PHYSICAL CONSTANTS OF METALS.

Metal.	Symbol.	Atomic Weight.	Atomic Volume.	Specific Gravity.	Specific Heat.	Melting Point. °C.	Coefficient of Linear Expansion.	Thermal Conductivity in cal. cm. secs.	Electrical Conductivity. Ag.=100.
Aluminium . .	Al	27·1	10·6	2·56	0·218	657	0·0000231	0·502	57·9
Antimony . .	Sb	120·2	17·9	6·71	0·051	630	0·0000105	0·042	4·2
Arsenic . .	As	75·0	13·2	5·67	0·081	450	0·0000055	..	..
Barium . .	Ba	137·4	36·3	3·78	0·047	850	..	..	..
Bismuth . .	Bi	208·0	21·2	9·80	0·031	266	0·0000162	0·019	11·3
Cadmium . .	Cd	112·4	13·2	8·60	0·056	322	0·0000306	0·219	14·7
Cæsium . .	Cs	132·9	71·1	1·87	0·048	26	..	..	..
Calcium . .	Ca	40·1	25·5	1·57	0·170	780	..	..	..
Cerium . .	Ce	140·2	21·0	6·68	0·045	623	..	..	..
Chromium . .	Cr	52·1	7·7	6·80	0·120	1482	..	..	..
Cobalt . .	Co	59·0	6·9	8·50	0·103	1464	0·0000123	..	..
Columbium . .	Cb	94·0	7·4	12·70	0·071	..	..	..	..
Copper . .	Cu	63·6	7·1	8·93	0·093	1084	0·0000167	0·924	94·2
Gallium . .	Ga	70·0	11·8	5·90	0·079	30	..	..	..
Glucinum . .	Gl	9·1	4·7	1·93	0·621	..	..	..	..
Gold . .	Au	197·2	10·2	19·32	0·031	1065	0·0000144	0·700	66·7
Indium . .	In	115·0	15·5	7·42	0·057	155	0·0000417	..	..
Iridium . .	Ir	193·0	8·6	22·42	0·033	1950	0·0000070	..	..
Iron . .	Fe	55·9	7·1	7·86	0·110	1505	0·0000121	0·147	16·4
Lanthanum . .	La	138·9	22·4	6·20	0·045	810	..	..	..
Lead . .	Pb	206·9	18·2	11·37	0·031	327	0·0000292	0·084	7·3
Lithium . .	Li	7·0	13·0	0·54	0·941	186	..	..	..
Magnesium . .	Mg	24·4	14·0	1·74	0·250	633	0·0000269	0·343	33·7
Manganese . .	Mn	55·0	6·9	8·00	0·120	1207	..	..	..
Mercury . .	Hg	200·0	14·7	13·59	0·032	−39	0·0000610	0·020	1·6
Molybdenum . .	Mo	96·0	11·2	8·60	0·072	2500	..	..	..
Nickel . .	Ni	58·7	6·7	8·80	0·108	1451	0·0000127	0·141	11·9
Osmium . .	Os	191·0	8·5	22·48	0·031	2500	0·0000065	..	..
Palladium . .	Pd	106·5	9·3	11·50	0·059	1535	0·0000117	0·168	14·5
Platinum . .	Pt	194·8	9·1	21·50	0·032	1710	0·0000089	0·166	13·4
Potassium . .	K	39·1	45·5	0·86	0·170	62	0·0000841	..	..
Rhodium . .	Rh	103·0	8·5	12·10	0·058	1660	0·0000085	..	..
Rubidium . .	Rb	85·5	55·9	1·53	0·077	38	..	..	..
Ruthenium . .	Ru	101·7	8·3	12·26	0·061	1800	0·0000096	..	..
Silver . .	Ag	107·9	10·2	10·53	0·056	961	0·0000192	0·993	100·0
Sodium . .	Na	23·0	23·8	0·97	0·290	95	0·0000710	0·365	..
Strontium . .	Sr	87·6	34·5	2·54	..	800	..	..	..
Tantalum . .	Ta	181·0	16·7	10·80	0·036	2910	0·0000079	..	..
Tellurium . .	Te	127·6	20·4	6·25	0·049	440	0·0000167	..	..
Thallium . .	Tl	204·1	17·2	11·85	0·033	303	0·0000302	..	..
Thorium . .	Th	232·5	20·9	11·10	0·028	..	..	..	..
Tin . .	Sn	119·0	16·3	7·29	0·055	232	0·0000223	0·155	11·3
Titanium . .	Ti	48·1	9·9	4·87	0·130	..	..	..	..
Tungsten . .	W	184·0	9·6	19·10	0·034	3100	..	..	..
Uranium . .	U	238·5	12·8	18·70	0·028	..	..	..	..
Vanadium . .	V	51·2	9·3	5·50	0·125	1680	..	..	..
Yttrium . .	Yt	89·0	23·4	3·80	..	..	..	..	..
Zinc . .	Zn	65·4	9·1	7·15	0·094	419	0·0000291	0·269	25·6
Zirconium . .	Zr	90·6	21·8	4·15	0·066	1500	..	..	..

ALLOYS.

CHAPTER I.

INTRODUCTION

THERE has been some difference of opinion as to the origin of the word alloy, but according to Roberts-Austen it is derived from the Latin word *alligo* (*ad ligo*), "to bind to," and refers to the union or binding together of the metals constituting the alloy.

From the earliest times alloys were produced accidentally by the simultaneous reduction of mixtures of metallic ores, but there is little doubt that the first metals to be intentionally alloyed were the precious metals, and more especially gold, and it is equally certain that these attempts to alloy the precious metal were of a fraudulent character, and carried out with the object of producing a metal which might be substituted for the pure metal. How long these fraudulent but successful practices were carried on without any adequate means of detection it is impossible to say, but they received their first check when Archimedes conceived the brilliant idea that all bodies when immersed in water must displace their own volume of water irrespective of their weights, and that their weights in water would be less than their weights in air by the weight of the water thus displaced. From this he argued that if gold were alloyed with another metal its presence could be detected by determining the displacement in water, and the story of his detection of the addition of an alloy to the gold used in making the king's crown is too well known to need repetition.

The alloying of gold and silver plays a prominent part throughout the entire history of the metals, and this probably accounts

for the fact that the word alloy, as ordinarily used in the English language, signifies a depreciation or lowering of value. Thus we frequently read of "unalloyed pleasure" and "unalloyed happiness," and the definition of the word in some dictionaries is "to add base metal." To the metallurgist, however, the word conveys a very different meaning, and the object he aims at in alloying metals is to produce a new metal whose properties shall be superior to those of the metals of which it is composed.

Probably the most satisfactory definition of an alloy is that which describes it as "a mixture of two or more metallic substances which, after melting, does not separate into two distinct layers." But commercial enterprise refuses to be bound by definitions, and so we find commercial alloys which on cooling *do* separate into layers, if special precautions are not taken to prevent them doing so ; and as the object of this volume is to deal with the commercial alloys we must perforce find a definition which will include them. For this purpose, then, we will define an alloy as "a coherent metallic mass produced by the intimate mixture, whether by fusion or otherwise, of two or more metals or metallic substances." By the addition of the words "metallic substances" the definition may be made to include those alloys of the type of phosphor-copper which are really alloys of a metal with a definite compound (such as phosphide of copper) whose appearance and properties may be regarded as metallic.

The importance of the study of metallic alloys is evident when we consider the extent to which they are employed and the comparatively limited uses of metals in the pure state. Iron, for example, in the pure state has a tensile strength of only 16 tons per sq. in., and even the use of wrought iron, which is the purest commercial form of iron, is comparatively insignificant compared with the use of steel, which must be regarded as an iron alloy. It is true that copper in a pure state is employed for a number of purposes, but the amount of pure copper used is only a fraction of the copper used in the form of bronze, brass, German silver, and a number of other copper alloys. Gold and silver are practically never employed in an unalloyed condition. Lead, zinc, tin, nickel, and aluminium are all used to a certain extent in the pure state, but their alloys account for a very large proportion of the annual consumption of these metals,

Preparation of Alloys.—In addition to the obvious method of melting together the component metals, alloys may be prepared in several other ways. Some of these are of purely theoretical interest, while others have been, and are still, used commercially. The methods of preparation may be regarded as six in number :—

(1) By sublimation or condensation of metallic vapours.

(2) By compression.

(3) By diffusion.

(4) By electro-deposition.

(5) By the simultaneous reduction of two or more metals.

(6) By simple melting of the constituent metals.

(1) **Sublimation or Condensation of Vapour.**—The formation of alloys by condensation of metallic vapour is rare, but such cases have been observed to occur in furnace products, and it is probable that certain alloys which are found in the native state have been formed in this way. By the decomposition of mixtures of the carbonyls of iron and nickel, alloys of these metals may be produced.

(2) **Compression.**—In 1878 Spring showed that if metals in a finely divided state are subjected to pressure the particles unite to form a solid mass, as though they had been melted, although the actual rise in temperature, due to the increase of pressure, is inconsiderable. The pressure required to cause particles of metals to unite in this way depends upon the nature of the metal, but the following figures have been determined for several of the common metals :—

Lead	unites at 13 tons per sq. in.		
Tin	,,	19	,,	,,
Zinc	,,	38	,,	,,
Antimony	,,	38	,,	,,
Aluminium	,,	38	,,	,,
Bismuth	,,	38	,,	,,
Copper	,,	33	,,	,,

With increasing pressure the metals can be forced through a hole in the base of the compression chamber in the form of wire. In the case of lead and tin the pressures required to effect this are 33 and 47 tons per sq. in. respectively.

If now, instead of compressing simple metallic powders, mixtures

of different metals are subjected to the same treatment it should be possible to produce alloys, and Spring showed that this is actually the case and that true alloys are so formed. Thus a mixture of bismuth, lead, tin, and cadmium in the proportions of 15, 8, 4, and 3 parts respectively gave a fusible alloy which melted at 98°, a temperature no less than 134° lower than the melting-point of the most fusible of the constituents, tin, which melts at 232°.

(3) **Diffusion**.—The diffusion of metals will be considered later in some detail, and it is only necessary to point out here that alloys can be formed by the diffusion of solid metals in contact with one another even at ordinary temperatures, as shown by Roberts-Austen in the case of lead and gold.

(4) **Electro-deposition**.—If an electric current is passed through a solution containing two metallic salts it is possible, under suitable conditions, to obtain the two metals deposited at the same time in the form of a true alloy. It is only possible to obtain the proper conditions with a few combinations of metals, but the method is used commercially to deposit brass from solutions containing copper and zinc, and was at one time employed for electro-plating with alloys of silver and cadmium in place of pure silver. From a commercial point of view the process presents many difficulties, and is only practicable in the case of a limited number of alloys.

(5) **Simultaneous Reduction of Metals**.—This is the primitive method by which alloys were made long before the metals of which they were composed were known in the free state. Thus brass was well known and largely used long before the metal zinc was known, and in later times the regular method of making brass, known as the "calamine method," consisted in reducing calamine in the presence of metallic copper. A still more recent application of the method is to be found in the production of aluminium bronze by the Cowles process, in which the reduction of aluminium was carried out in an electric furnace in presence of metallic copper which immediately alloyed with the reduced aluminium.

Although many of these processes are now obsolete, a number of alloys are still manufactured by the simultaneous reduction of two metals. Ferro-manganese and spiegeleisen are manufactured

in the blast furnace by the simultaneous reduction of iron and manganese ores, while ferro-chrome, ferro-silicon, and ferro-phosphorus are made both in the blast furnace and in the electric furnace; and ferro-titanium, ferro-aluminium, and more complex alloys (such as ferro-aluminium silicide and ferro-calcium silicide) are made in the electric furnace.

Another method of producing alloys by simultaneous reduction to which some reference must be made is that commonly known as the Goldschmidt or thermit process, which depends on the powerful affinity of aluminium for oxygen, whereby it is able to combine with the oxygen of many other metallic oxides, leaving the metals in a free state. The reaction may be represented thus :—

$$3CuO + 2Al = 3Cu + Al_2O_3.$$
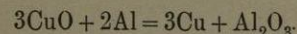
The heat produced by the reaction is so great that if the oxide is merely mixed with granulated aluminium and heated in a furnace the reduction often takes place with explosive violence and a method must be adopted of controlling the reaction. The usual procedure is as follows :—A small quantity of the oxide or oxides to be reduced is mixed with the calculated quantity of granulated aluminium and placed in a crucible which has been previously lined with magnesia in order to resist the high temperature. On the top of the mixture is placed a small heap of an ignition powder made by mixing powdered aluminium with an easily reducible oxide, such as barium or sodium peroxide, and into this heap is inserted a short piece of magnesium wire or cordite. The ignition of the magnesium wire is sufficient to start the reaction in the ignition powder, which is then communicated to the mixture in the crucible. When the reaction is fairly started the remainder of the oxide to be reduced, mixed with the requisite amount of aluminium, is slowly charged into the crucible. If this is carried out properly the reduced metal will settle to the bottom of the crucible under a layer of slag consisting of fused alumina. This method is of much service in preparing alloys, as many of the oxides of the rare metals are readily reduced by aluminium; but it is often difficult to obtain the metals free from a certain amount of aluminium. The calorific values given in the table on p. 6 will indicate the relative reducibility of the oxides, and a

simple calculation will give the heat evolved during the reaction. Thus in the case of the reduction of nickel oxide

$$3NiO + 2Al = 3Ni + Al_2O_3$$
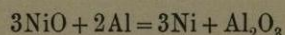
we have the heat of formation of Al_2O_3 $(131\cdot2 \times 3 = 393\cdot6)$ less the heat of formation of 3NiO required for the reduction $(61\cdot5 \times 3 = 184\cdot5)$, leaving $209\cdot1$ calories. This excess heat has been employed in the welding of tram rails, etc., as the operation can be carried out wherever required and quite independently of the existence of furnaces.

(6) **Melting the Constituent Metals.**—All the well-known alloys, such as bronze, brass, German silver, pewter, and other white metal alloys, gold and silver alloys, etc., are made by melting together the metals which are to be alloyed. The melting is nearly always performed in crucibles; but in a few cases, where large ingots are required, reverberatory furnaces are employed. The crucibles used are either made of fireclay or of a mixture of fireclay and graphite. The former are used for the melting of iron alloys, where carbon plays an important part in the composition of the alloy; while the latter, which are known as graphite or plumbago crucibles, are used for all oxidisable alloys, such as those of copper. Alloys with low melting-points, such as those of lead and tin, are often melted in cast-iron pots.

The furnaces in which the crucibles are heated may be either coke or gas-fired. The coke-fired furnace is the most generally used and is of the simplest design, being practically identical with the ordinary assay furnace. Gas-fired furnaces have been more largely used within the last few years, and where a large number of furnaces are required they possess many advantages over those fired by coke.

Heat of Formation of Metallic Oxides.

Magnesium (MgO)	145·5 calories.
Calcium (CaO)	145·0 ,,
Strontium (SrO)	131·0 ,,
Aluminium $\left(\dfrac{Al_2O_3}{3}\right)$	131·2 ,,
Barium (BaO)	124·2 ,,
Sodium (Na_2O)	100·9 ,,
Potassium (K_2O)	98·2 ,,

Silicon $\left(\dfrac{SiO_2}{2}\right)$	90·9 calories.
Boron $\left(\dfrac{Bo_2O_3}{3}\right)$	90·9 ,,
Manganese (MnO)	90·0 ,,
Zinc (ZnO)	84·8 ,,
Tin $\left(\dfrac{SnO_2}{2}\right)$	70·6 ,,
Cadmium (CdO)	66·3 ,,
Iron $\left(\dfrac{Fe_2O_3}{3}\right)$	65·9 ,,
Tungsten $\left(\dfrac{WO_2}{2}\right)$	65·7 ,,
Cobalt (CoO)	64·5 ,,
Nickel (NiO)	61·5 ,,
Antimony $\left(\dfrac{Sb_2O_3}{3}\right)$	55·6 ,,
Arsenic $\left(\dfrac{As_2O_3}{3}\right)$	52·1 ,,
Lead (PbO)	50·8 ,,
Bismuth $\left(\dfrac{Bi_2O_3}{3}\right)$	46·4 ,,
Copper (Cu_2O)	43·8 ,,
Mercury (HgO)	21·5 ,,
Silver (Ag_2O)	7·0 ,,

In the manufacture of alloys on a large scale it is not always easy to produce a mixture of uniform composition even with careful stirring, and in practice it is often considered desirable, if not necessary, to re-melt the alloy a second time. The difficulty is greatest when the metals to be alloyed have widely different melting-points, and is still further increased if one of the metals is volatile. In order to reduce this difficulty to a minimum the pure metals are not melted together, but previously made alloys, whose composition is known, are used to make the final alloy. For example, in the case of German silver, which is composed of copper, nickel and zinc, the zinc melts at 419° and the nickel at 1451°, and it is evident that if the three metals were placed in a crucible and raised to the necessary temperature most of the zinc would be lost by volatilisation before a uniform alloy was obtained. To overcome this difficulty German silver is made by melting together an alloy of copper and nickel usually containing 50 per cent. of each metal and brass. The copper nickel alloy has a lower melting-point than pure nickel, while the brass has a higher melting-point than zinc, and the melting-points being

thus more nearly alike the metals are more readily alloyed and the loss of zinc by volatilisation is very materially reduced. Another difficulty met with in melting metals to form alloys is the liability of the metals to become oxidised, and this subject is of such importance that it deserves some consideration. It is well known that some metals are capable of absorbing, dissolving, or alloying with considerable quantities of their oxides with most injurious results, but this behaviour of metals towards their oxides is of more common occurrence than is generally supposed. The influence of oxide on a molten metal may be readily seen by melting a small quantity of copper in a crucible without taking any precautions to prevent oxidation. The metal will be found to be moderately fluid, but if a small quantity of phosphor-copper is now added to the molten metal the increase in the fluidity of the metal is remarkable, and cannot fail to be noticed. For some time this increase in the fluidity of a metal was not properly understood in its practical applications, and when aluminium was first used as a deoxidiser for steel it was commonly stated that the effect of the aluminium was to lower the melting-point of the steel. Measurements of the melting-point, however, proved that there was no such lowering, but merely an increase in the fluidity, which was made more apparent by the heat produced by the combination of the oxygen with the aluminium.

In order to prevent oxidation as far as possible the metals are melted in graphite crucibles and covered with a layer of charcoal, resin, or other carbonaceous material. In some cases borax is used as a covering, as it melts easily and forms a protecting layer, while at the same time it combines with any metallic oxides present and keeps the molten metal clean. The alloy is stirred with a carbon stirrer, or in some cases with a green pole, the gases evolved from the wood serving to reduce any oxides present. In spite of these precautions, however, oxides are frequently formed which are not reduced by carbon, and the difficulty then presents itself of deoxidising the metal. In order to effectually free a molten metal or alloy from oxide it is necessary that the deoxidiser used shall have a stronger affinity for oxygen than the metal to be deoxidised; and, secondly, that any excess of the deoxidiser over that necessary to completely remove the

oxide shall have no injurious effect upon the metal itself. A large number of deoxidisers are now manufactured, and the following list gives those most commonly used, together with the alloys for which they are most suitable and the form in which they are employed :—

Alloy.	Deoxidiser.	Used in Form of
Iron alloys . .	Manganese . .	Ferro - manganese and spiegeleisen.
,, ,, .	Silicon . . .	Ferro-silicon and silicides.
,, ,, .	Calcium . . .	Ferro-calcium silicide.
,, ,, .	Aluminium . .	Aluminium and ferro-aluminium silicide.
Bronze . . .	Phosphorus . .	Phosphor - copper and phosphor-tin.
,, . .	Aluminium . .	Aluminium.
,, . .	Silicon . . .	Cupro-silicon.
,, . .	Zinc . . .	Zinc.
,, . .	Manganese . .	Cupro-manganese.
German silver .	Magnesium . .	Cupro-magnesium.
Silver-copper alloys	Cadmium . .	Cadmium.
Aluminium alloys	Magnesium . .	Magnesium.

Pouring and Casting.—It has long been known that the temperature at which metals and alloys are poured has an important influence on their mechanical properties, and the most suitable casting temperature for any particular alloy has been determined entirely by practical experience. There is a lack of definite information on the subject, but Longmuir is responsible for some interesting observations and experiments which deserve attention. He cites the case of a number of cast-iron test pieces cast from a 5-ton ladle during an interval of fifteen minutes. Transverse tests on bars 2 ins. by 1 in. placed on supports 3 ft. apart varied from 22 to 35 cwt.

Another series of experiments on a special alloy, whose composition is not given, showed a tensile strength varying from 12·5 to 26·2 tons per sq. in., and corresponding elongations varying from 5·0 to 51·6 per cent. on a length of 6 ins. Two examples are also quoted of castings which failed to meet the required specification, but when broken up and re-melted, without any further addition of metal, and cast at a proper temperature, gave perfectly satisfactory results.

Alloy.	No.	Casting Temperature.	Elastic Limit. Tons per sq. in.	Maximum Stress in Tons per sq. in.	Extension per cent. on 2 ins.	Contraction of Area per cent.	Bending Angle in Degrees.
Gunmetal	1	1173	6·468	8·376	5·5	4·23	30°; broken half through.
	2	1069	8·482	14·838	14·5	16·71	40°; cracked.
	3	965	8·984	11·018	5·0	6·36	40°; „
Yellow brass	4	1182	4·432	11·484	37·75	31·405	Parallel over ¾-in. radius.
	5	1020	3·974	12·713	43·00	35·66	„ „ „
	6	850	4·150	7·447	15·00	15·25	„ „ „
Red brass	7	1308	4·284	6·855	13·25	12·65	Parallel over ¾-in. radius; badly cracked.
	8	1073	4·263	12·649	26·00	30·285	105"; cracked. then hammered flat.
	9	1058	4·376	5·670	5·5	6·64	105"; „ „
Muntz metal	10	1038	8·753	12·454	6·0	10·60	80°; broken.
	11	973	9·637	18·889	15·0	16·10	180°; unbroken.
	12	943	9·526	16·287	9·5	14·81	180°; broken.
Cast iron	13	"Hot"	…	12·271	…	…	
	14	"Fair"	…	13·104	…	…	
	15	"Cold"		11·094			
Malleable iron	16	"Hot"	17·41	24·335	1·75	…	Broke in shoulder.
	17	"Fair"	16·16	26·937	5·75	10·16	„ „ „
	18	"Cold"	12·24	24·02	3·50	6·24	„ „ „

Longmuir has made a number of experimental castings with various alloys, and the figures in the foregoing table show his results. The figures explain themselves, and it is only necessary to add that the quantity of alloy melted was in every case over 50 lbs. in weight. Three bars were cast at a high temperature, and the metal allowed to cool in the crucible for a few minutes. A second set of three bars was then cast, followed after an interval by a third set of three, these last being cast at a temperature at which the metal would just flow.

If the alloy is cast at too high a temperature it possesses the coarse structure characteristic of a slowly cooled metal; whereas if it is poured at too low a temperature, not only is there risk of the alloy becoming partially solid, or the less fusible constituents separating out, before pouring, but also it solidifies immediately on coming in contact with the mould, with the result that there is a lack of cohesion in the ingot. Moreover, on account of the decrease in the fluidity of the alloy at temperatures only slightly above the melting-point, it is liable to enclose scum, slag, or charcoal, which is unable to float to the surface. The result is an unsound ingot which cracks when rolled.

The proper temperature of casting would appear to be such that the mould is entirely filled with molten metal, which begins to solidify almost immediately after the pouring is completed. Determinations of the casting temperature of standard silver carried out at the Royal Mint showed that the average temperature was nearly 100° above the initial freezing-point of the alloy, or about 980°, and this would seem to be a suitable difference in temperature for alloys melting in the neighbourhood of 900°. In the case of alloys with much lower melting-points, which would cool more slowly, the difference between the melting-point and the casting temperature can with advantage be decreased. Thus with aluminium alloys such as magnalium, and alloys of lead and tin, the casting temperature should be only slightly higher than the initial freezing-point.

Closely connected with the casting temperature is the rate of cooling of the alloy, a matter of very great importance. Generally speaking, slow cooling produces a large grain, a coarse structure, and relatively weak alloys; while rapid cooling gives a fine structure and a stronger, but more brittle, alloy. The rate of

cooling is to a great extent controlled by the temperature of the moulds. These are frequently heated in order to prevent too rapid cooling, and in some cases it has been found that the temperature of the moulds is of great importance in determining the quality of the alloy. An example of this occurs in the casting of certain antifriction alloys, which will be considered later.

Moulds.—Owing to the extended range of temperatures through which different alloys melt, a variety of materials are available for making moulds. Iron, brass, sand, plaster of Paris, and a number of other materials may be employed; but those most commonly used are iron and sand compositions. Alloys intended for rolling or drawing, such as steel, bronze, brass, German silver, magnalium, gold and silver alloys, etc., are cast in iron moulds; while those which are to be cast into objects of various shapes, merely requiring to be finished by turning or filing, are cast in sand moulds.

Iron moulds are made in two pieces, which are usually held together by clamps or by a ring and wedge device, intended to facilitate the removal of the ingot. The interior of the mould is either oiled, blackleaded, or smoked before the alloy is poured in. The foregoing remarks do not apply to ingot moulds used in casting steel, which are of special form and do not receive any oiling or other treatment previous to casting. They are made of grey hæmatite iron in the form of truncated pyramids of any desired section, with just sufficient tapering to allow the mould to be easily removed from the solid ingot. The second part of the mould, in this case, consists of a cast-iron bottom plate upon which the moulds stand.

The material used in making moulds for "sand castings" is a mixture of somewhat variable composition, but usually contains about 5 per cent. of clay, 1 to 2 per cent. of iron oxide, and the remainder of clean sand. Where fine castings with a specially good surface are required, the surface of the mould is "faced" with flour or a mixture of flour and charcoal.

The "pattern" round which the sand is moulded is usually made of hard wood, and is varnished or blackleaded to enable it to leave the sand easily. Allowance must also be made for the shrinkage of the metal on cooling. In casting alloys sharp

corners or angles should be avoided, as far as possible, for a double reason. In the first place, such patterns are difficult to mould; and, in the second place, sharp angles give rise to a line of weakness in the casting which may result in fracture. This line of weakness is due to the fact that crystallisation takes place in a line at right angles to the face of the mould, and it follows that if two faces form a sharp angle the crystallisation starting from both faces will meet and produce a line of separation which bisects the angle. Prof. Turner states that a moderate internal pressure will frequently force out the bottom of a cylinder in a single piece if it has been cast with sharp corners. For this reason rounded curves should be adopted wherever possible.

After-treatment of Alloys.—When an alloy leaves the ingot mould it is subjected to a number of operations, all of which affect its properties to a greater or less degree. These operations may be described as (1) mechanical treatment, such as rolling, drawing, spinning, etc.; (2) thermal treatment, such as annealing, chilling, tempering, etc.; and (3) chemical treatment, which may be merely a cleaning of the surface by pickling in acid or alkali, or an actual alteration in the composition and character of the surface of the alloy by pickling or by cementation.

The influence of these operations will be considered separately.

1. **Influence of Mechanical Treatment.**—All metals are more or less compressible, and in the light of recent research it would appear that compressibility is a periodic property, and closely connected with, if not proportional to, the atomic volume. When subjected to mechanical treatment, such as rolling, hammering, or drawing, metals and alloys undergo compression and their mechanical properties are altered. The metal becomes stronger, harder, and more brittle, or, in other words, the tensile strength is increased and the elongation decreased. The practical application of alloys hardened by mechanical treatment may be seen, to take a single example, in the use of standard silver for the blades of dessert knives, fish knives, etc. These are manufactured by hammering, or, in the cheaper varieties, by "hard rolling." In the case of alloys experimental data are wanting; but it has been shown with pure metals that the greater the compressibility the more rapidly does it decrease with increasing pressure, and,

according to Le Chatelier, the tensile strength of metals hardened to their maximum extent is almost exactly double their strength in their normal or softened condition. His figures for five metals are as follows :—

Metal.	Tensile Strength in Tons per sq. in.	
	Minimum Hardness.	Maximum Hardness.
Copper	15·87	32·38
Nickel	34·92	66·66
Aluminium . . .	7·62	15·87
Silver	11·43	24·12
Cadmium	1·58	3·17

As regards alloys it is probable that those consisting of solid solutions which, as will be seen later, have structures similar to those of pure metals and are the only alloys capable of receiving much mechanical treatment without being previously heated, will behave in much the same way as pure metals. In some cases alloys are rolled while hot, and in others they are rolled cold. Cold rolling produces a greater degree of hardness than hot rolling, and the maximum hardness is produced by cold drawing to form wire or rod. The condition of maximum hardness, however, is not a stable one, and Le Chatelier has shown that a metal which has attained a state of maximum hardness becomes gradually softer in the course of time. Thus wires of silver and copper tested some hours after drawing showed a decrease in strength of 2 to 2·5 tons per square inch from those tested immediately after drawing. It is evident that this change, which Le Chatelier has aptly described as "spontaneous annealing," is of the utmost importance, and renders tests made on hardened metals of more than doubtful value.

2. **Influence of Thermal Treatment.**—After being subjected to mechanical treatment metals and alloys are usually too hard and brittle to be of use, and it is necessary to soften them by reheating or annealing. This operation is usually carried out either in closed furnaces of the muffle type or in reverberatory furnaces (under reducing conditions) when the size of the pieces to be annealed does not permit of the use of a muffle furnace. Very

small objects, such as pieces of standard silver to be used for jewellery, are sometimes annealed by simply resting them on the hot coke in the open furnace.

Annealing is usually followed by slow cooling, but in some cases rapid cooling produces a softer metal. Examples of this are to be found, in the case of pure metals, with silver; and in the case of alloys, with magnalium. The alteration produced by annealing requires time, and takes place more rapidly as the temperature is raised. On the other hand, impurities render the process of annealing slower.

The properties of some alloys are profoundly altered by chilling, quenching, or rapidly cooling from a high temperature. The object of such treatment is to fix or maintain, as far as possible, the structure possessed by the alloy at the temperature from which it is quenched, and it follows that the treatment is only applicable to alloys which undergo a transformation or molecular change on heating or cooling. It also follows that the effect produced by quenching will vary with different alloys. Steel, for example, is hardened by quenching; whereas the same treatment applied to bronze renders the alloy softer and more malleable, the rapid cooling preventing or hindering the formation of a hard constituent, which is always formed in a slowly cooled sample. The temperature from which the alloy is quenched depends upon the temperature at which the molecular transformation takes place, and must, of course, be above that temperature.

The structure of an alloy can never be absolutely fixed by quenching, for the simple reason that the quenching can never be instantaneous and the efficiency of the quenching depends on the size, or, more strictly speaking, on the weight, specific heat, and conductivity of the alloy to be quenched; and also on the temperature and nature (and more especially the conductivity) of the bath in which the quenching takes place.

Quenching is usually carried out in water, solutions of salts in water, oils, lead, or the more fusible alloys of lead and tin.

Tempering consists in reheating a quenched alloy to a temperature below that from which it was quenched with the object of destroying the internal strain produced by the quenching, without affecting its molecular structure. The softening effect of this reheating is greater as the temperature is raised, but the tempera-

ture must be well below the point of transformation. A better example of the influence of heat treatment on the structure of an alloy could hardly be chosen than that given by Roberts-Austen and reproduced in photograph 1. The photographs all represent a steel containing 1·5 per cent. of carbon. The centre photograph shows the structure of the metal as it comes from the cementation furnace. No. 1 shows the structure after heating to 1000°, working and slowly cooling. In No. 2 the metal has been heated to 850° and cooled in air. In No. 3, instead of cooling in air, the metal has been quenched from the same temperature, 850°, in water. The steel is thus hardened and the pearlitic structure has been entirely replaced by martensite. In No. 4 the metal has been raised to a higher temperature, 1050°, and more rapidly cooled by quenching in iced brine. The structure now consists of bands of martensite, alternating with lighter and softer bands of austenite. If this metal is now cooled to the temperature of liquid air the structure is profoundly altered as shown in No. 5. In No. 6 the steel has been quenched from a temperature near its melting-point and the result is a "burnt" steel. The structure shown in No. 7 is the result of prolonged annealing at 650°. The cementite and pearlite are well defined. Lastly, No. 8 shows the original structure produced by heating any of the samples, except No. 6, to 850°, working, and slowly cooling.

Influence of Chemical Treatment.—After an alloy has been subjected to mechanical and thermal treatment it is necessary to remove the surface deposit of oxide which is formed on most alloys, and this cleaning is usually effected by "pickling" in an acid bath which is frequently heated. Now, this pickling has a decidedly prejudicial effect upon the mechanical properties of the alloy, and is so well recognised in the case of iron and steel that some specifications, including those demanded by the Admiralty, require that tests should be made upon the pickled metal. In the pickling of thin steel sheets intended for tin-plate manufacture, the decrease in strength and ductility of the metal is often accompanied by the formation of blisters on the surface; and in the pickling of hard steel rod containing about 0·8 per cent. of carbon the metal sometimes flies to pieces when immersed in the acid. The following figures by Baker and Lang illustrate the falling-off in the quality of steel rod by pickling. The first

sample was pickled in a 38 per cent. sulphuric acid bath for one hour, the second in an 11 per cent. bath for forty-five minutes, and the third in a 10 per cent. bath for one hour ten minutes, the temperature of the bath in each case being 100°.

	Tensile Strength in lbs. per sq. in.			Percentage Contraction.		
	1.	2.	3.	1.	2.	3.
Before pickling . .	65,700	59,700	69,100	63	66	67
After pickling . .	61,400	59,700	64,200	38	44	47

On reheating, the metal returns partially, but not entirely, to its former state.

There is no doubt that these results are due to the hydrogen, which is evolved in considerable quantity during the operation of pickling, and the action is more readily understood when we consider the following facts. Hydrogen at the normal temperature is easily capable of penetrating steel, and at 100° the penetration must be *greater*. Moreover, the action of the acid leaves a rough surface on the metal which favours the penetration of the gas. Nascent hydrogen is a powerful reducing agent, and is capable of reducing metallic oxides, whether formed in the process of melting, or rolled into the metal during subsequent mechanical treatment, and the author has shown that this reduction can take place at a temperature of 100°. The reduction of oxides is accompanied by the formation of water, and the water being unable to pass out of the metal where the hydrogen entered, gives rise to an internal pressure, which may cause a blister in soft metal, a fracture in hard metal, or, at least, a falling-off in the mechanical properties. But at higher temperatures the action is reversed; metallic iron decomposes water vapour, and the hydrogen so formed is able to pass through the metal again.

The alteration in composition due to pickling must not be overlooked. For example, in the case of standard silver, which in the hands of the silversmith undergoes repeated annealings and cleaning in acid, the copper is almost entirely removed from

the surface of the alloy, leaving a coating of almost pure silver. This is a point which has to be considered by the assayer in taking an average sample of the metal.   A change of composition in the surface layer of an alloy may also be produced by the ancient process of cementation.   This process, which is still used in the hardening of steel, consists in heating the alloy, in the presence of a substance with which it is capable of alloying, at a temperature below its melting-point.   Thus steel is superficially hardened by packing it in charcoal, and maintaining it at a high temperature for some time.   The steel gradually alloys with the carbon, with the result that the surface is much harder than the interior.   A similar result is obtained by heating copper alloys in zinc dust, or even in zinc vapour, which alloys with the copper.   A similar method is employed in the production of what is known as malleable cast iron; in this case the result aimed at is not the addition of a new element, but its extraction. Cast iron is heated with oxide of iron, which decarburises the iron and renders castings softer and less brittle.

CHAPTER II.

PROPERTIES OF ALLOYS.

Density.—The density of an alloy is influenced (1) by the purity of the metals of which it is composed; (2) the mechanical treatment it has undergone; (3) the temperature at which it has been cast; and (4) the rate of cooling.   These facts may to a great extent account for the disagreements shown in the work of Mallet, Calvert and Johnson, Matthiessen and Riche.   Their work shows, however, that the density of an alloy is seldom the mean of the densities of its constituent metals, sometimes being greater and sometimes less than the mean.   The mean density of an alloy may be calculated from the formula

$$M = \frac{(W + w)Dd}{Dw + dW},$$

where M is the mean density, W and w the weights of the constituent metals, and D and d their respective densities.   The following alloys have frequently been given as examples of cases in which the densities are respectively greater and less than the mean :—

Alloys whose Density is less than the Mean of their Constituents.	Alloys whose Density is greater than the Mean of their Constituents.
Au and Zn	Au and Ag
Au ,, Sn	Au ,, Fe
Au ,, Bi	Au ,, Pb
Au ,, Sb	Au ,, Cu
Au ,, Co	Au ,, Ir
Ag ,, Zn	Au ,, Ni
Ag ,, Sn	Ag ,, Cu
Ag ,, Bi	Fe ,, Bi
Ag ,, Sb	Fe ,, Sb
Cu ,, Zn	Fe ,, Pb
Cu ,, Sn	Sn ,, Pb
Cu ,, Pd	Sn ,, Pd
Cu ,, Bi	Sn ,, Sb
Pb ,, Sb	Ni ,, As
Pt ,, Mo	Zn ,, Sb
Pd ,, Bi	