usually permits their use directly without any machining or polishing operation, or an electroplated finish can be applied directly. The dimensional accuracy of die castings is very high and thin sections or intricate shapes can be cast readily. Assembly costs can be kept low by the use of inserts of other alloys or nonmetallic materials. A large number of small castings can be made in one die, depending on the melting temperature of the casting alloy used. Up to half a million zinc-alloy die castings or 50,000 to 200,000 aluminum alloy castings are normally made in a die under favorable conditions.

By far the most important die-casting alloys are those of zinc, although alloys of aluminum, magnesium, lead, tin, and, to some extent copper, are also die cast. Modern zinc die-casting alloys are very much superior to the zinc alloys produced some years ago, particularly from the standpoint of stability. These alloys are made from zinc of very high purity, 99.99% Zn, and such impurities as tin, cadmium, and iron are held to extremely low limits. The three common alloys each contain approximately 4% Al and 0.05 Mg, and the copper content is 0, 1, and 3% respectively. The copper-free alloy has the best dimensional stability whereas the alloys with copper have higher tensile properties, ranging up to 48,000 psi tensile strength and about 19% elongation for the 3% Cu alloy. None of the zinc-base alloys is suitable for service at temperatures above approximately 200°F, particularly in humid atmospheres.

The serviceability of good zinc-base die castings is well known in the automotive field for radiator grills, door handles, and miscellaneous hardware on the modern automobile.

### NICKEL AND NICKEL ALLOYS

Nickel is a very useful metal both in the commercially pure form and as an alloying element in ferrous and nonferrous alloys. The useful properties of nickel include resistance to corrosion and oxidation, white color, fairly good resistance to tarnish, good mechanical properties, and

TABLE 31. COMPOSITION AND

Form	A.S.T.M.	Am. Mg. Corp.	Dow Chem. Co.	Composition, Per Cent Magnesium-Remainder				Uses and Characteristics
	Alloy No.			Al	Mn	Zn		
Sand castings	4	265	H	6.0	0.2	3.0		General casting use. Sand and permanent mold castings.
	17	260	C	9.0	0.1	2.0		Pressure-tight castings.
	2	240	G	10.0	0.1			Sand and permanent mold castings.
Die castings	3	246	B	12.0	0.1			Hard castings. Pistons. Best salt water resistance. Aircraft tank fittings.
	11	403 244	M	4.0	0.3			
	12	230	K	10.0	0.1		Si 0.5	Thin section die castings. General die castings.
Extruded bars and rods	13	263	R	9.0	0.2	0.6		
	8	57S	J	6.5	0.2	0.7		Improved strength.
	8	57S	J	6.5	0.2	0.7	(S)	Screw machine rod. Best salt water resistance.
	11	3S	M		1.5			Bars of high strength. Heat-treatable bar.
	9	58S	O	8.5	0.2	0.5	(S)	
	15	74S	X	3.0	0.2	3.0		
	15	74S	X					
2(e)	59S	G	10.0	0.1			Highest hardness and strength. Good ductility and impact toughness.	
18	52S	FS	2.8	0.3	1.0			
Extruded structural shapes	8	57S	J	6.5	0.2	0.7	(S)	Good strength and weldability. Best salt water resistance. Heat-treatable shapes.
	11(e)	3S	M		1.5			
	15	74S	X	3.0	0.2	3.0	(S)	
	15	74S	X					
	9(e)	58S	O	8.5	0.2	0.7	(S)	Improved strength. Highest hardness and strength. Good ductility and impact toughness.
	2(e)	59S	G	10.0	0.1			
18	52S	FS	2.8	0.3	1.0			
Extruded tubing	8(e)	57S	J	6.5	0.2	0.7	(S)	Good strength and weldability. Best salt water resistance. Heat-treatable tubing.
	11(e)	3S	M		1.5			
	15(e)	74S	X	3.0	0.2	3.0	(S)	
	15(e)	74S	X					
	9(e)	58S	O	8.5	0.2	0.7		Highest strength tubing. Good ductility.
18(e)	52S	FS	2.8	0.3	1.0			
Press forgings	8	57S	J	6.5	0.2	0.7	(S)	General forging. Good ductility. Weldable forgings.
	11(e)	3S	M		1.5			
	9	58S	O	8.5	0.2	0.5	(S)	Forgings, simple design. Strong. Heat-treatable forgings.
	15	74S	X	3.0	0.2	3.0	(S)	
15	74S	X						
Hammer forgings	16	65S	L	3.5	0.2		Sn 5.0 Cd 3.5	Hammer forgings. Hammer forgings.
				3.0	0.2			
Rolled plate, sheet and strip	11	3S-H 3S-O	Mh Ma		1.5			Sheet with best formability and salt water resistance.
	8(e)	57S-H 57S-O	J-1h J-1a	6.5	0.2	0.7	(f)	Sheet with best combination of strength and salt water resistance. General-purpose sheet alloy. Good formability and strength.
	18(e)	52S-H 52S-O	Fsh Fsa	2.7	0.3	1.0		

(a) In 1000 psi. Yield strength is the stress at which the stress-strain curve deviates 0.2% from the modulus line.

(b) Endurance or fatigue limit for 500 million reversals of the load, in 1000 psi.

(c) Solution heat treatment: Soaking at about 630 to 810°F followed by air quenching.

## PROPERTIES OF MAGNESIUM ALLOYS

A.S.T.M. Alloy No.	Condition	Tensile Strength (a)		Yield Strength (a)		Elongation in 2 in. %		Brinell Hardness	Shear Strength (a)	Endurance (b)
		Typical	Min	Typical	Min	Typical	Min			
4	As cast	27	24	11	10	5	4	51	17	10
	Cast; soln. T. (c)	37	30	12	10	10	6	53	18	10
	Cast; soln. T.; aged (d)	37	32	18	16	4	2	70	19	9
17	As cast	23	20	14	10	1		62	18	10
	Cast; soln. T. (c)	39	30	14	10	10	6	61	20	10
	Cast; soln. T.; aged (d)	38	32	20	18	3	1	77	22	10
2	As cast	21	18	12	10	2	1	53	18	8
	Cast; soln. T. (c)	33	29	12	10	8	5	52	20	10
	Cast; soln. T.; aged (d)	34	29	19	17	1		69	22	8
3	Cast; soln. T.; aged (d)	32	27	20	17	0.5		85	19	7
	As cast	14	12	4	5	5	3	33	11	
11	As cast	24	20	9	8	6	4	44	14	
	As cast	30		22		1		68		
13	As cast	33		20		3		66		
8	As extruded	43	40	30	26	17	12	54		17
11	As extruded; stretched	44	40	32	26	15	12	55	20	15
9	As extruded	42	32	27	20	6	5	42		10
15	As extruded	47	43	33	28	11	9	61		17
15	As extruded	42	39	30	26	19	15	51		18
2(e)	As extruded; aged	44	41	34	30	13	10	54		17
18	As extruded; stretched	51	45	38	33	9	6	70	23	16
	As extruded; stretched	40	37	30	25	17	12	50	19	12
11(e)	As extruded	35	30	23	16	6	3	42		
15	As extruded	42	39	25	22	17	10	59		
15	As extruded; aged	43	40	28	25	14	8	62		
9(e)	As extruded	44	40	29	25	11	8	58		
2(e)	As extruded	48	45	37	30	9	6			
18	As extruded	39	35	28	22	15	11			
8(e)	As extruded	40	36	19	17	9	7	55		
11(e)	As extruded	35	32	17	17	5	3	40		
15(e)	As extruded	40	36	19	17	9	7	55		
15(e)	As extruded; aged	41	37	22	19	7	6	59		
9(e)	As extruded; aged	42	39	29	25	5	4	60		
18(e)	As extruded	35	32	16		11		50		
8	As forged	41	38	25	22	9	6	56	21	17
11(e)	As forged	33	29	19	12	6	2	43		
9	As forged	45	42	30	24	7	5	69	22	18
15	As forged	41	38	24	20	16	9	59		17
15	As forged; aged	42	38	28	22	14	7	62		17
16	As hammer forged	38	35	22	20	12	6	52	16	10.5
	As hammer forged	37	34	26	19	11	6	51		10.5
11	As hard rolled	37	32	27	24	9	4	53		
	Annealed	32	(35 max)	16		15	12	44	17	
8(e)	As hard rolled	45	40	35	28	8	3		21	8
	Annealed	40	(45 max)	25		15	8		20	
18(e)	As hard rolled	45	38	35	26	9	4			
	Annealed	36	32	22		18	12			

(d) Solution treatment followed by artificial aging at about 350°F (precipitation hardening).

(e) This form not listed in the A.S.T.M. specifications.

(f) Dowmetal J-1, O-1, X-1, and AMC-57s limited to 0.005% Fe max and 0.005% Ni max for improved resistance to salt water.

TABLE 32. PROPERTIES OF

Alloy	Composition						Form		
	Ni + Co								
"A" nickel	99.4						Sheet		
"Z" nickel	98 + (C, Ti, Mg)						Wire		
Ni-Mn, "E"	97.5	Mn	2				Hot-rolled rod		
Ni-Mn, "D"	94.5	Mn	4.7				Hot-rolled rod		
Ni-Mn, 15%	84.3	Mn	15						
Cast nickel	97 +	Si	1.25,	Mn	0.5,	Fe	0.5	Cast	
Monel "B"	67	Cu	30	Fe	1.4	Mn	1	Wrought	
Monel free machining "R"	67		30		1.4	1	(S 0.035)	Wrought	
Monel hardenable "K"	66		29		0.9	0.4	(Al 2.75)	Hot rolled	
Cast Monel	67		29		1.5	0.9	(Si 1.25)	Cast	
Cast Monel H	65		29.5		1.5	0.5	(Si 3)	Cast	
Cast Monel S	63		30		2	0.5	(Si 4)	Heat treated	
Cupro-nickel	70-85	Cu	15-30 (Sn 0-1)				Wrought		
Nickel silver	18	Cu	64	Zn	18			Wrought	
Nickel silver	16		60		16	Pb	5	Sn 3	Cast
Nickel silver	20		65		6	5		4	Cast
Nichrome	62	Cr	15	Fe	23				
Inconel	79		13.5		7				
Hastelloy A	60	Mo	20		20				
Hastelloy B	65		30		5				
Hastelloy C	60		17		8	Cr	15		
Westinghouse K-42-B	45 Ni	Co	25	Cr	20	Ti	2	Fe 7	Heat treated
									Test at 1100°F

good working properties. It is one of the most useful of alloying elements since it forms tough and ductile solid solution alloys with many of the common metals. In many alloys a relatively small addition of nickel produces important changes in properties. For use in the preparation of alloys it is available in the form of electrolytic cathode nickel, remelted electrolytic nickel blocks or shot, carbonyl nickel pellets, cubes or rondules reduced from the oxide without fusion, and powdered nickel. The purity of the electrolytic grade is about 99.5% nickel or 99.95% nickel plus cobalt.

### Wrought-Nickel and High-Nickel Alloys

Small amounts of sulfur cause brittleness in nickel and the so-called malleable or "deoxidized" grades of nickel which are used in the wrought form are produced by adding manganese; this converts the sulfur into a less harmful form. Sulfide embrittlement is likely to occur in any of the alloys containing substantial amounts of nickel if these are exposed to sulfur-bearing gases at elevated temperatures.

NICKEL ALLOYS

Tensile Strength, 1000 psi	Yield Strength, 1000 psi	Elongation, % in 2"	Brinell Hardness Number	Characteristics
75-120	20-110	48-5	100-200	Wrought nickel
90-240	28-150	50-2	150-380	High strength wrought nickel
81	32	45	140	Spark plug electrodes
86	34	40	147	Spark plug electrodes
95	38	38	155	Spark plug electrodes
55	21	22	120	Nickel castings
65-130	25-115	50-2	120-220	Original Monel Metal
75-100	35-90	45-5		Free machining. Hot short.
97-130	58-112	38-5	38-215	Soln. H. T. Quench from 1425°F; 14 hr at 1080°F, slow cool
70	35	30	140	Corrosion-resistant castings
85	50	15	190	Strong castings, hardened by H. T. 4 hr 1100°F, slow cool
110	80	2	300	Strong castings, hardened by H. T. 4 hr 1100°F, slow cool
140-170	100-120	18-6	250-290	Ppt. H. T. Quench from 1425°F 4 hrs at 1100°F, slow cool
40-83	14-80	50-3	80-145	Marine condenser tubes
50-95	16-80	43-3	RB 30-90	White alloys very similar to brasses, nickel brasses
35-45	17-24	15-30	65-80	White alloys very similar to brasses, nickel brasses
42-48	25-30	12-16	90-100	White alloys very similar to brasses, nickel brasses
95-175		35-0.5	155-275	Heat- and corrosion-resistant
85-170	28-140	53-10	115-350	Heat- and corrosion-resistant
69-120	42-52	48-8	153-215	High corrosion resistance
75-140	55-65	45-6	190-235	High corrosion resistance
72-80	45-48	15-10	210-235	High corrosion resistance
165	104	29		High strength, oxidation resistance at elevated temperatures
127	86	21		High strength, oxidation resistance at elevated temperatures

The common commercial grade of wrought nickel is known as "A Nickel"; it contains about 99.4% nickel plus cobalt, and is available in many forms including hot-rolled or cold-drawn rod, bar, wire, sheet, strip, plate, and special shapes. Nickel-clad steel is also available. The mechanical properties of A Nickel are given in Table 32.

A precipitation-hardening alloy known as "Z Nickel," containing over 98% nickel plus cobalt with small amounts of carbon, titanium, and magnesium, is capable of developing very high tensile properties. The recommended heat treatment includes an "annealing" or solution heat treatment at 1950°-2000°F, followed by quenching, after which the alloy can be cold worked readily. The precipitation heat treatment for hardening consists of heating to 910°F for 8 to 16 hours. The mechanical properties of Z Nickel are given in Table 32.

Cast Nickel

Nickel is sometimes used for corrosion-resistant castings, particularly for applications where contamination with copper or iron must be

avoided. Small amounts of silicon, manganese, and magnesium are added to facilitate the production of sound, ductile castings. Lead, tin, and zinc should be absent and the sulfur content should be below 0.01%. The composition and properties of cast nickel are given in Table 32.

**Nickel-Manganese Alloys.** Resistance to sulfur gases is improved by manganese additions to nickel and several wrought alloys, containing

TABLE 33. ELECTRICAL RESISTOR ALLOYS

Trade Names	Compo- sition	Resistivity 68°F		Temp. Coeff. Resistivity, 68-212°F	Maximum Operating Temp., °F	Melt- ing Point, °F	Uses and Characteristics
		Ohms C.M.F.	Microhms Cu cm				
Nichrome II Chromel A Tophet A	Ni 80 Cr 20	650	104	0.00009*	2100	2540	Electrical heating elements.
Nichrome Chromel C Tophet C	Ni 62 Cr 15 Fe bal.	675	109	0.000094	1850	2460	Electrical heating elements.
Cromin D Comet	Ni 30 Cr 5, Fe 65	575	96	0.00038			Low temperature controls.
Climax	Ni 28, Fe 72	525	87	0.0006	1500	2550	Cheap heating ele- ments.
Smith alloy #10 Hoskins #10 Kanthal A	Cr 37.5 Al 7.5 Fe 55 Cr 25, Al 5 Co 3, Fe 67	1000	164	0.00012†	2600	2830	Brittle at room temp. Weak at operating temperature.
Ohmaloy	Cr 15 Al 5, Fe 80	850	139	0.00005‡	2375	3000	Heating elements. Weak at operating temp.
Constantan, Copel, advance, Ideal, cupron.	Ni 45 Cu 55	750	123	0.00005	2100	2910	Resistors. Weak at elevated tempera- tures.
Manganin	Cu 84, Mn 12 Ni 4	294	49	±0.00001	800	2400	Low temp. coeffi- cient rheostats.
Commercial platinum		290	(44) 48	±0.00001	95		Shunts. Resistors. Low temp. only
Commercial molybdenum		72	12	0.0021	3190	3224	Resistors high temp.
Ni " A "		33	5	0.0025	1300	4748	Used in reducing atm.
		65	92	0.0025	900	2646	High temp. coef- ficient

\* 68-800°F approximately zero above 800°F. † Negative above 1700°F. ‡ 68-1650°F.

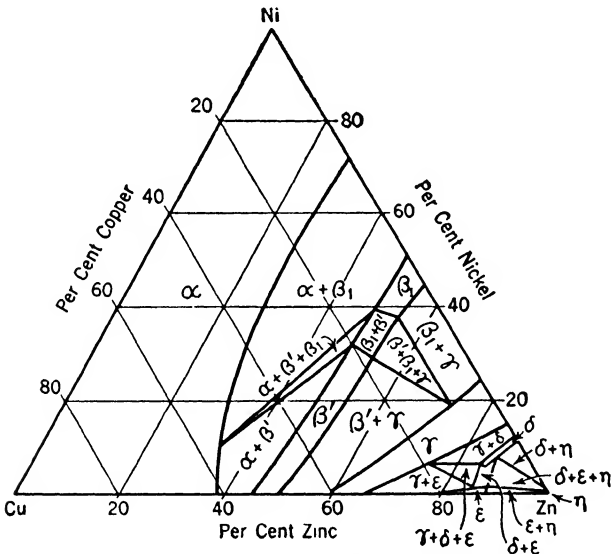
respectively 2, 4.65, and 15% Mn, are available for such applications as spark plug electrodes and ignition tubes.

**Nickel-Beryllium Alloys.** Nickel-beryllium alloys which have been developed recently are susceptible to the precipitation-hardening type of



heat treatment and have very high tensile properties. An alloy containing 1.9–2.5% Be, 0.5–1.0% Mn, balance Ni, has a tensile strength of up to 260,000 psi.

**Nickel-Copper Alloys.** Nickel and copper dissolve in each other in all proportions in the solid state to form a series of useful alloys having good corrosion resistance, mechanical properties, and working properties. The alloys containing over 15 or 20% nickel are white in color, and the copper-rich alloys in this series are in some respects closely related to other copper-base alloys such as brasses. Cupro-nickel containing 20 to 30% nickel is used chiefly for marine condenser tubes. The composition of American nickel coins is 25% nickel, 75% copper. Constantan, 45% nickel and 55% copper, is used in the form of wire for rheostats and thermocouples (Table 33).



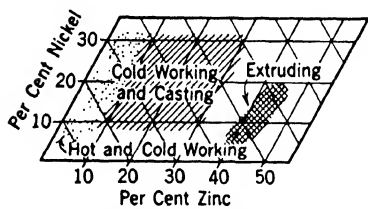
*Courtesy Schramm, A.S.M. Handbook*

FIG. 118. Constitution of copper-nickel-zinc alloys at 25°C.

**Monel Metal.** Monel metal is a natural alloy of about two-thirds nickel and one-third copper, the proportion in which these two metals occur together in some Canadian ores. The alloy resembles nickel in color and corrosion-resisting properties. Several grades of Monel metal are available, each especially suited for certain applications; some are susceptible to a precipitation-hardening heat treatment; some are special casting alloys; one is free-machining, and another has the best ductility. The properties of these alloys are given in Table 32.

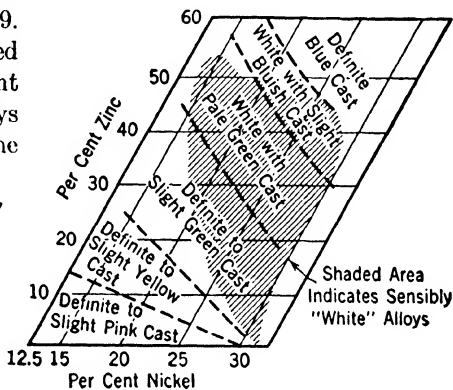
**Nickel Silver.** Nickel silver, German silver, or nickel-brass is an alloy of copper, zinc, and nickel, and can be regarded as a brass to which enough nickel has been added to change the color to white (usually 7 to 30% Ni). The constitution of the ternary system at room temperature is given in Fig. 118.

Most commercial nickel-silver alloys fall in the alpha solid solution range of compositions, the only important exception being the  $\alpha + \beta$  extrusion alloy. In working and mechanical properties, summarized in Table 32, these alloys are analogous to the corresponding  $\alpha$  and  $\alpha + \beta$  brasses. Nickel has a mild hardening effect, increasing tensile properties slightly at the expense of a slight decrease in ductility. The composition ranges of commercial alloys are given in Fig. 119. The 18% nickel alloy is used widely since this nickel content represents a minimum for alloys substantially white in color. The



Courtesy Kùhlgrèn, A.S.M. Handbook

FIG. 119. Composition ranges of nickel silvers.



Courtesy A.S.M. Handbook

FIG. 120. Color trends of nickel silvers.

relation between composition and color of the copper-nickel-zinc alloys is given in Fig. 120.

The copper content of most wrought nickel-silvers ranges between 60 and 65% whereas most casting alloys contain 55 to 65% Cu, 12 to 25% Ni, 2 to 4% Sn, 1 to 10% Pb, balance zinc. Lead promotes machinability and is sometimes added to wrought nickel-silvers (1 to 2% Pb) used for keys, screws, bolts, nuts, valves, and lock parts. Leaded nickel-silvers are hot short and have inferior cold-working properties.

The uses of nickel silver are based on its white color, fair resistance to tarnish, a resistance to corrosion slightly better than that of brasses, and good working properties. Some of the important uses are: silver-

plated tableware, food-handling equipment, architectural trim, hardware, and marine fittings.

**Electrical Resistance Wires.** Electrical resistance wires for heating elements and rheostats are made of special alloys with high electrical resistivity (which should remain fairly constant with temperature changes) and resistance to oxidation with suitable strength at operating temperatures. For heating elements, long life at high temperatures is most important, whereas for rheostats and resistors operating at lower temperatures a nearly constant resistivity is desirable. Table 33 lists a number of the more important commercial alloys and metals used for this purpose together with their characteristics.

### BEARING-METAL ALLOYS

The desirable characteristics of a bearing metal are extremely diverse and no single alloy possesses all of them. For instance, one requirement is resistance to wear, a quality normally associated with high hardness, and another useful property is plasticity, usually found in soft alloys. Depending upon the type of service for which it is intended, a bearing metal may be required to have several of the following characteristics to various degrees: wear resistance, sufficient plasticity to facilitate uniform load distribution, high compressive strength and resistance to pounding at operating temperatures, capacity for retention of an oil film on the bearing surface, low coefficient of friction with the shaft material (important primarily during metal-to-metal contact when lubrication is imperfect), low tendency toward galling or seizing, high thermal conductivity, good bonding characteristics with the backing material, high melting temperature, corrosion resistance, low tendency to scratch or wear the shaft, self-lubricating properties, and low cost of installation and maintenance. Data obtained from tensile and hardness tests are often misleading when used as a basis for judging the merits of a bearing metal alloy.

Special alloys have been developed for various types of service, but the demands of the designing engineer are constantly changing and new alloys or new methods of application are sometimes required to meet these demands. The former custom of using thick linings of bearing metal is being changed and there is a definite trend toward the use of much thinner linings. Extremely thin coatings of silver, tin, or lead over steel or other special backing alloys have been used successfully for bearings.

A microstructure which includes both a hard, wear-resistant constitu-

ent and a softer, more plastic constituent has long been regarded as the ideal structure for a bearing alloy. The facts that ordinary bearing bronze is used in the "as cast" condition with a dendritic and segregated structure, and that any sort of homogenizing treatment definitely lowers its performance as a bearing alloy tend to confirm this theory. At least the rule seems to hold true for almost all the successful bearing alloys which are used in the form of thick linings. In pure metals used as very thin coatings, it is possible that the structure of the backing material may be an important factor.

### White-Metal Bearing Alloys

The bearing alloys of tin, lead, and cadmium are characterized by a high degree of plasticity and relatively low fusing temperatures. The lead- and tin-base alloys are used very widely and both are frequently

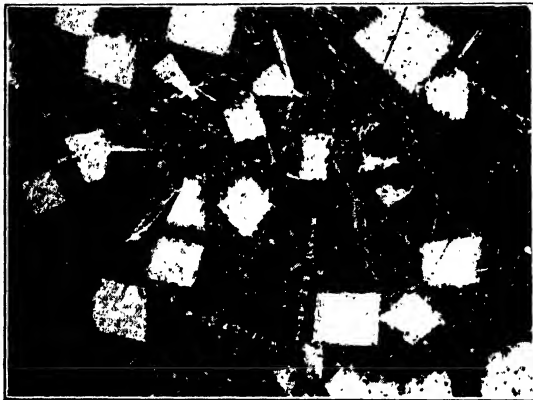


FIG. 121. Tin-base babbitt.  $\times 100$ .

called "babbitt metal," although the original alloy developed by Babbitt was a tin-base alloy. The tin-base babbitts have been used for over a century with only slight modifications in composition. The principal hardening elements are antimony, usually 4.5 to 12%, and copper, 1.5 to 8.3%. The present trend is toward standardization on alloys falling near the middle of these ranges. Two typical alloys are the S.A.E. No. 11, about 7 Sb, 5.7 Cu, and A.S.T.M. No. 2, 7.5 Sb and 3.5 Cu. Alloys containing less antimony and copper are used mainly for very thin linings in shells of steel or bronze. Lead tends to lower the melting temperature of tin-base alloys and in high-grade alloys is kept below 0.35%.

The microstructure of tin-base babbitt is illustrated in Fig. 121. Two

hard and wear-resisting compounds are present,  $\text{SbSn}$  cubes and  $\text{CuSn}$  needles, embedded in a plastic tin-rich matrix (actually a fine eutectic). Proper distribution of these constituents is obtained by control of the casting temperature and the use of preheated molds.

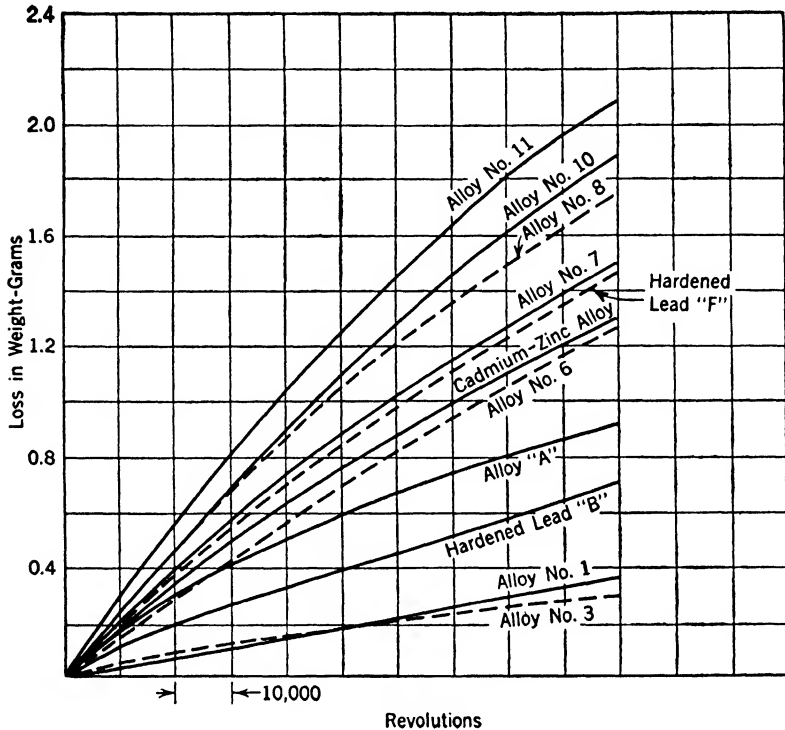
In spite of their relatively high cost, the tin-base babbitts are used for a wide variety of applications, particularly where high speeds and moderately high bearing pressures are involved. The operating temperature can be slightly higher than for lead-base alloys, and the tin-base alloys have better resistance to deformation under impact.

Because of their low cost, lead-base bearing alloys are used most extensively and they are especially suitable for lightly loaded bearings. There are two main groups of lead-base alloys in use: for the first group, antimony, or more often antimony and tin, are the principal alloying elements; the second group includes alloys hardened with calcium and related elements.

Simple, binary lead-antimony alloys are the cheapest but are very inferior in wear resistance. The 90-10 and 85-15 alloys are sometimes used for slow-moving machinery with light bearing pressures. The eutectic in the lead-antimony system occurs at 12% Sb and alloys containing over this amount of antimony have a microstructure consisting of some primary antimony crystals in a matrix of the lead-antimony eutectic.

Tin additions to the lead-antimony alloys have a beneficial effect, particularly with respect to wear resistance and toughness. Even small additions, on the order of 2 to 5%, are very much worth while and it is doubtful if the straight binary lead-antimony alloys are economical to use in any application. Most of the alloys used fall in the following composition range: lead 63 (min), antimony 10-15, tin 2-20. The microstructure of these alloys is similar to that of the binary lead-antimony alloys but an additional microconstituent is present, the compound  $\text{SbSn}$  in the form of cubes. Both the primary antimony and the  $\text{SbSn}$  crystals are lower in specific gravity than lead, and since these freeze first during the solidification of the alloy there is a tendency toward segregation of these constituents in the upper portion of the casting. Proper control of casting temperature and mold temperature are required in order to obtain the correct particle size and distribution of these constituents. Small amounts of copper (1-2%) are added to alloys containing near the maximum amount of tin for the purpose of limiting the degree of segregation. Arsenic has a similar effect, but tends to cause brittleness. Wear resistance can be improved by the addition of about 1% nickel. A commercial alloy of this type known as "Thermit" metal contains about 15 Sb, 1 Cu, 6 Sn, 1 Ni, 1 Cd, and 0.5 As.

The relative wear resistance of several tin-, lead-, and cadmium-base bearing metals was determined by the National Bureau of Standards in cooperation with the War Department, and service tests in the U. S. Army Class B trucks indicated results similar to those obtained with a



Courtesy National Bureau of Standards

FIG. 122. Relation between wear and revolutions for white-metal bearing alloys tested on Amsler wear-testing machine. Alloys tested against S.A.E. 1045 steel heat-treated to Brinell hardness of 240.

“ universal Amsler wear-testing machine ” modified for rolling resistance at low loads with kerosene as a medium. Table 34 gives the chemical analysis of the metals and Fig. 122 shows their relative wear resistance.

### Lead-Calcium Bearing Alloys

This type of alloy is used extensively in Germany especially for railroad service, but is not very popular in this country. The German alloy known as *Bahnmetall* contains about 98.6% Pb, 0.7% Cu, 0.6% Na, 0.04% Li, and 0-0.02% Al. The best known American alloy of this type, Satco, contains a fraction of one per cent calcium, about 1% tin,

and a small amount of magnesium as the principal hardening elements. Other alloying elements which have been used to a lesser extent are Ba, Sr, K, Cu, and Hg. The mechanical properties of these alloys are very

TABLE 34. RESULTS OF CHEMICAL ANALYSES OF WHITE-METAL BEARING ALLOYS

Alloy Designation	Lead %	Tin %	Anti-mony %	Copper %	Cadmium %	Zinc %	Other Constituents %
No. 1		90.9	4.6	4.5			
No. 3		83.8	8.1	8.1			
No. 6	62.3	20.8	15.5	1.4			
No. 7	78.8	8.4	12.8				
No. 8	79.7	5.0	15.3				
No. 10	87.0	1.2	11.8				
No. 11	88.1		11.9				
Hardened lead F*	96.93	0.18		0.1			Hg 0.33, Ba 1.70, Ca 0.70
Hardened lead B†	98.0						Na 0.65, K 0.3, Ca 0.75, Li 0.4
Cadmium-zinc‡					82.0	18	
A**	80.6	3.8	13.5	1.0	0.2		Ni 0.2, As 0.6

\* Analysis by the National Lead Co.

† Nominal composition as given by the Maywood Chemical Co.

‡ Nominal composition.

\*\* Analysis made by J. A. Scherrer, Bureau of Standards.

good, but their poor corrosion resistance, difficulty in casting and remelting, and relatively high cost as compared with other lead-base alloys have limited their usefulness.

### Cadmium-Base Bearing Metals

Cadmium-base bearing metals have been used to some extent to replace tin-base babbitts. They can be used at higher bearing pressures and better wear resistance is also claimed. High cost and susceptibility to corrosion by certain types of lubricating oils containing fatty acids are their chief disadvantages. The hardening elements are Cu 0-3%, Ag 0-3%, Ni 0-3%, and small amounts of indium and magnesium have also been added. The two types most commonly used in this country are the cadmium-copper-silver (0.7-2.9 Ag) and the cadmium-nickel (1-3 Ni). The cadmium-nickel alloys have very good bonding characteristics with steel.

## BEARING BRONZES

### Copper-Base Bearing Alloys

A wide variety of copper-base alloys has at times been specified for service in bearings and bushings, but the leaded tin bronzes have been found the most useful. Compared with the white-metal bearing alloys, the bearing bronzes have a much higher load-carrying capacity and re-

sistance to pounding, but have much less plasticity. They also tend to wear a soft steel shaft and are therefore recommended only for use with hardened steel journals. The compositions of the most widely used alloys fall in the range Sn 5-10, Pb 5-30, Zn 0-3, Cu 63-85. Tin bronzes without lead, of the gun metal, gear bronze, or phosphor-bronze types, have also been used for low speed bearings but have poorer resistance to wear and lower plasticity.

The most widely used bearing bronze is the 80-10-10 composition which has good resistance to wear and to pounding and fair plasticity. It can be used for most applications where bearing bronze is required. This alloy may also contain up to about 3% zinc. High zinc alloys (brasses) have inferior resistance to wear and are not used for bearing purposes. Phosphor-bronzes are not good bearing metals but the term phosphor-bronze is used occasionally to mean a leaded tin-bronze.

Both tin and lead tend to improve wear resistance and the effect is greater when both elements are present. Antifriction properties are improved by lead additions but lowered by tin, particularly if the tin content exceeds approximately 10%. Resistance to pounding is increased by tin, especially in the range above about 6% tin, and is affected only slightly by the lead content. Plasticity is improved by high lead content and two common high-lead alloys are the 78-7-15 and the 70-5-25 compositions. The high-lead alloys can be used at higher bearing speeds. Some difficulty is encountered in obtaining uniform distribution of lead in alloys containing over approximately 15% lead, and chill casting or the addition of nickel or other element are sometimes found necessary. Lead is almost insoluble in bronze in the solid state and should be uniformly distributed in the form of small globules of free lead. Bearing bronzes are always used in the cast condition and have a dendritic or cored structure which seems to be beneficial for this type of service. Alloys containing over approximately 7% tin also contain some of the hard delta phase.

Copper-lead or "tin-free leaded bronze" is used in place of tin- or cadmium-base bearing alloys when high mechanical properties at elevated temperatures are required, as in connecting rod bearings in aircraft and automotive truck engines. They have also been used to some extent in rolling mill and railroad service. The properties of these alloys may be considered as intermediate between those of bearing bronzes and white-metal alloys. Since the lead content is always high, usually 25 to 40%, these alloys have more plasticity than the bronzes. The problem of obtaining uniform lead distribution in their manufacture is even more severe than in high lead-tin bronzes. Lead segregation can be reduced by small additions of tin, nickel, silicon, zirconium



sulfide, etc., and chill casting is also beneficial. These alloys are often used in the form of thin coatings on a steel shell. Some trouble has been encountered with corrosion by lubricating oils containing fatty acids.

### **Graphite-Bronze and Oil-Impregnated Bearings**

Bearings which are likely to be operated with irregular or interrupted lubrication are usually made of an alloy containing graphite or some other lubricant impregnated in a porous alloy or of bearing bronze with a graphite paste lubricant inserted in slots or holes in the bearing surface. The most common bearing material of this type, graphite-bronze, is made by powder metallurgy. Powdered copper and tin or powdered tin-bronze are mixed with graphite, compressed into the form of a bushing or bearing under high pressure and finally sintered to consolidate the metal particles. The porosity of the product can be controlled accurately and some of these alloys are capable of absorbing substantial amounts of oil. The strength of these alloys is usually low, particularly alloys of high porosity or high graphite content, so they need to be supported by a strong backing material.

Many other materials have been used for special types of bearings, including aluminum bronze, brass, cast iron, cast aluminum alloys, zinc-base die castings, and some nonmetallic substances such as wood, plastics, impregnated fabrics, hard rubber, and *lignum-vitae*.

## CHAPTER XI

### CORROSION

The highly important subject of the corrosion of metals is considered briefly here with special emphasis on the type of corrosion known as electrolytic or galvanic. The types of corrosion commonly encountered may be classified as: direct chemical attack or solution; pitting corrosion; and galvanic or electrolytic corrosion involving the principle of the electric battery or electrolytic cell.

**Electrolytic Corrosion.** When two dissimilar metals or alloys, in electrical contact with each other, are exposed to an electrolyte, one of the metals is corroded much more rapidly than if there were no contact between them. The electrolyte may be a very weak one, even ordinary tap water. The two metals become the electrodes of a small battery and an electric current actually flows through the electrical contact while one of the metals, the anodic electrode, goes rapidly into solution.

The driving force in this type of corrosion is the voltage developed by the electrolytic cell. Two metals or alloys listed far apart in Table 35 develop a high voltage and corrosion is very rapid when they are present together in an electrolytic cell. Of the two, the metal listed nearer the top of the table is the one which is corroded whereas the other, sometimes called "more noble," is actually protected against corrosion by the cell. The table is McKay and Worthington's modification of the well-known "electrochemical series" built upon actual experience with corrosion problems.

This type of corrosion takes place only when the electrical circuit is complete through the metals and solution. Distilled water and air are such poor conductors that the metal ions of the anode do not readily go in solution but when impure water and various salts are added galvanic corrosion may take place rapidly as in sea water, strong acids and alkalis. Joints well insulated keep an open circuit and frequently inhibit galvanic action or stop it completely.

Frequently an interference to the passage of current results from formation of insoluble films (*polarization*). Galvanic corrosion is usually closest to contact points of dissimilar metals except in electrolytes of highest conduction. Small anodes are rapidly corroded but large anodic areas give increased protection.

TABLE 35. THE GALVANIC SERIES OF METALS\*

CORRODED END (ANODIC)	
Magnesium	This series is based upon actual experience with corrosion and laboratory measurement. Metals grouped together have no strong tendency to produce galvanic corrosion on each other; connecting two metals distant on the list from each other tends to corrode the one higher in the list. Voltage figures are not given because these vary with every new corrosive condition. Relative positions of metals change in many cases but it is unusual for changes to occur across the spaces left blank. The chromium-iron and chromium-nickel-iron change positions as indicated depending on oxidizing conditions, acidity and chlorine in solution. The series as it stands is correct for many common dilute water solutions such as sea water, weak acids and alkalies.
Aluminum	
Duralumin	
Zinc	
Cadmium	
Iron	
Chromium iron (active)	
Chromium-nickel-iron (active)	
Soft solder	
Tin	
Lead	
Nickel	
Brasses	
Bronzes	
Nickel-copper alloy	
Copper	
Chromium (passive)	
Chromium-nickel-iron (passive)	
Silver solder	
Silver	
Gold	
Platinum	

\* McKay and Worthington, "Corrosion Resistance of Metals and Alloys," A.C.S. Monograph 71, 1936.

There are actually four possible types of electrolytic corrosion caused by:

1. Two different metals in the same electrolyte.
2. Two different metals in different electrolytes.
3. One metal in two different concentrations of the same electrolyte.
4. One metal in different electrolytes.

**Pitting.** Pitting, as the name implies, usually results from localized corrosion and may be from two causes: (1) when the corrosion product or film covers and protects most of the metal, thereby forming holes or pits where the film is broken and there is no protection, and (2) when metals have inclusions or are not too homogeneous structurally they may corrode galvanically or directly. Inclusions may hold moisture and

other solutions different from the corroding medium and pitting may also occur from different concentrations of the solution (concentration cell). This latter case is considered to be most destructive and most common in the formation of pits.

**Nonhomogeneity vs. Corrosion.** When metals are homogeneous there is less chance for corrosion, as evidenced by high-purity iron, zinc, aluminum, and other high-purity metals when there is present only one solid phase. Segregation in metals and concentration of inclusions, therefore, aid in electrolytic corrosion. The dispersion of carbides in troostite aids in lowering its corrosion resistance when compared to other microconstituents of steel, according to Speller.

The susceptibility to intergranular corrosion of 18-8 stainless steels (in all commercial carbon contents) after being heated above 850°F for long periods of time is probably caused by precipitation of a chromium carbide phase at the grain boundaries, and lowering the chromium content of the austenite in these zones. Likewise, the intergranular corrosion of duralumin-type alloys is caused by some grain boundary precipitation of the compounds, mostly  $\text{CuAl}_2$ .

The intergranular corrosion of a lead-shot alloy containing only 1% magnesium proceeds because there is a eutectic of a lead-magnesium solid solution and  $\text{PbMg}_2$  which is surrounding the  $\alpha$  phase.

In the above cases it should be noted that lack of homogeneity, especially when there is a high difference in potential, is the cause of electrolytic corrosion.

**Effect of Stress on Corrosion.** Cold-worked metals are anodic to those same metals in the annealed state. The *season cracking* of  $\alpha$ -brass, 70-30 cartridge cases, may result when there is too much cold working in the forming operations, causing high internal stress. This intergranular corrosion may take place in storage and readily results in brasses from 20 to 40% zinc after exposure to ammonia gas. Cold-worked Monel has also been known to crack when handling mercury and some of its salt solutions, whereas annealed Monel is satisfactory.

A well screen made of cold-drawn Everdur bronze was found to have disintegrated by intercrystalline corrosion when exposed to mercury which had escaped from a pump. Its structure is shown in Fig. 123. Generally, the higher the residual stress the greater is the tendency to crack. The austenitic stainless steels have a strong tendency to crack with high stress and this susceptibility can be checked by boiling specimens in a 10%  $\text{H}_2\text{SO}_4$ -10%  $\text{CuSO}_4$  solution.

The embrittlement of cold-worked boiler steel of 0.18-0.24% C, which has frequently been termed "caustic embrittlement" but has since been found to be intergranular corrosion not caused by high-

purity caustic soda, is caused by small amounts of many different salts in boiler waters. Here, again, a thorough stress-relieving anneal removes the embrittlement.

Welded mud drums for high pressure steam are now thoroughly annealed in large furnaces and have given no trouble from embrittle-



FIG. 123. Intercrystalline corrosion cracks in Everdur bronze. Cu 96%, Si 3%, Mn 1%. Cold drawn and exposed to mercury at bottom of well 100 ft deep.  $\times 100$ .

ment. In this modern construction there are no cold-worked rivets, holes, or girth straps which may concentrate harmful salts and cause electrolytic corrosion due to a concentration cell.

#### SOLID SOLUTIONS FOR CORROSION RESISTANCE

In making inexpensive alloys for high resistance to corrosion in certain media, it is desirable to have solid solutions where the solute atoms are either more noble or else behave as such by a film action. Stainless steel, for example, has about 18% of chromium atoms by weight which are in sufficient concentration to prevent the dissolving away of the iron atoms by radicals having large atomic volumes such as  $\text{NO}_3$  and  $\text{SO}_4$ .

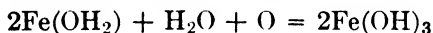
It is recognized that chromium atoms give the stainless irons and steels their relatively high corrosion resistance ("passivity") by the forma-

tion of an oxide film. They are far more resistant with oxidizing conditions than with reducing conditions. Anodized films on aluminum-base alloys, sodium dichromate films on magnesium-base alloys, and oxide films of copper, brass, and bronze aid materially in protecting these metals. Alpha brasses frequently corrode in localized areas by de-zincification when exposed to salt water having good conductivity with slight acidity in the presence of oxygen. This occurs only when the protective film is broken.

Tammann<sup>1</sup> found that when gold alloys containing copper or silver from  $\frac{9}{10}$  (100 at.%) down to  $\frac{1}{10}$  (50 at.%) were parted in hot nitric acid there was no appreciable solution of the copper or silver. Alloys of  $\frac{5}{10}$  copper or silver and above were readily parted and only the gold remained. This example shows the importance of a sufficient number of the more noble atoms in protecting a baser lattice for corrosion resistance for a definite set of conditions.

#### CORROSION OF IRON AND STEEL

The rusting of iron and steel is commonly caused by the combined action of moisture and oxygen. The reddish iron rust does not offer much film protection against further corrosion. Iron dissolves to a very limited extent in distilled water to form a saturated solution of ferrous ions if the water is free of  $O_2$  and  $CO_2$  and in a stoppered bottle. If the stopper is removed oxidation begins



and ferric hydroxide forms as a reddish brown precipitate which eventually forms a hydrous ferric oxide,  $Fe_2O_3$ , or rust. Both water and oxygen are always required for the formation of rust.

**Protective Coatings.** Metallic coatings are usually applied to iron and steel by hot dipping, electroplating, cementation, or metal spraying. One of the most satisfactory and inexpensive coatings for atmospheric exposure is zinc applied by hot-dip galvanizing. Zinc is anodic to iron, so the coating need not be perfect, and the protection offered is almost directly proportional to the weight of coating applied. A coating of tin, which is cathodic to iron, must be relatively free of porosity to give good protection. Tin plate, used extensively in the canning industry, has been produced mainly by the hot-dipping process, but recently the electroplating process has been improved to give a thin coating of low porosity. Other coatings commonly applied by electroplating include nickel, chromium, zinc, cadmium, copper, silver, gold, and rhodium.

<sup>1</sup> Tammann, *Lehrbuch der Metallkunde*, 4th ed., Leopold Voss, Leipzig, 1932.

Other metallic coatings such as sherardizing (Zn), calorizing (Al), chromizing, siliconizing, and metal spraying are more expensive than hot-dipped coats but offer advantages in certain cases.

There are many nonmetallic film coatings such as parkerizing, bonderizing, blueing, blacking, etc., offering some protection for indoor service. Paints, lacquers, and greases offer fair protection, but for general outdoor corrosion resistance none of them compares with hot-dip galvanizing.





## APPENDIX

### BINARY CONSTITUTION DIAGRAMS \*

PLATES						
I	II	III	IV	V	VI	VII
Ag-Al	Al-Cr	Au-Pb	C-Mn	Cu-Fe	Fe-O	Mg-Zn
Ag-Au	Al-Cu	Au-Pd	C-Ni	Cu-Mg	Fe-B	Mn-Ni
Ag-Cd	Al-Cu	Au-Pt	C-W	Cu-Ni	Fe-S	Mo-Ni
Ag-Cu	Al-Fe	Au-Sn	Ca-Pb	Cu-O	Fe-Si	Mo-W
Ag-Hg	Al-Mg	Au-Zn	Cd-Cu	Cu-B	Fe-Sn	Na-Pb
Ag-Mg	Al-Mn	B-Fe	Cd-Hg	Cu-Pb	Fe-Ti	Ni-P
Ag-Ni	Al-Ni	Be-Cu	Cd-Pb	Cu-Pd	Fe-V	Ni-Pb
Ag-Pb	Al-Pb	Be-Fe	Cd-Sn	Cu-Pt	Fe-W	Ni-Pd
Ag-Pd	Al-Sb	Be-Ni	Cd-Zn	Cu-S	Fe-Zn	Ni-Pt
Ag-Pt	Al-Si	Bi-Cd	Co-Cr	Cu-Si	Fe-Zr	Ni-Si
Ag-Si	Al-Sn	Bi-Pb	Co-Cu	Cu-Sn	Hg-Na	Ni-Sn
Ag-Sn	Al-Zn	Bi-Sb	Co-Fe	Cu-Zn	Hg-Pb	Ni-W
Ag-Zn	As-Pb	Bi-Sn	Co-Ni	Fe-Mn	Hg-Sn	Ni-Zn
Al-Bi	As-Sb	C-Co	Co-W	Fe-Mo	Hg-Zn	Pb-Sb
Al-Be	Au-Cu	C-Cr	Cr-Cu	Fe-N	Li-Pb	Pb-Sn
Al-Cd	Au-Hg	C-Fe	Cr-Fe	Fe-Ni	Mg-Mn	Pb-Zn
Al-Co	Au-Ni		Cr-Mo		Mg-Ni	Pt-Rh
			Cr-Ni		Mg-Pb	Sb-Sn
					Mg-Si	Sb-Zn
					Mg-Sn	Sn-Zn

\* For more complete information on these and other binary systems consult the *A.S.M. Metals Handbook* or Hansen's "Der Aufbau der Zweislofllegierungen," published by Julius Springer, 1936.

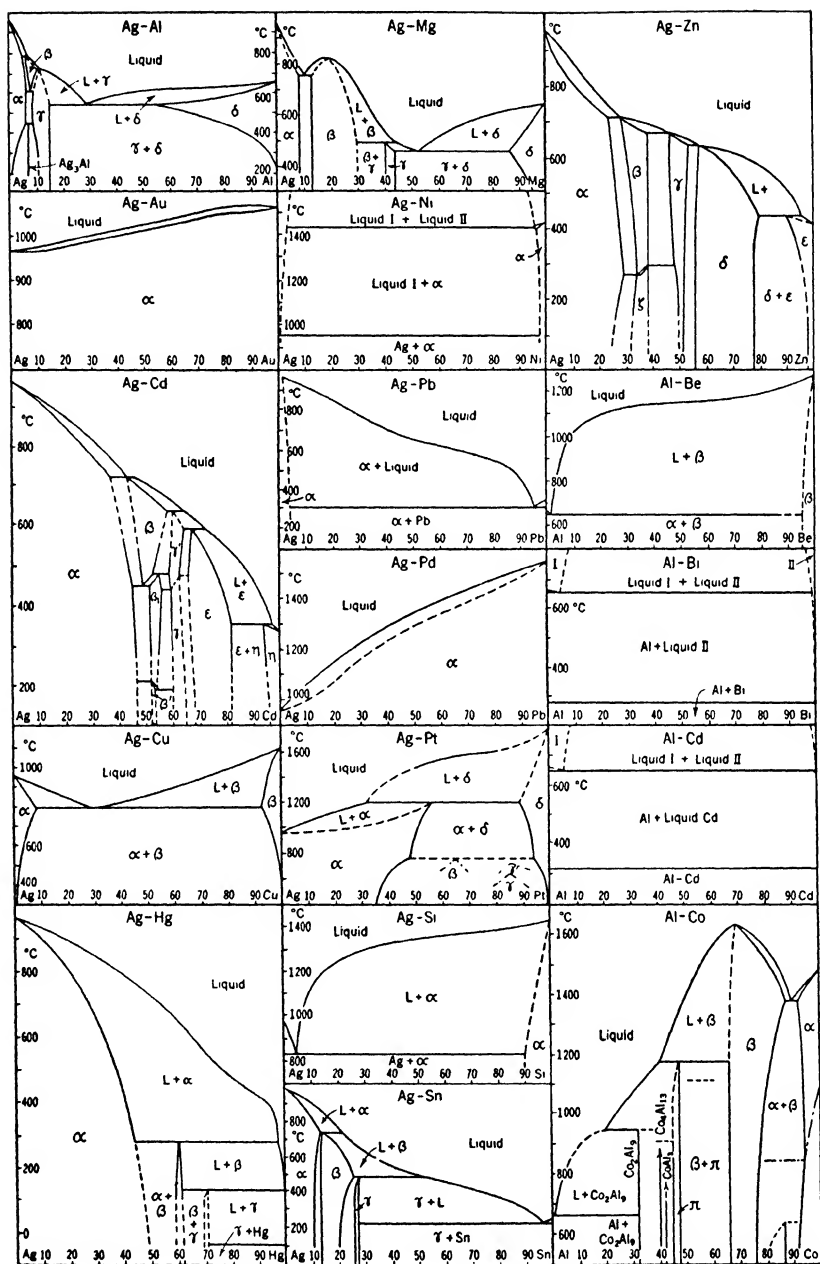


PLATE I. Ag-Al to Al-Co.

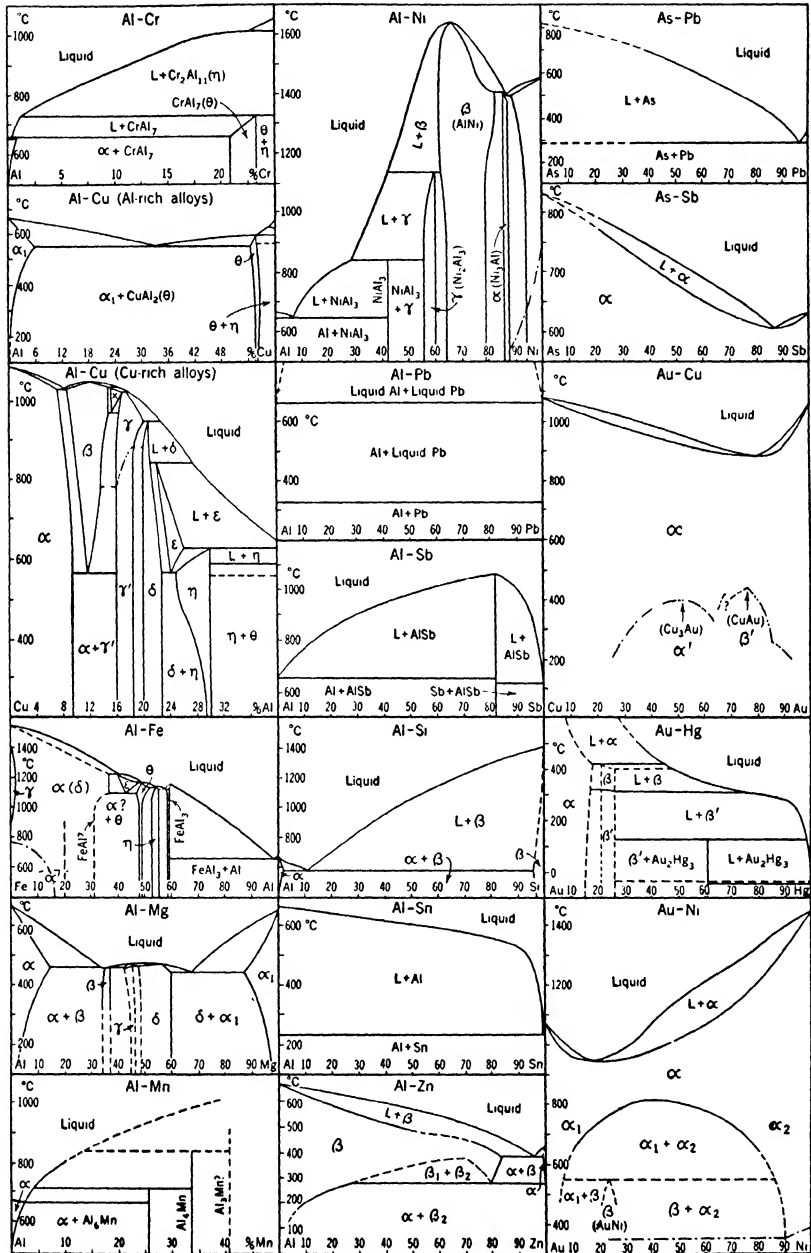


PLATE II. Al-Cr to Au-Ni.

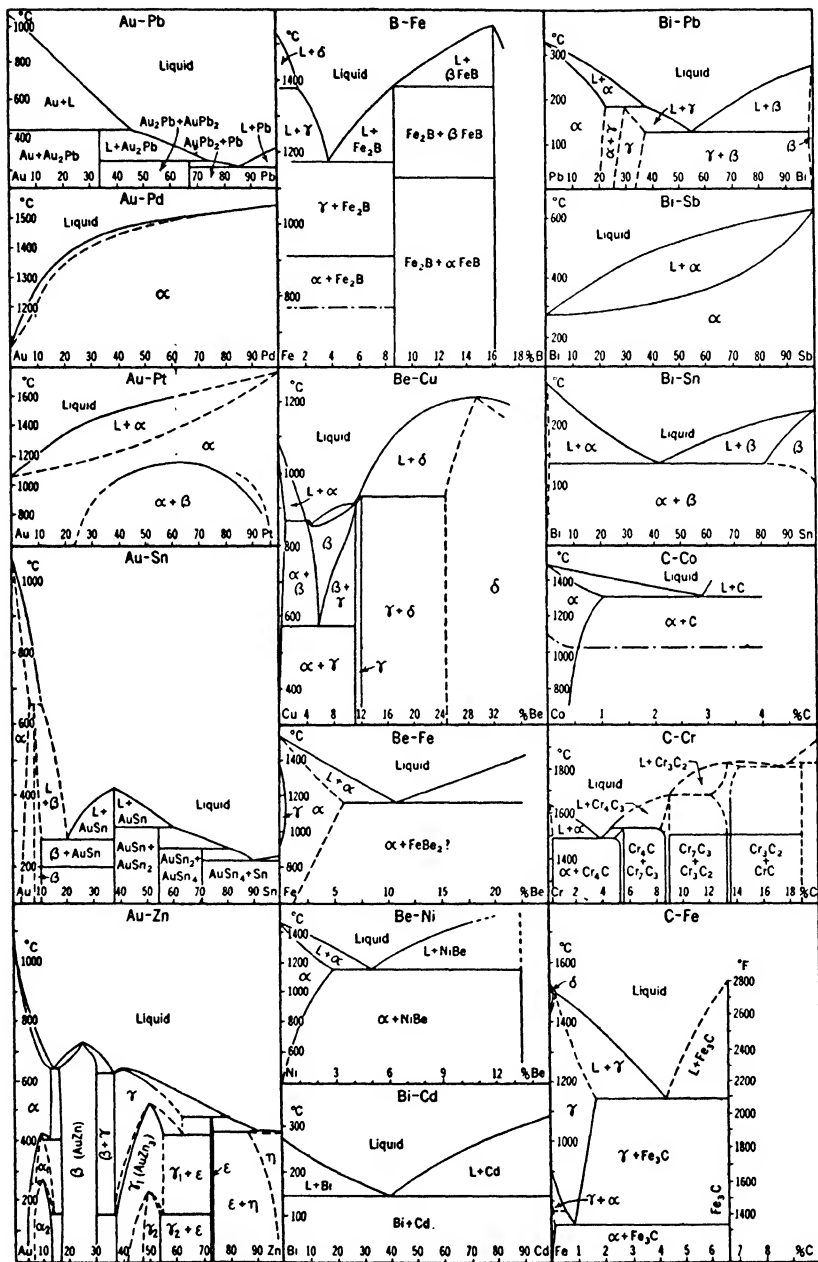


PLATE III. Au-Pb to C-Fe.

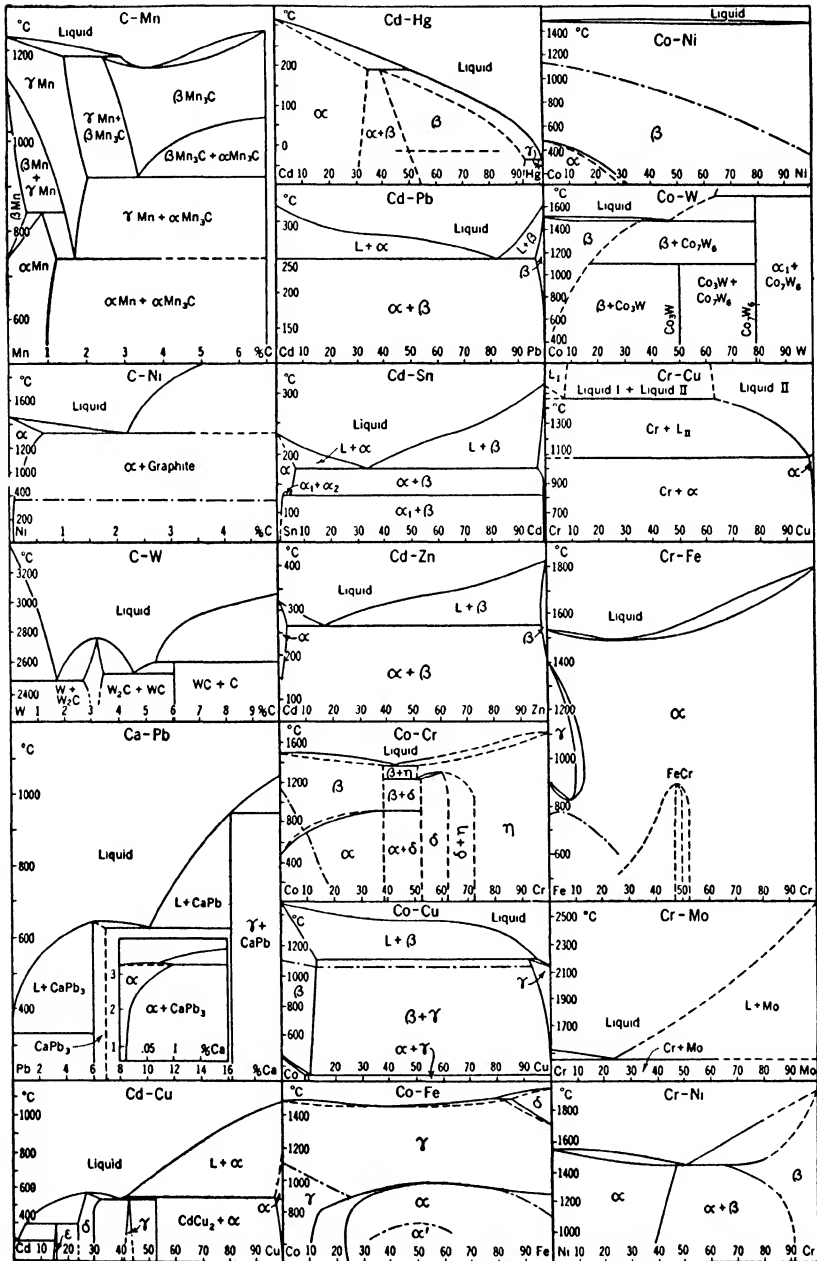


PLATE IV. C-Mn to Cr-Ni.

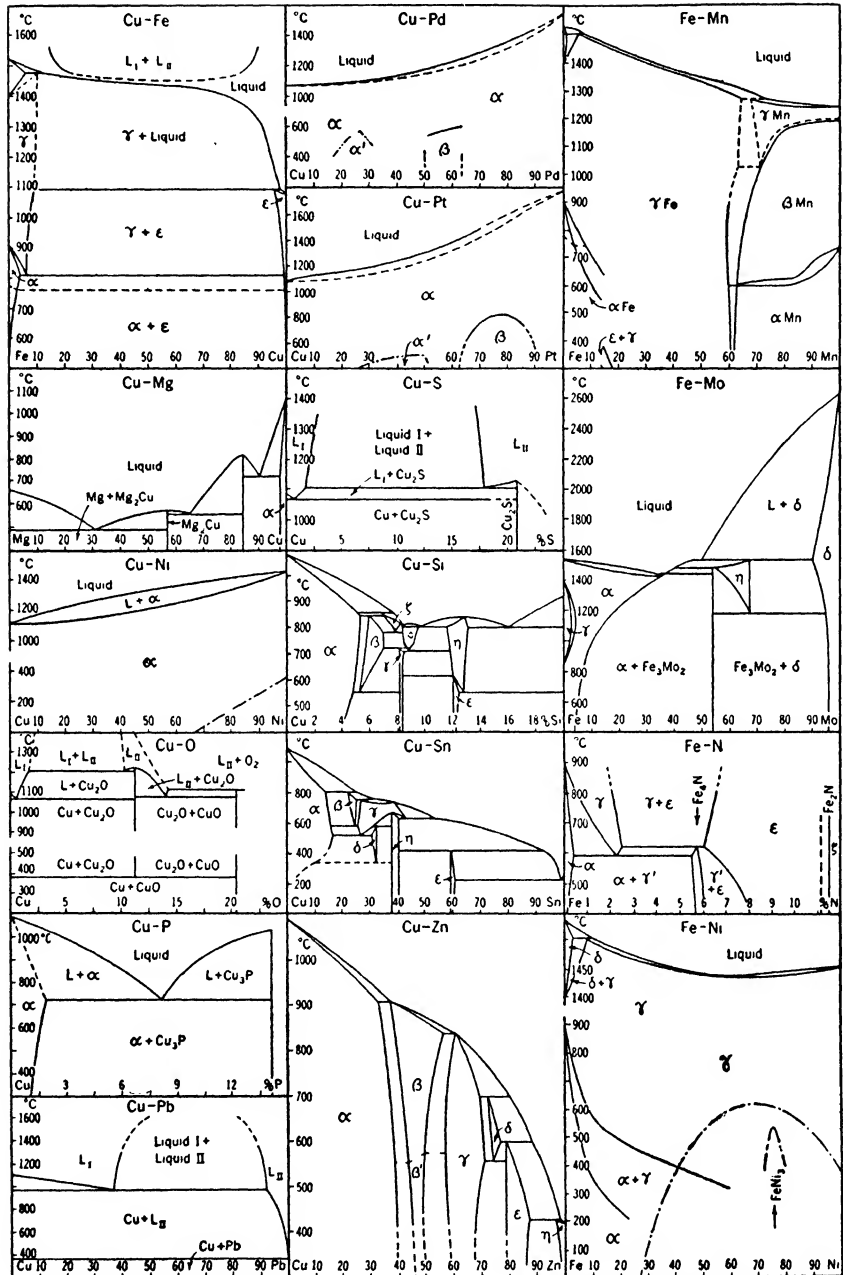


PLATE V. Cu-Fe to Fe-Ni.

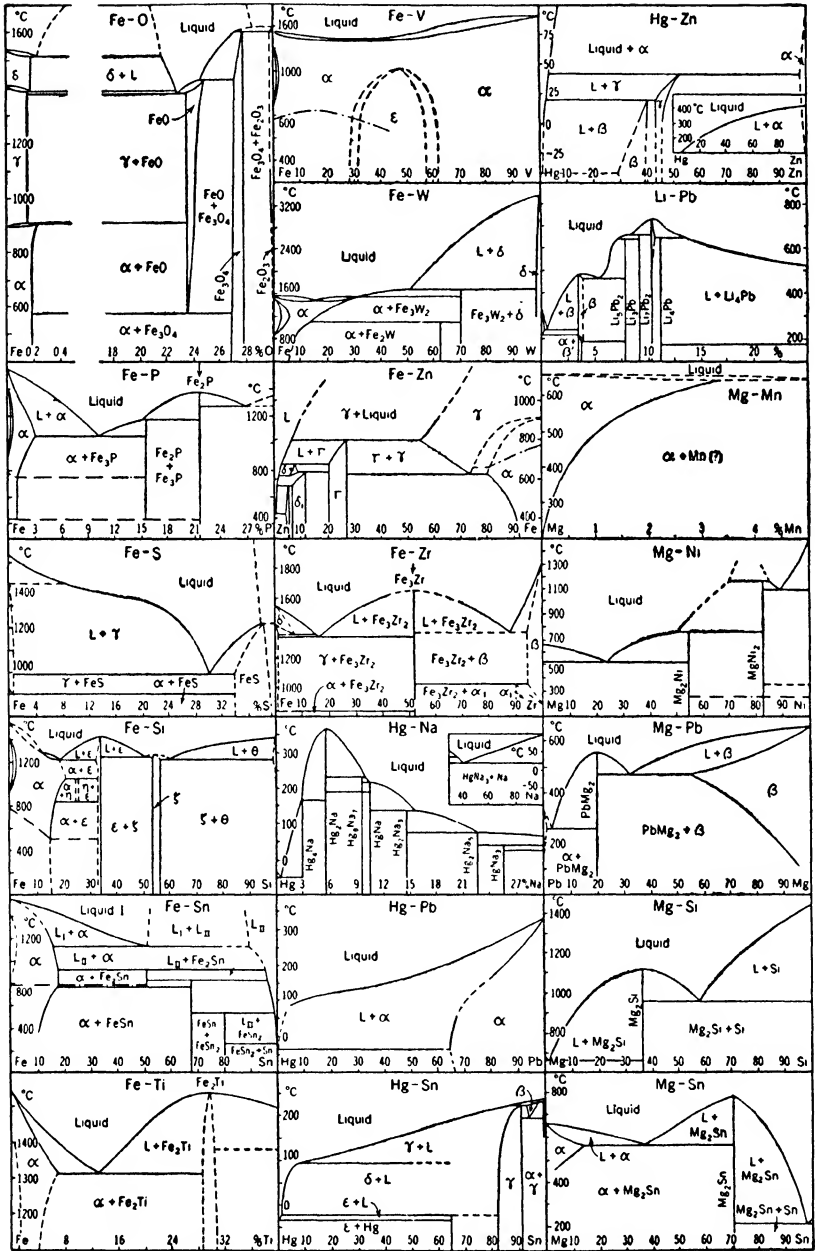


PLATE VI. Fe-O to Mg-Sn.

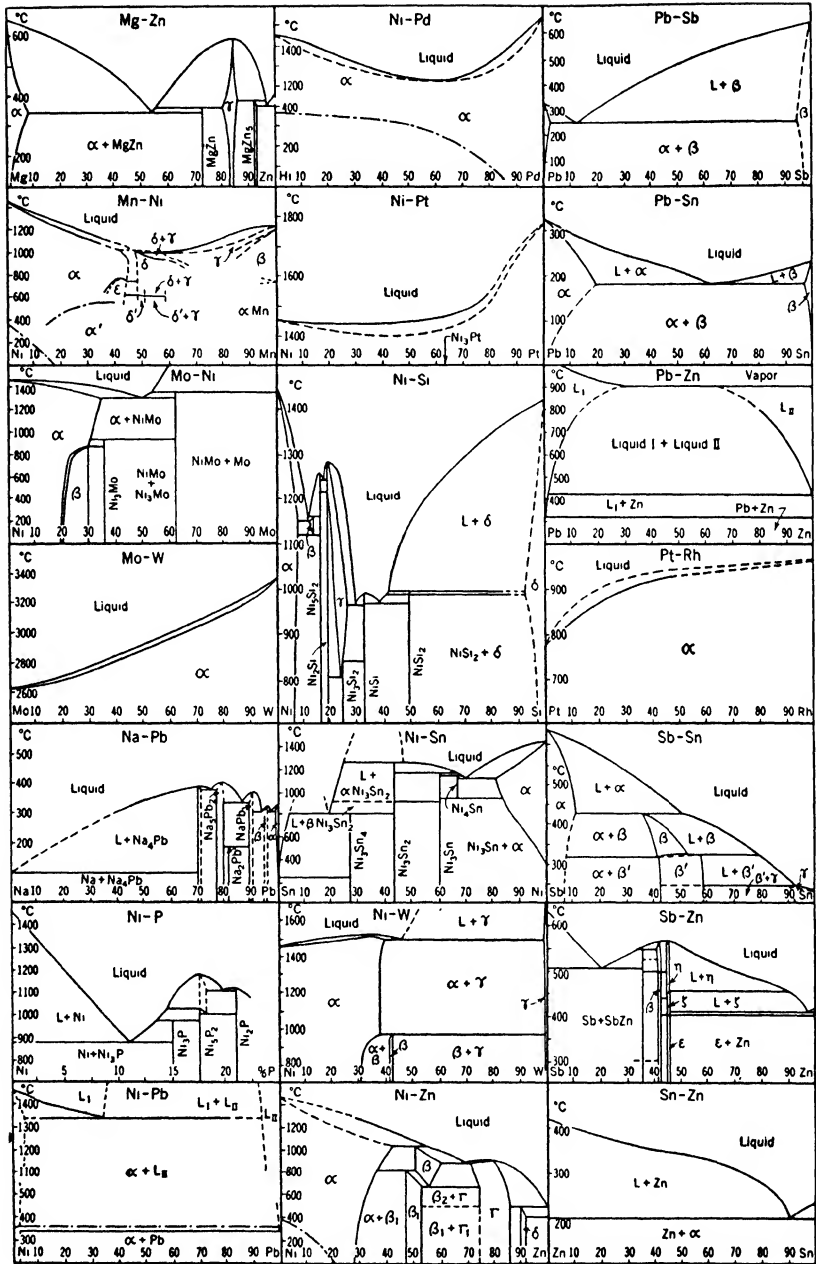


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