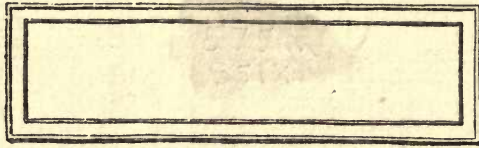


Vining dept.



71 (300)





**ALLOYS** (Non-ferrous).



# ALLOYS

(NON-FERROUS)

— BY —

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MINING DEPT.

TO  
Professor E. MARION HOWE, LL.D.,  
Columbia University, New York, in recognition of the help  
and stimulus derived from his various works on Metallurgy.

U.S. DEPT. OF THE INTERIOR  
BUREAU OF MINES  
WASHINGTON, D. C.



## PREFACE.

THE literature of Alloys is not very large, and such great advances have been made during the last few years that little apology is needed for the preparation of another book on the subject.

The object which the author had in view in the preparation of this book was to provide for students, and more particularly for makers and users of alloys, a brief account of some of the advances which have recently been made in the study of Alloys. His object has not been in any sense to provide a complete account of what has been done, but rather to indicate the direction in which research is going on, and to give to the maker and user of alloys such information as may be of practical utility, and which will enable him to clearly understand the current literature of the subject, and to see in what direction he must look for further developments that may be of use to him.

A good deal of the work which has been published can only be regarded as a preliminary explanation, and in many cases the results await confirmation or modification by fuller research on a larger scale than has yet been attempted. The work of Dr. Carpenter and Mr. Edwards for the Alloys Research Committee on the Alloys of Aluminium and Copper is an example of the work which needs to be undertaken for the various other groups of alloys.

The scope of the work did not allow of the consideration of many important points which are not yet fully worked out, such, for instance, as the meaning of some of the thermal changes of a minor character noticed during the cooling of alloys, or of some recent methods of

research such as the use of ultra violet light, from which important results may be obtained in the future. The alloys of iron are so many and so important that a separate volume would be needed to consider them in anything like useful detail. It has, therefore, been thought better to omit them altogether in this work.

At present the results of the researches that have been made are scattered through the journals of many Scientific and Technical Societies and the Technical Journals, and as there is no Society specially devoted to this work, the field which has to be travelled over is unusually large, and many valuable papers have been published in the journals of societies which are difficult to obtain. It is quite likely, therefore, that the author may have overlooked valuable papers, and in some cases he has had to depend on abstracts as the papers themselves were not available. Much of this information is, therefore, quite inaccessible to the general reader, and the author hopes that the bringing of a good deal of it together into one book may not be altogether useless.

To previous writers on the subject the author is, of course, deeply indebted, and he has not scrupled to quote from them when necessary. To them and to the Societies (especially the Society of Mechanical Engineers), authors of papers, and publishers who have kindly allowed him to use their results and illustrations, he gives his best thanks. Acknowledgments have been made in the text, and if by oversight any have been omitted, he here expresses his regret.

His best thanks are also due to his assistants, Messrs. J. S. G. Primrose, A.G.T.C., and J. A. C. Edmiston, for the valuable help they have given in various ways.

# CONTENTS.

## CHAPTER I.

INTRODUCTION .. .. .	1
----------------------	---

## CHAPTER II.

THE PROPERTIES OF ALLOYS AS RELATED TO THOSE OF THEIR CONSTITUENTS .. .. .	7
---	---

## CHAPTER III.

THE PHENOMENA OF SOLIDIFICATION .. .. .	20
---	----

## CHAPTER IV.

WHAT THE MICROSCOPE CAN TEACH .. .. .	43
---------------------------------------	----

## CHAPTER V.

CHANGES IN THE STRUCTURE OF ALLOYS IN THE SOLID CONDITION .. .. .	64
--	----

## CHAPTER VI.

METALS USED IN THE PREPARATION OF ALLOYS .. .. .	75
--	----

## CHAPTER VII.

THE BRASSES (THE COPPER-ZINC SERIES) .. .. .	87
--	----

## CHAPTER VIII.

THE BRONZES (THE COPPER-TIN SERIES) .. .. .	120
---	-----

## CHAPTER IX.

MACHINERY BRASSES AND BRONZES, BEARING BRONZES, AND OTHER COPPER ALLOYS .. .. .	147
--	-----

## CHAPTER X.

WHITE ALLOYS ; ALLOYS IN WHICH TIN IS THE PRINCIPAL CONSTITUENT .. .. .	172
--	-----

## CHAPTER XI.

WHITE ANTI-FRICTION ALLOYS .. .. .	184
------------------------------------	-----

## CHAPTER XII.

LIGHT ALLOYS; FUSIBLE ALLOYS .. .. .	197
--------------------------------------	-----

## CHAPTER XIII.

NICKEL ALLOYS .. .. .	209
-----------------------	-----

## CHAPTER XIV.

ALLOYS OF THE PRECIOUS METALS .. .. .	217
---------------------------------------	-----

## CHAPTER XV.

PREPARATION OF ALLOYS .. .. .	244
-------------------------------	-----

# ALLOYS.

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## CHAPTER I.

### INTRODUCTORY.

WHEN two or more metals are melted together they, as a rule, remain intimately mixed, showing little tendency to separate according to their densities, or as it may be otherwise expressed, they remain in solution one in the other, whilst they are in the liquid condition. When the mass solidifies this state of uniform distribution or mixture may continue, or it may be broken up. In the former case the solidified mass will contain the constituent metals in a condition of more or less uniform diffusion, and such a mass is called an alloy. In the latter case the metals will separate according to their specific gravities, the heavier metal going to the bottom and the lighter rising to the top, such separation being as a rule the more complete the slower the solidification. The separated metals in this case are rarely if ever pure, but each retains a small quantity of the other, and strictly speaking both are therefore alloys. In practice, however, the term alloy is restricted to those cases in which neither of the metals is present in very small proportion; the other cases being simply considered as metals containing an impurity.

**An Alloy is neither a Mechanical Mixture nor a Chemical Compound.**—An alloy is, then, an intimate mixture of two or more metals, and the term mixed metals has sometimes been used in place of alloys. This is, however, very misleading, as the alloys are much more than mere mixtures, and mixtures of metals may exist which are not alloys.

If lead and copper be melted together, and the mixture be slowly cooled, the metals will separate. If, however, the mixture be quickly cooled separation cannot take place

and the metals will remain mechanically mixed the one with the other, they not having had time to separate into distinct layers, but the mass will consist of intermixed particles of the two metals, and if it be heated up to the melting point of lead this metal may be, to a large extent, melted out. This, then, would be a case of a mixture of metals, but not of an alloy. In an alloy, the mixture must be of such a character that the constituent metals lose their individuality, and become blended into a new substance which has properties, to some extent at least, unlike those of its constituents.

As a rule, substances which are not elements are divided into the two classes, chemical compounds and mechanical mixtures, but the metallic alloy cannot be made to fit exactly into either group.

In a mere mixture the particles, however small and however intimately they may be mixed, always retain their individuality, and the properties of the mixture are always a mean of those of its constituents. If the constituents be black and white the mixture will be grey, if red and white, a paler shade of red, and so on through all the other properties. This, as is well known, is not the case with alloys. Brass containing, say, 50 per cent. of copper and 50 per cent. of zinc, is yellow, and this yellow colour is certainly not a mean between the red of the copper and the bluish white of the zinc; nor is the specific gravity, or indeed any other property of the brass, a mean between those of its constituents. The only point in which alloys always resemble their constituents is that they are distinctly metallic.

Alloys, therefore, are not mechanical mixtures.

A chemical compound contains the elements in fixed proportions, these being always simple multiples of the atomic weights, and some of the physical properties follow from the molecular weight of the compound. This is not the case with alloys. As a rule, the metals are not present in any simple atomic proportion, and further the proportions can be varied often within wide limits without producing any great change in the properties of the alloy.

The metals do not show any strong chemical affinity one for another, but there is no doubt that in some cases

definite chemical compounds of the metals do exist, but in no case do they form alloys of any industrial importance.

**Solutions.**—There is still another form in which substances can exist which, while not a mere mechanical mixture, is something less than chemical combination. If salt or any other soluble substance be stirred up with water it disappears, or dissolves in the water, and the result is a solution of the salt. This solution has some of the properties of the salt; it has, for instance, a salt taste, yet its properties cannot be said to be a mean between those of water and salt. The salt dissolves without increasing the volume of the solution, so that the solution is denser than the mean between salt and water. The addition of the salt also lowers the freezing point of the water, so that the freezing point of the solution, instead of being a mean between that of water and salt, is lower than that of either, and by the addition of proper proportions of salt it may be reduced to about  $-22.5^{\circ}$  C.

The essential character of a solution is that the constituents are so intimately blended that they cannot be separated or detected by mechanical means, whilst at the same time they have not entered into true chemical combination.

**Solid Solutions.**—As a rule, when a solution is frozen, the constituents separate one from another to a larger or smaller extent, but this is not always the case. We can imagine a solution to become solid without any other change, and the result would be a solid solution in which the constituents would still be so intimately mixed that no mechanical separation would be possible, and in which the properties would not be a mean of those of its constituents, but in which these constituents would not be present in the definite proportions required for a chemical compound.

**Alloys.**—True alloys are never mere mechanical mixtures of metals, and though in some cases the metals do combine, yielding definite chemical compounds which often retain their metallic properties, none of these are of any use in the arts. Alloys are very frequently solid solutions of one metal in another, or of

a chemical compound of the metals in the metal which is in excess. Many consist of mixtures of such solutions with definite substances that have crystallised out during cooling, so that the actual composition and structure may vary very widely; and each alloy, or rather group of alloys, must be studied separately, as it is impossible to lay down any except the most general rules.

**Importance of a Knowledge of the Structure of Alloys.**—It may be thought that the structure of alloys, whilst interesting enough as a scientific study, will be of very little importance to the practical maker and user of alloys. This is, however, far from being the case. The properties of alloys depend to such a large extent on their structure, that without a knowledge of the latter the former cannot be understood. Many of the failures in the making of alloys are due to changes in structure brought about by small changes in the method of treatment or in other ways, and failures cannot be prevented till the causes which produce them are known; and therefore such knowledge is of great practical importance to all who have to deal with alloys.

**Methods of Investigation.**—Chemical analysis is, of course, of primary importance, as giving the proportions in which the various constituents are present; but its uses are limited to that, and that alone is not enough, for it is often important to know not only what elements are present, but how these are united; that is, to know not only the ultimate but the proximate composition. At present the proximate analysis of metals and alloys has made little progress, and only in a few cases has it been found possible to separate any of the proximate constituents by analysis. For chemical analysis it is necessary to attack the whole alloy, and the reagents used for this purpose have such a vigorous action that they break up all the constituents of the alloy into their elements, which then enter into new forms of combination.

**The Microscope.**—Within the past few years the application of the microscope to the examination of metals has developed very rapidly. Accurate methods of work are now known, and a vast amount of data has been gathered. The microscope can supplement chemical analysis. It



does not enable us to determine what chemical elements are present, but it enables the structure of the body to be made out, and particularly the constituents that may have separated as the alloy has solidified, and therefore to determine some at least of the facts which chemical analysis leaves undetermined.

**Phenomena of Solidification.**—If alloys, when melted, can be considered as being solutions of one metal in another, then a study of the phenomena which take place during the solidification and cooling of solutions should throw great light on the changes which take place during the solidification of alloys. This has actually been found to be the case. Many solutions which solidify at a moderate temperature are much more easily studied experimentally than the alloys which melt at a high temperature, and it is comparatively easy, with due care, to reason from the one to the other.

**Physical Properties.**—The physical properties of alloys are found to vary with changes in their composition and methods of treatment, though the changes are often complex, and in many cases do not seem to bear any simple relation to the composition. Nevertheless, they throw much light on the points at which changes take place.

**Four Methods of Research.**—These four methods of research—viz., chemical analysis, microscopic examination, study of the phenomena of fusion and solidification, and study of the physical properties of the alloys—have now been applied to most of the important series of alloys. They supplement one another, and, taken together, enable very many valuable inductions to be made, so that what may be called a theory of alloys can now be formulated.

**Scope of this Book.**—In this book it is intended first to describe briefly the methods by which the structure and character of alloys have been determined, and then to give a brief account of the more important groups of alloys and the methods of preparing them. The object will be to give an account of the investigations that have been made and the facts that have been discovered during the last few years, in so far as they are likely to be of any practical importance to the maker and

user of alloys. In some cases it may be unavoidable that the subjects discussed should be to some extent theoretical, and perhaps appear somewhat far away from practical utility ; but the needs of the practical worker are always kept in view, as it is for him that the book is mainly intended. At the same time, it will be a more or less complete account of the present condition of our knowledge of alloys.

## CHAPTER II.

### THE PROPERTIES OF ALLOYS AS RELATED TO THOSE OF THEIR CONSTITUENTS.

ALLOYS contain two or more metals in some form of mixture or combination, and at the outset it will simplify matters to consider such as contain two metals only. The properties of the alloy will, of course, differ from those of its constituents, but it remains to inquire how the two sets of properties are related. It is evident that the properties of an alloy must to some extent depend on those of its constituents, for this is true even in the case of chemical compounds; but alloys, as remarked above, are not definite chemical compounds, and therefore we should expect a much closer resemblance between the properties of the alloy and those of its components.

It must be remembered that a series of alloys can usually be obtained in which the percentage of one metal can be increased from 0 to 100, and that of the other diminished from 100 to 0; the two extreme members of such a series being the pure metals. And it is of interest to study how the properties of such a series will vary.

If the alloy be a mere mixture, then the variation should be always in the same direction, and should be proportional to the amount of the second metal added; if it be a chemical compound, or set of chemical compounds, sudden breaks or changes in properties might be expected when compositions are reached corresponding to the definite compounds; if it be a solid solution, variations might be expected continuously in the same direction, but not necessarily proportional to the amount of the added metal, as changes in solubility may take place as the solvent metal becomes more nearly saturated, and if, as is possible, two, or perhaps all these conditions may co-exist, we should expect more or less irregular variations. In this chapter some of the principal properties will be con-

sidered, the alloys being selected so as to best illustrate the property under consideration, and later the alloys of commercial importance will be separately dealt with.

**Colour.**—There is no property which is subject to more striking variations by admixture of metals than colour. Unfortunately, we have no quantitative method of valuing colour, so that comparisons can only be general and qualitative.

Most of the metals are white, though the shade of whiteness varies very much, from the silver-white of silver or aluminium to the very bluish-white of lead. There are only two metals in common use with well-marked colours—gold, which is yellow, and copper, which is usually said to be red, but which may best be defined as being copper-coloured.

All alloys of the white metals one with another are white, but the shade of white bears little or no relation to the shade of the metals themselves. When a white metal is alloyed with a coloured metal, great changes of colour are often produced. These changes may be looked at from two points. Starting with the white metal, the gradual change of colour which is produced by the addition of increasing quantities of the coloured metal may be noted; or starting from the coloured metal, the changes in colour produced by the addition of increasing quantities of the white metal may be considered. In general, the second method is the most satisfactory, because, strange though it may seem, the alteration of colour produced by the addition of a comparatively small quantity of a white metal to a mass of the coloured metal is usually far greater than that produced by the addition of a small quantity of the coloured metal to a mass of the white one, and in either case the resulting colour seems to bear little relation to that of the constituent metals.

Almost any series of such alloys might be taken as an example. In the case of the aluminium-copper series for instance, whilst 5 per cent. of copper makes very little difference to the colour of aluminium, 5 per cent. of aluminium changes the red colour of copper to a fine yellow.

The most striking colour series, however, is probably that of the copper-zinc alloys. Five per cent. of zinc added to copper destroys the red colour and gives a yellow alloy; as more zinc is added the yellow colour becomes more intense, though by no means uniformly so with each addition of zinc, till the composition 50 per cent. copper and 50 per cent. zinc is reached, this being the composition of common yellow brass. As the proportion of zinc is increased to about 60 per cent. a silver-white alloy, white brass, is obtained, and with still increasing zinc this silver-white gives place to the bluish-white colour of zinc itself.

There are other cases where the colour change is still more striking, such as the alloy of about 51 per cent. of copper with 49 per cent. of antimony, known as *Regulus of Venus*, which has a fine violet colour, and the alloy of gold with 10 per cent. of aluminium, discovered by Sir W. Roberts-Austen, which has a ruby-red colour.

**Specific Gravity.**—When metals are melted together and solidified, the volume of the mixture is rarely the same as that of the metals separately. There is either contraction or expansion, and the specific gravity of the alloy is

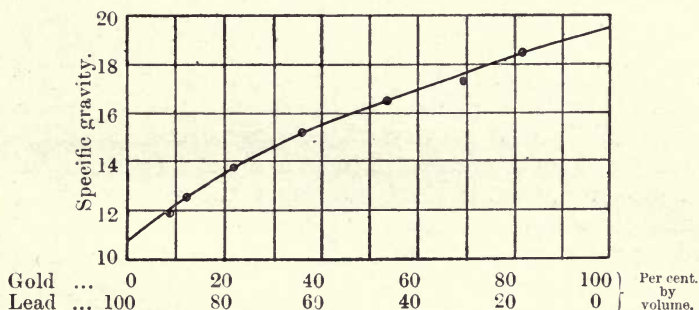


FIG. 1.—SPECIFIC GRAVITY OF LEAD-GOLD ALLOYS.

therefore either greater or less than the mean of that of its constituents in the same proportion. In most cases the specific gravity of an alloy is greater than the mean of that of its constituents, as is also usually the case with solutions.

As a rule, the specific gravity falls as the quantity of the lighter metal increases, but not in direct proportion

to the quantity of the lighter metal present; in such cases a curve representing the densities of a series of alloys will be a continuous curve rising above a straight line connecting the specific gravity of the two constituent metals, as is shown in the curve Fig. 1, which represents the densities of gold-lead alloys as determined by Matthiesen.\* On the other hand, antimony and tin expand on alloying so that the specific gravity of the alloy is less than the mean of its constituents, and therefore the curve lies below the straight line, as shown in Fig. 2. In other

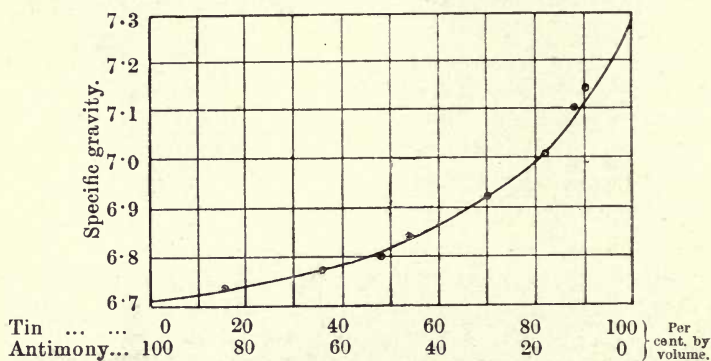


FIG. 2.—SPECIFIC GRAVITY OF ANTIMONY-TIN ALLOYS.

cases the increase or decrease is not regular, but there are breaks at certain points. In the case of the copper-tin series, the specific gravity of the alloy decreases as the quantity of tin increases, till there is about 28 per cent. of tin present; then it rises till, when the percentage of tin is about 38, it reaches 8.9, and therefore the alloy is denser than copper, then as the tin is further increased, the specific gravity falls continuously. Riche† states that the curve of densities has two maxima corresponding to  $\text{Cu}_4\text{Sn}$  (68.12% Cu) and  $\text{Cu}_3\text{Sn}$  (61.58% Cu).

It is quite obvious, therefore, that the specific gravity of an alloy cannot be calculated from that of its constituents, unless we know exactly what changes take place when the metals are alloyed, and that experiment alone can decide.

\* Phil. Tran. Royal Soc., 1860, p. 183. † Comp. Rendu, 55, 162.

Except when alloys are prepared specially for experimental work it is difficult, if not impossible, to obtain a series of varying composition, under exactly similar conditions, so that an accurate comparison can be made, and as the treatment to which the alloy has been subjected, such as work put on it, annealing, rate of cooling, &c., all may influence its specific gravity, concordant results are very often not obtained by workers working under different conditions.

The densities of the various alloys of commercial importance will be considered later.

**Tenacity.**—The tensile strength of an alloy may be greater or less than that of its constituents. Alloys of copper and zinc, or copper and tin, in certain proportions, are much stronger than either of the metals; but, in other proportions, they are much weaker. Here, again, no definite rule as to the influence of one metal on another can be laid down.

**Ductility.**—As a rule, increase of tensile strength is accompanied by decreased ductility, but such is not always the case. The addition of a foreign metal to a soft ductile metal will as a rule harden it, and decrease its ductility, but this is certainly not the case in every instance, some alloys being not only stronger, but also more ductile than either of their constituents. In some cases the hardening influence of even a small quantity of foreign element is well marked, as in the case of antimony on lead, bismuth on gold, and carbon on iron.

The influence of foreign metals in diminishing the tenacity and ductility of other metals seems to depend on their atomic volume.\* The larger the atomic volume of the added metal the greater as a rule is the reduction of tenacity and ductility. The late Sir W. Roberts-Austen made a large number of experiments on the influence of foreign metals on gold, and found that the elements of high atomic volume reduced the tenacity and also the ductility of gold, whilst the

---

\* The atomic volume is the proportional volume occupied by this molecule, and is  $\frac{\text{Atomic weight}}{\text{Specific gravity}}$ . In the case of gold the atomic volume is  $\frac{197.2}{19.3} = 10.2$ .

That of bismuth is  $\frac{208.5}{9.82} = 21.2$ . That of aluminium is  $\frac{27}{2.5} = 10.6$ .

metals of low atomic volume either have no influence or increase the tenacity. Pure gold has a tenacity of about 7 tons, and elongates about 30 per cent. before breaking, with a test piece of the length used for the experiments. When the gold was alloyed with bismuth, only  $\cdot 21$  per cent. of that metal being added, the tensile strength was only  $\cdot 5$  ton, and the elongation was imperceptible. When alloyed with  $\cdot 186$  per cent. of aluminium, which stands at the other end of the series, the tensile strength was 8.87 tons and the elongation 25.5 per cent. Silver, which has the same molecular volume as gold, has little effect one way or the other. It is not certain whether a similar rule holds for all the other metals.

**Fusibility.**—The melting point of an alloy is invariably lower than a mean of those of its constituents, and in some cases is even lower than that of the most fusible. There is, however, great uncertainty as to the exact meaning of the melting point of an alloy, as the term is usually used, and as will be seen later, many alloys have no distinct melting point, but a longer or shorter melting range.

**Expansion by Heat.**—The expansion of alloys by heat is very irregular, and does not seem to bear any definite relation to that of their constituents.

**Electric Properties.**—The electric properties of alloys have been in many cases carefully studied, and are of very great interest. The electric properties can be accurately measured and are thus capable of giving, not only qualitative but quantitative results, and at the same time the relation between electric properties and composition in substances other than alloys has been so fully investigated that light may be thrown by analogy on the structure of alloys. There are three electric properties that are of importance in this connection.

- (1) Electric conductivity ;
- (2) Action of an electric current on fused alloys (electrolysis) ;
- (3) Potential difference set up by the contact of alloys with metals.

**Electric Conductivity.**—The influence of the addition of one metal to another on the conductivity is well marked,



and as a rule the conducting power is considerably reduced. Alloys in general may be divided into two groups, according to the way in which the conducting power of the alloy is related to that of the constituent metals. In the first group the alloy behaves exactly as if it were a mere mixture of the two metals, the conducting power rising or falling as the percentage by volume of the second metal is increased, according as the starting point is the metal of less or greater conductivity. The curve for conductivity when plotted, is therefore a straight line. This may perhaps be called the normal curve, though as a matter of fact a comparatively small group of alloys gives it. As an example the tin-zinc series may be taken, and the curve for these is plotted in Fig. 3.

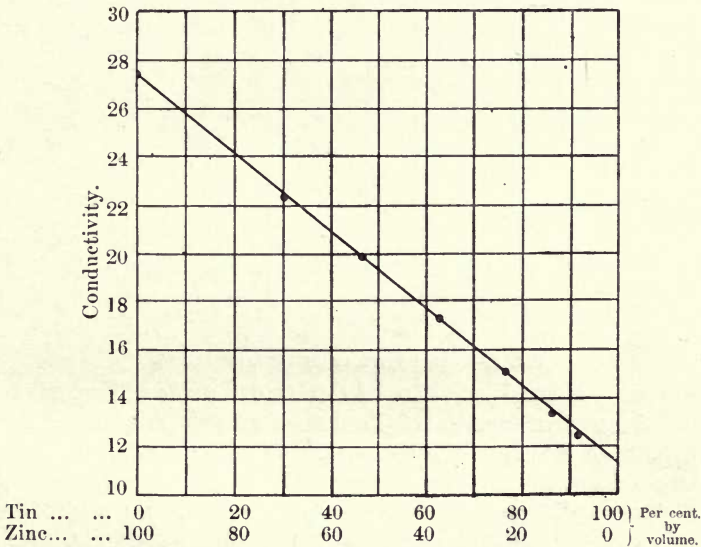


FIG. 3.—CONDUCTIVITY OF ZINC-TIN ALLOYS.

The metals belonging to this group are lead, zinc, tin, and cadmium, and the rule applies to alloys one with another.

It is obvious that the addition of a small quantity of one of these metals to another can have a very small effect on the conducting power, because the resulting

conductivity will be proportional to the volumes of the constituents present.

With alloys of the other metals with the members of this group or with one another, the result is very different. The conducting power of the alloy is always less than what it would be if the metals all behaved like the metals of the zinc-lead group. That is, when the curve is plotted, it will always lie entirely below the straight line

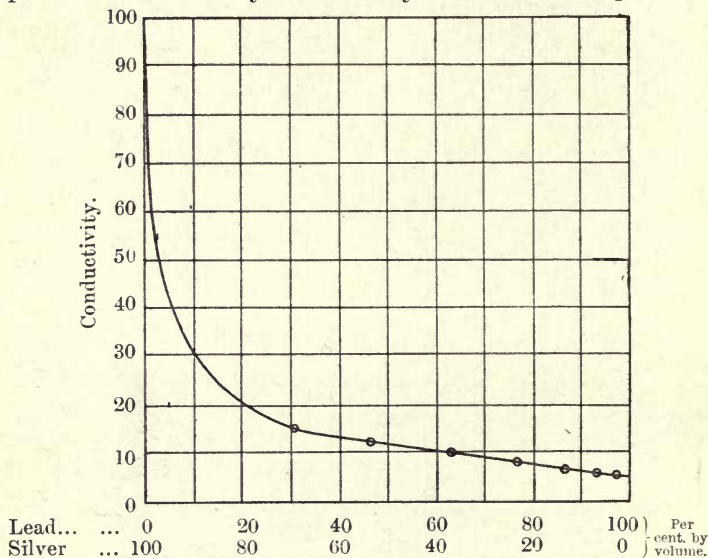


FIG. 4.—CONDUCTIVITY OF SILVER-LEAD ALLOYS.

joining the conductivities of the two metals. The curve itself may in general take two forms. Alloys of the metals of the lead-zinc group with other metals show a somewhat curious behaviour. If a small quantity of a metal of the lead-zinc group, say lead, be added to a metal not belonging to the group, say silver, it causes a very rapid diminution of conducting power, whilst the addition of a small quantity of silver to lead has a small effect on its conducting power. When the curve for such an alloy is plotted, it takes, therefore, somewhat of an L form, the vertical portion falling sharply, it may reach a minimum, in which case the continuation of the curve will rise, or it may continue to fall at a much reduced rate. The curve is

not always continuous, but may show a sharp break or change of direction, and these breaks do not seem to correspond to the formation of definite chemical compounds.

The curve for the silver-lead series is shown in Fig. 4.

With metals not of the lead-zinc series alloyed with one another the curve is somewhat different, for here the

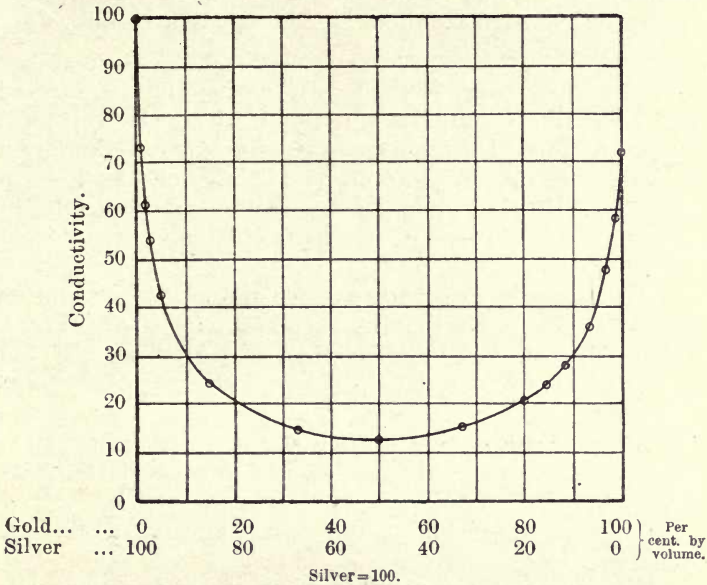


FIG. 5.—CONDUCTIVITY OF SILVER-GOLD ALLOYS.

addition of a small quantity of either metal to the other causes a rapid diminution of conductivity, and the curve therefore assumes a roughly U shape, the length of the two vertical arms being unequal and in the proportion of the conducting power of the constituent metals. The curve for the gold-silver series is shown in Fig. 5.

These curves can only be taken as examples, for in no two alloys are the curves the same. It may be that the curves in cases 2 and 3 are not true curves, but rather series of straight lines, the alloy behaving between each turning-point like an alloy of the lead-zinc series.

The bearing of these facts on the constitution of alloys will be discussed later.

**Electrolysis.**—When an electric current is passed through a compound either melted or in solution in a suitable solvent, the compound is broken up, and the two “ions,” which may be either elements or groups of elements, are separated at the electrodes. All attempts to electrolyse fused alloys have failed, they seeming to conduct in all cases like elements, *i.e.*, not to undergo decomposition. If any conclusion can be drawn from a merely negative result, it is that apparently alloys are not chemical compounds.

**Potential Difference.**—When two metals are connected by a metallic conductor and put into an electrolyte, a certain potential difference is set up between them and a current is set in motion. The behaviour of alloys in contact with their component metals may thus be of importance in throwing some light on the constitution of the alloys.

A. P. Laurie† has made a series of experiments on this subject. He found that in a cell—a cuprous iodide cell was used—using plates of copper, and of copper having pieces of zinc soldered to them, the electromotive force produced was the same as that produced with plates of copper and zinc, even when the quantity of zinc exposed was not more than  $\frac{1}{2000}$  of the area of the plate exposed.

He then tried alloys of copper and zinc, and he remarks :—

“There are three possible ways in which zinc-copper alloys may be constituted :—

“First : They may be merely mixtures of zinc and copper. In that case they would give the electromotive force of zinc in the voltaic cell.

“Second : They may be of the nature of the solution of sulphuric acid in water” (*i.e.*, solid solutions); “in that case a series of such alloys beginning with 100 per cent. of copper and ending with 100 per cent. of zinc would probably show a gradual rise of electromotive force in the cell, from the value for copper to that for zinc.

“Third : One or more of the series may be a definite atomic compound, the rest being solutions of this

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† Journal Chem. Soc., vol. liii., 1888, p. 105.

compound or compounds in an excess of zinc or copper ; in that case the electromotive force would probably rise by a jump when a series of alloys were tested a slight excess over that necessary for the compound, causing a great alteration of electromotive force in the cell. Further, this jump would probably occur where the percentage of zinc and copper corresponded with some simple molecular formula."

Fig. 6 shows the curve as actually obtained by Laurie. The upper portion is very irregular, this being

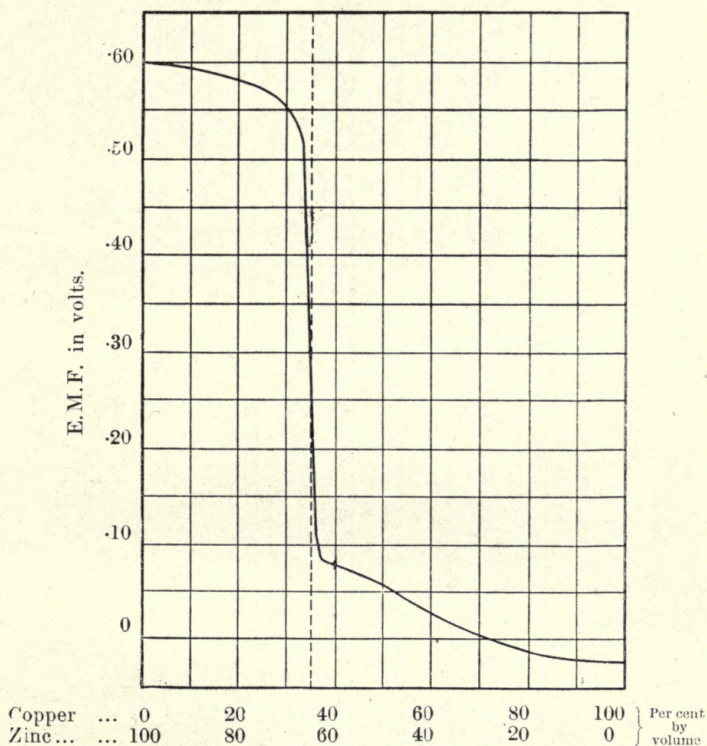


FIG. 6.—ELECTROMOTIVE FORCES OF COPPER AND COPPER-ZINC ALLOYS IN CUPROUS IODIDE.

due to irregularities in the alloy (these irregularities are not shown in the figure), but the general character of the curve is well marked. The electromotive force

remains constant at nearly that due to pure copper and zinc till about 32 per cent. of copper is present in the alloy, then it suddenly drops to a very small amount, and finally becomes nil, or, rather, in this case it becomes negative and the current is reversed.

There are many difficulties in obtaining perfectly concordant results with such experiments, but the general result is quite clear; and Laurie infers from this and other experiments the existence of a definite compound  $\text{Cu Zn}_2$  (32.71 per cent. Cu). In the case of copper-tin

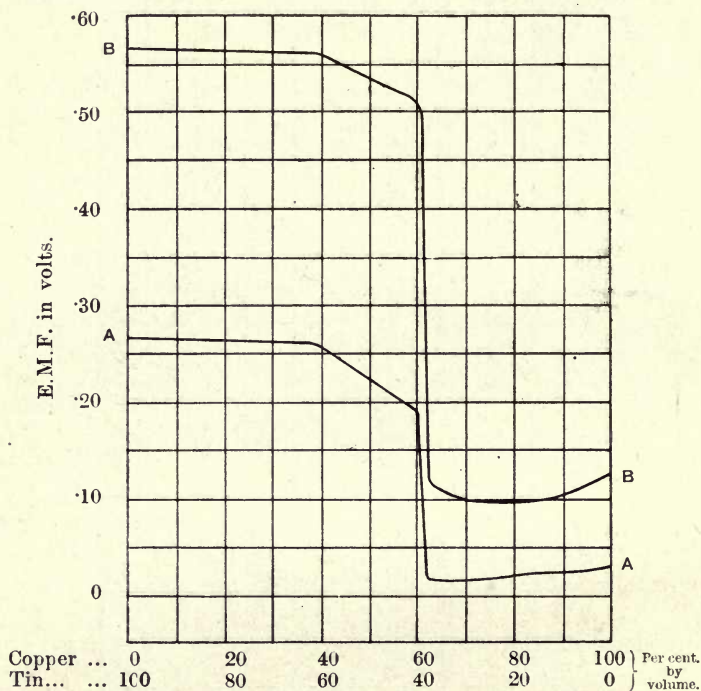


FIG. 7.—ELECTROMOTIVE FORCE OF COPPER AND COPPER-TIN ALLOYS.

AA in Stannous chloride.

BB in Stannous sulphate.

alloys (Fig. 7) exactly similar results were obtained, and he inferred the existence of a definite compound  $\text{Cu}_3 \text{Sn}$  (Cu 61.58 per cent.) and  $\text{Cu}_4 \text{Sn}$  (68.12 per cent. Cu).

Putting all these considerations together, it will be quite obvious that the constitution of alloys is not by

any means simple, and that the physical properties of the alloys do not enable us to form any conclusion as to what that constitution really is.

## CHAPTER III.

### THE PHENOMENA OF SOLIDIFICATION.

WHATEVER may be the exact nature of an alloy in the solid condition, in the liquid condition it is comparatively simple, and may be regarded as being a mixture of the two liquid metals, or, rather, as a solution of the one in the other. It therefore follows the law of solution, the two constituents tend to diffuse until the composition is uniform, and this diffusion can, of course, be greatly accelerated by agitation, by stirring, or otherwise. The few cases which are not solutions, but mere mixtures, and in which, therefore, the constituents will tend to separate according to their specific gravity, may be neglected as being of little importance.

The essentials of a solution, as far as they are of importance here, are :—

- (1) The constituents are uniformly distributed, so that the composition at all points is the same, and the constituents do not tend to separate even when very different in specific gravity ;
- (2) The constituents are in such a fine state of division that they cannot be detected by physical tests, and therefore the solution is essentially one substance.

When the solution solidifies this condition of things may or may not continue. The solution may solidify as a whole, in which case the resulting solid still retains some, at least, of the properties of the solution, and is called a solid solution, but more usually the conditions of equilibrium are disturbed, and a re-arrangement of the constituents takes place during solidification.

The phenomena of solidification have been studied in detail during the last few years, and much light has been thrown on the structure of complex bodies which have solidified from fusion, or from solution, for the



conditions which hold in the two cases are much the same, the principal difference being the actual temperature at which the solidification takes place. It is quite obvious that the fact that the solvent and the substance in solution are metals, and that a high temperature is required to keep the solvent in the liquid condition, cannot in any way alter the laws according to which the solidification will take place; so that the solidification of igneous rocks, alloys, and solutions of salts will follow exactly the same principles.

**Solidification of Pure Substances from Fusion.**—When a pure substance, whether it be an element or a compound, solidifies from fusion, the thermal phenomena

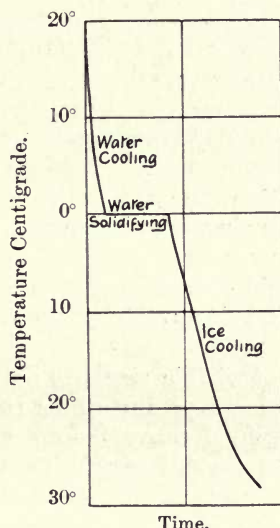


FIG. 8.—FREEZING CURVE OF WATER (DIAGRAMMATIC).

are very simple. The temperature falls steadily till solidification begins, then it remains constant till all the substance has solidified, then it once more begins to fall, and falls steadily. There is thus always a fixed and definite melting point, and either when the solid is melting or the liquid is freezing the temperature remains constant at that point, till the change is completed. If, therefore, a freezing

curve be drawn, the ordinates being the temperatures, and the abscissæ times of cooling, it will take the form represented in Fig. 8, which represents diagrammatically the freezing curve of water.

Solidification, of course, always begins at the points where cooling is most rapid, that is, almost invariably at the outside. Crystals begin to form, and these grow inwards into the still liquid mass, very likely crossing and interlacing so as to form a net-work, and ultimately the liquid within the net-work solidifies and binds the whole together; but there is no difference in composition between the substance which freezes first—that is, the first formed crystals—and that which freezes last, the inter-crystalline material. Whether the resulting solid mass will show a distinctly crystalline structure or not will depend largely on the size of the crystals which form and on their character. In the case of a metal, if the crystals are large and have a good cleavage, the fracture will almost always appear crystalline, but if not it will probably be granular.

When crystallisation begins, as it very frequently does, at many centres throughout the mass, the crystals as they grow will press against one another, the true crystal form will be obliterated, and a granular structure will result, the grains being allotriomorphic or distorted crystals.

Distinct crystals of visible size will only be produced when, owing to shrinkage or any other reason, the still liquid material is drained away before solidification is complete, leaving the crystal projecting into a cavity. Occasionally, large crystals of metals are formed in this way.

**Solidification of Solutions.**—A solution may be considered as a homogeneous liquid mixture of two substances with different solidifying points, it matters not whether one or both be solid at ordinary temperatures. The way in which a solution will solidify will vary very much with the way in which the constituents behave to one another in the solid condition.

As an example, the behaviour of a solution of common salt (sodium chloride) in water will be considered, as

this will give a key to the more complex phenomena which take place in the solidification of alloys.

**Solidification of a Solution of Salt.**—Salt will dissolve in water in varying proportions up to about 25 per cent., the exact amount required for saturation depending on the temperature. The phenomena which occur during solidification depend on the amount of salt present.

First: The case of a very dilute solution, one containing not more than, say, about 1 per cent. of salt. Suppose a thermometer capable of indicating small changes of temperature to be immersed in it, and the temperature to be slowly reduced. The temperature falls, and when it reaches  $0^{\circ}$  the water does not freeze. At  $-0.6^{\circ}$  C., however, solidification begins, the curve representing the thermal change being exactly similar to that representing the freezing of water, except that the halt in the fall of temperature takes place at a slightly lower temperature than in the case of pure water. The solid mass is no longer pure ice, but contains salt, and is, in fact, a solid solution of salt in ice.

This is one of the fundamental phenomena of the solidification of solutions. The solution always solidifies at a lower temperature than the freezing point of the solvent. The lowering of the freezing point depends on the quantity of the foreign substance present, and on its molecular weight, the lowering being the same for the molecule of any soluble substance, so that the lowering of the freezing point gives a means of determining the molecular weight of solid bodies in solution. The molecular depression of the freezing point in the case of the solution of salt in water is given as  $35.1^{\circ}$  C. That is, if the molecular weight (58.5) in grammes of salt could be dissolved in 100 grammes of water the freezing point would be reduced to  $-35.1^{\circ}$ . This is impossible, as water will not dissolve such a large amount of salt, but the reduction by the solution of any given weight of salt will be in the same proportion, so that 1 per cent. of salt will lower the freezing point to  $-0.6^{\circ}$  C.

Now consider a solution containing, say, 10 per cent. of salt. On cooling, the temperature will fall to about  $-6^{\circ}$  before solidification commences. Then there will be a

halt of cooling as before, and when the mass has apparently solidified, the temperature will continue to fall, but when a temperature of  $-22.5^{\circ}$  is reached, there is another halt in the cooling. In fact, the solution has no longer solidified as a whole. At the higher temperature the ice containing a small quantity of salt solidified, or rather, commenced to solidify, the solidification then going on continuously, the mother liquor still left liquid being gradually enriched in salt, till at  $-22.5^{\circ}$  it solidified. So that it is hardly correct to

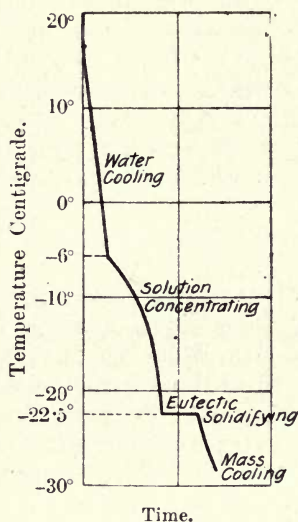


FIG. 9.—COOLING CURVE OF 10% SALT SOLUTION (DIAGRAMMATIC).

say that a solution containing 10 per cent. of salt has a definite freezing point unless it be the point at which solidification is completed. It has, in fact, two freezing points, the one that at which solidification begins, the other that at which it is completed. The former varies with the percentage of salt, the latter is fixed.

Fig. 10 shows diagrammatically the phenomena of the solidification of a solution containing 10 per cent. of salt.

If now a still stronger solution be examined, an exactly similar result will be obtained, the first freezing point

will be a good deal lower, but the second will be as before at  $-22.5^{\circ}$ . If a solution containing 23.6 per cent. of salt be taken, the temperature will fall continuously to  $-22.5^{\circ}$ , when it will remain constant till the whole has solidified, exactly as is the case with pure water.

If a solution slightly stronger in salt be used, salt will crystallise out till the temperature falls to  $-22.5^{\circ}$ , when the mother liquor containing 23.6 per cent. of salt will solidify as a whole.

The solidifying temperatures, or freezing points, of a series of salt solutions are shown in Fig. 10, the freezing point curve. The ordinates represent temperatures,

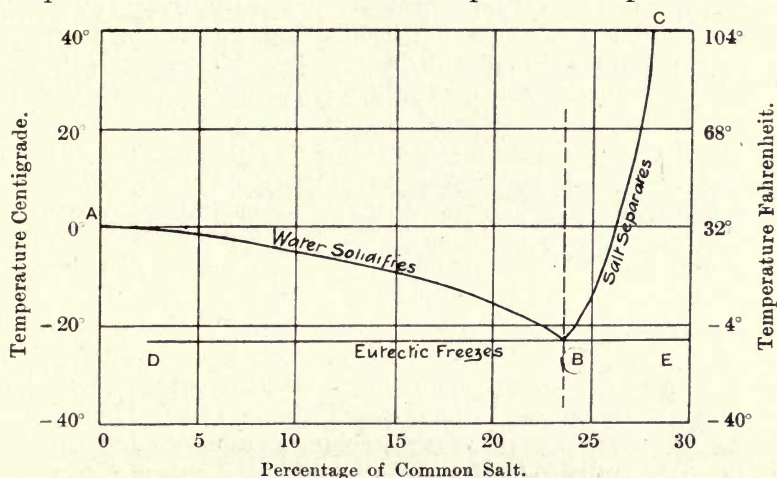


FIG. 10.—FREEZING-POINT CURVE OF SALT WATER.

the abscissæ the percentages of salt in the solution. The line A B shows the temperature at which freezing begins, and B C the temperature at which the precipitation of salt begins, whilst D E shows the temperature at which the mother liquor finally solidifies, which, as will be seen, is constant, and begins to be observed as soon as the total quantity of salt is in excess of that which the solid ice can hold in solution.

The actual phenomena in the case of salt and water must be carefully considered, as an understanding of them will help to make the changes which take place during the solidification of alloys clear.

Consider again, what happens when a solution of salt containing, say, 10 per cent. of salt freezes. As soon as the freezing point, due to the percentage of salt present, is reached, the water begins to freeze, and as it does so it ejects some of the salt from solution, thus making the remaining solution stronger in salt, and therefore, having a lower freezing point. As the temperature continues to fall the freezing point of this solution is reached, and more salt is ejected, and this continues till the residual solution or mother liquor contains 23.6 per cent. of salt, when it solidifies as a whole. It will thus be seen that the upper freezing point is that which is determined by the percentage of salt actually present, and is the temperature at which the solidification begins, but this temperature does not remain constant during solidification, as in the case of pure water, because the freezing point is gradually falling. As the water solidifies heat is evolved, so that the fall of temperature is retarded, but the temperature line does not remain horizontal; it rather slopes downwards in the form of a curve convex upwards, as is shown in Fig. 9. The mother liquor, which freezes at  $-22.5^{\circ}$ , is of peculiar character. It has a definite percentage composition, but it is not a chemical compound, for the constituents are not present in simple atomic proportions. It is found to consist merely of an intimate mixture of salt and ice, the two being arranged in more or less parallel plates of microscopic size. Such a solidified mother liquor is called in the case of aqueous solutions a cryohydrate, or more generally in the case of all solutions a eutectic.

**Eutectic.**—A eutectic is the portion of any solution or alloy which is the last to solidify as the solution is slowly cooled. It has a definite composition and freezing point, depending only on the substances which it contains, and this is the same from whichever end of the series it is approached. For example, in the case of salt and water, whether it is reached by the cooling of a dilute solution or a very strong solution. The constituents of a eutectic are very rarely, and then only accidentally, present in proportions approaching a simple atomic ratio, and the eutectic is always a mixture of the two substances in distinct portions which have separated in contact.

Eutectics in the case of metallic alloys will be fully discussed later, but it is very important at the outset to have a clear idea of the meaning of the term.

**Solidification of Metallic Alloys.**—The idea of a solid solution has already been alluded to, and it is one that must be kept in mind in considering the phenomena now to be described. Molten alloys may be considered as being solutions of the one metal in the other, but whether this condition will be retained during solidification will depend on circumstances.

Three possible conditions may be considered :—

- (1) The metals are quite insoluble one in the other in the solid condition.
- (2) The metals are soluble to some extent the one in the other in the solid condition.
- (3) The metals are soluble one in the other in the solid condition in all proportions.

Conditions 1 and 3 are probably not to be met with, but they are limiting conditions which may be approached if not actually reached, and which for simplicity may be considered in illustration of the subject.

(1) **Metals which are insoluble one in another in the solid condition.**—It is assumed that they are soluble in one another in all proportions whilst in the liquid condition, but that they are insoluble one in the other in the solid condition ; and that, therefore, whilst the melted metals will form a homogeneous solution, they will separate from one another completely on solidifying.

Let the metals be called A and B, and consider first the case of an alloy consisting mainly of B, but containing a small percentage of A, B being the metal of higher solidifying point. What will happen as the mass solidifies will be something as follows : As the temperature falls, solidification will begin at a temperature somewhat below the actual freezing point of B, because A being in solution in B will lower its freezing point. As B solidifies A will be ejected, and thus the mother liquor will become richer and richer in A, and the freezing point will continue to fall, the cooling curve, owing to the evolution of heat during solidification, being convex upwards. As the temperature

continues to fall A will continue to be ejected, and therefore the mother liquor to become still richer in A, and therefore its freezing point to fall, until a point may be reached when the freezing point of the mother liquor is the same as that of A, then A and the remainder of B will solidify at once, separation, of course, taking place at the moment of solidification, and a solid eutectic, consisting of a mixture of the two metals, will be formed. Or, if the freezing point of the mother liquor, even when containing an unlimited quantity of A, should be above the freezing point of A, then the material to solidify last will not be a true eutectic but pure A.

In either case, on the solidification of an alloy of A and B in any proportions whatever there will be two solidifying points, the upper one depending on the quantity of A in solution; the lower one being the freezing point of A, and the material however solidified will be merely a mixture of the two metals A and B. Such cases are not by any means common, but the condition is nearly approached in the case of a mixture of copper and bismuth, the latter metal always separating, and thus rendering copper containing it very brittle.

An alloy which contains a eutectic is said to be "eutectiferous," and in the case of metals related as A and B are supposed to be, it will be eutectiferous in whatever proportions the metals may be present.

(2) **Metals which are soluble one in another.**—Now, the other extreme case, that in which the metals are soluble one in the other in all proportions both in the solid and liquid conditions, may be considered. In this case the conditions will obviously be very different from those in the first case. In considering the changes which take place, a liquid solution of a small quantity of a metal C in a larger quantity of a metal D of higher melting point may be taken as an example.

As the solution cools, solidification will begin at a temperature below the freezing point of D, the exact temperature being determined by the amount of C present. As solidification goes on, the solidified mass will not be pure D, but will be D containing a certain amount of C



in solution, but it will be poorer in C than the original liquid mixture, some C being ejected and the mother liquor becoming richer and richer in C, and each layer or portion of D as it solidifies being richer in C than that which solidified before it, so that if a sample could be taken it would be found that the percentage of C in the alloy gradually increases from the first to the last portion solidified, so that the alloy will not be homogeneous. If a eutectic be defined as solidified mother liquor, or as the portion of the alloy which solidifies last, then, of course, there must be a eutectic in every alloy, but in this case it will not have the true eutectic structure, *i.e.*, it will not be a mixture

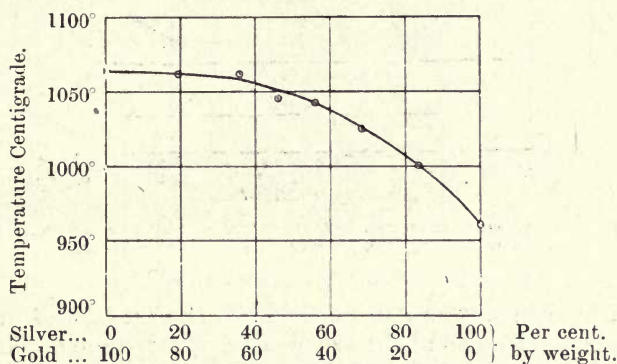


FIG. 11.—FREEZING POINT CURVE OF SILVER-GOLD ALLOYS.

of the two metals, but will be simply a more concentrated solution of the one metal in the other, and such an alloy is best called a non-eutectiferous or solid-solution alloy.

Such an alloy can have no fixed freezing point, but a more or less extended freezing range. There will be a definite point at which freezing begins, and a definite point at which it ends, and the first of these will always be more sharply marked than the latter, indeed, the latter may hardly be noticeable.

The best marked series of alloys of this character is that containing gold and silver, the freezing points of which are shown in Fig. 11, and these freezing points, of course lie between those of pure gold and of pure silver.

**Metals which are More or Less Soluble one in the Other.**—The two cases already considered are of a somewhat special character, and are of rare occurrence. The case now to be considered is one which is much more general.

An alloy consists of two metals, A and B, each of which is to a certain extent soluble in the other in the solid condition. Let it be assumed that A in the solid condition

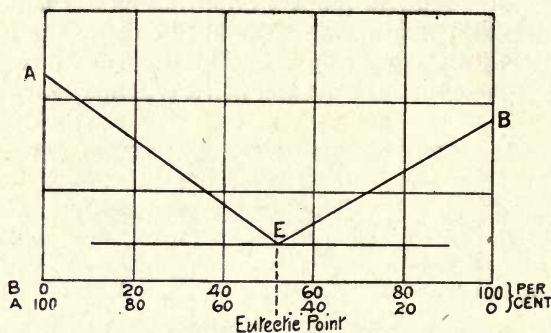


FIG. 12.—DIAGRAM OF FREEZING POINTS OF ALLOY OF A AND B WHEN A AND B ARE EACH TO SOME EXTENT SOLUBLE IN THE OTHER.

can hold in solution 10 per cent. of B, and that B in the solid condition can hold 10 per cent. of A; here obviously will be a combination of the two conditions previously considered.

If an alloy of A and B contains less than 10 per cent. of B it will behave exactly like the alloy of the metals which were soluble in all proportions. The solidification will begin at a temperature dependent on the quantity of B present, and will continue with a continuously falling temperature till the whole is solid. There will be a comparatively short freezing range, and no eutectic in the ordinary sense will be formed, since the portion of lowest freezing point will be a solid solution. If the alloy contains more than 10 per cent. of B the phenomena will be exactly the same up to the 10 per cent. point, then the solidification will continue, the mother liquor becoming more and more concentrated till at last a point is reached where the mother liquor will solidify, separating at once into its two constituents

A saturated with B and B saturated with A, a true eutectic in either case. If the start be made at the other end of the series the phenomena will be exactly similar, and the eutectic solidifying point will be reached at the same temperature and with the same proportions as when the start is made from the A end. The freezing point curve will be of the form shown in Fig. 12A. At either end alloys rich in one metal and poor in

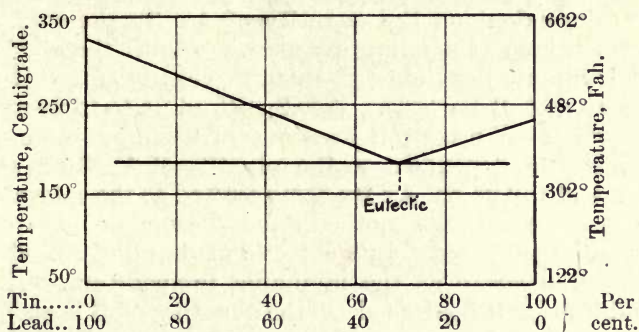


FIG. 13.—FREEZING POINT CURVE OF LEAD-TIN ALLOYS.

another will solidify as solid solutions; in the intermediate range there will be a definite eutectic formed which will, of course, always solidify at the same temperature. There will be a range of solidification in which the alloys of A and B will be non-eutectiferous, and an intermediate range in which they will be eutectiferous.

This is a very common condition. It is the condition of ice and salt, and it is well shown in the freezing point curve of alloys of tin and lead shown in Fig. 13.

#### ALLOYS OF METALS IN WHICH A DEFINITE CHEMICAL COMPOUND IS FORMED.

It has been assumed in the cases already considered that the metals do not form any chemical compound, but in many cases they do so combine, and this complicates still further the conditions of solidification by the introduction of new conditions. It is quite obvious that the chemical compound formed may be completely soluble, partially soluble, or quite insoluble in either or both of the metals in the solid condition.

It will be sufficient to consider one case. Suppose two elements A and B to form a compound  $A_x B_y$ , and that this compound is to some extent soluble in both the metals.

Now, starting with an alloy containing a small quantity of B and a large quantity of A, the whole of B will unite with some of the A to form the compound  $A_x B_y$ , and if there be not too much of this it will remain in solution in the solid condition. Freezing will begin at a temperature dependent on the quantity of  $A_x B_y$  present, and will continue at a falling temperature until the whole is solid, the mother liquor gradually concentrating. If the quantity of B be larger, it will still all unite to form  $A_x B_y$ , which will dissolve. Freezing will begin as before at a temperature dependent on the quantity of  $A_x B_y$  in solution, and will go on,  $A_x B_y$  being ejected as the saturation point is passed, the mother liquor becoming more concentrated till ultimately a eutectic made up of A and  $A_x B_y$  will separate at the minimum temperature. These conditions will hold good till the quantity of B is such as

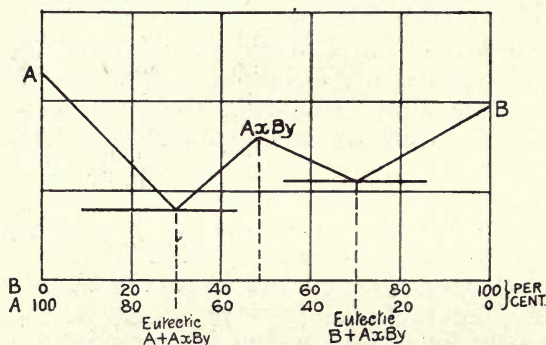


FIG. 14.—DIAGRAM OF FREEZING POINTS OF ALLOYS IN THE CASE OF METALS A AND B, WHICH FORM A DEFINITE COMPOUND  $A_x B_y$ , WHICH IS TO SOME EXTENT SOLUBLE IN BOTH METALS.

to give the eutectic composition for A and  $A_x B_y$ , when the mass will solidify as a whole. As the quantity of B is increased, the conditions will be different, the quantity of  $A_x B_y$  will be greater than the eutectic proportion; the freezing will therefore begin at a temperature higher than the eutectic point, but lower than the freezing point of

the compound  $Ax By$ . When the quantity of B in excess is so small that it can remain in solid solution in  $Ax By$ , the eutectic will disappear, and when the proportions are such as to exactly form  $Ax By$  this will solidify as a whole at a definite point. Alloys containing more B will be first solutions of B in the compound  $Ax By$ , till the point is reached when a eutectic of  $Ax By$  and B is formed; then  $Ax By$  will be in solution in B, and so on, so that ultimately the curve will take the form shown in Fig. 14.

There are, of course, other possible conditions, but the cases explained will serve as illustrations, and will enable the changes which take place under other conditions to be understood.

When there are three or more constituents present, the conditions may become more complex.

#### CONDITIONS OF HOMOGENEITY.

It will be seen that, as a rule, a solidified mass of metal will not be homogeneous, there being indeed only three conditions when perfect homogeneity may be expected, viz., when the substance is a pure metal, when it is a definite chemical compound, and when it consists of two constituents either or both of which may be elements or compounds in the exact eutectic proportion.

**Conditions of Solidification.**—The heterogeneity of a solidifying solution must, of course, lead to a corresponding structure of the solidified alloy, but what will be the practical result will depend on the way in which solidification takes place.

For simplicity, it may be best to assume first of all a cylinder or sphere of the liquid material cooling uniformly from outside, so that the solid material is formed in thin layers or shells, one within the other. In that case, at any moment there will be a solid mass outside, and a liquid mass within separated by a thin layer just in process of solidification. Using geographical terms, Prof. Howe suggests that the portion already solidified should be called the solid continent, the liquid portion the sea, and the zone just between the two the littoral or shore region. In the case under consideration, the solid

continent will gradually extend inwards, the sea gradually shrinking and ultimately disappearing. It is quite evident that the centre of the mass will be the last to solidify.

If the alloy solidifies as a whole, and yields a perfectly homogeneous solid, the portion which solidifies last will not differ in any respect from the portion which

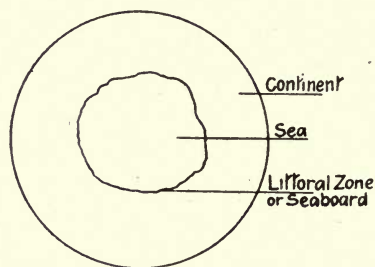


FIG. 15.—IDEAL SECTION OF A COOLING INGOT.

solidifies first, and it will remain liquid to the last simply because being surrounded by a mass of hot metal it can only cool more slowly.

On the other hand, if the alloy be not one that has a definite freezing point, the mass in the middle which last solidifies will be that of lowest melting point, either the solid solution of lowest melting point or the eutectic as the case may be. In the former case, there will be a gradual transition from the composition of the outer layers to that of the inner, with no line of demarcation between the two; whilst in the latter there will be a more or less sharp line of demarcation between the first solidified solution outside and the eutectic mixture within.

In either case, the segregation or separation into portions of different composition will be more or less well marked, and chemical analysis would show a progressive change in composition inwards. For very many reasons, solidification never takes place in quite such a simple way.

The line bounding the continent and the sea is never a plane surface parallel to the cooling surface, for the solidification takes place by the irregular growth inwards of crystals of the solidifying materials, so that the continent becomes extended into peninsulas projecting

inwards into the sea, and the sea thereby becomes broken up into bays, and as the crystal growth does not take place by any means regularly, the crystals grow not only directly inwards, but cross from one side of the bays to the other, so ultimately the mother liquor becomes broken up into a series of pools, or it may be squeezed into

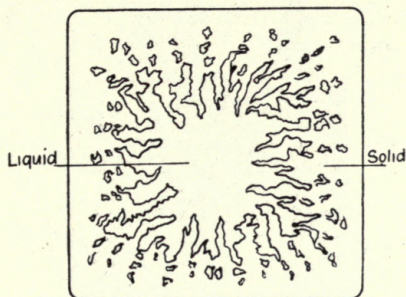


FIG. 16.—IDEAL SECTION OF A SOLIDIFYING INGOT, SHOWING HOW LAKES OF LIQUID MATERIAL MAY BE ENTANGLED IN THE SOLID MASS.

thin strings. In this way, whilst there is still the separation of the various constituents, there is not the same distinct segregation that would be under the conditions described above.

These can only be regarded as examples, for there are many other ways in which solidification may take place. It may, for instance, begin at many places in the mass at once, the solid matter growing from these solidifying

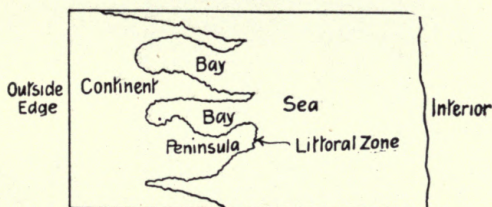


FIG. 17.—DIAGRAM OF MODE OF SOLIDIFICATION.

centres until they meet, the last solidifying mother liquor being squeezed into the spaces between the solidifying masses, and forming a network which may, of course, be reduced to mere strings.

Examples of these will be seen later.

**Segregation.**—From what has been said it is evident that as an alloy solidifies, there may be more or less of segregation or actual separation of the parts. If the mode



FIG. 18.—CRYSTALLISED IRON.

of solidification at all approaches to the first condition described above this may be very marked. It may happen that the solidifying mass may be more or less



free in the mother liquor, that is, unattached to the already solidified continent, and in that case if there be any great difference in specific gravity the heavier mass will tend to sink and the lighter to rise, so that there may be a distinct segregation in the casting not inwards but upwards. The phenomena of segregation are well known to the makers and users of certain alloys, and cause no little trouble.

**Prevention of Segregation.**—From what has been said, it is clear that the lack of homogeneity of the alloy cannot be prevented, because it depends on the natural laws of cooling, but the injurious segregation may be minimised if not prevented. As a rule, the more slowly the mass is frozen the more perfect will be the separation, whilst the more rapid the freezing the better will be the mixture of the constituents. For example, zinc will only retain in solid solution about 1.5 per cent. of lead, and yet if a mass of zinc be cast in such a way that it cools very rapidly, a much larger quantity will apparently be retained, but this excess consists of lead, containing a small amount of zinc in solution, scattered through the mass in very minute shots or masses. On remelting and cooling very slowly, a considerable portion of the heavy lead alloy may separate out.

**Liquation.**—As most solidified alloys consist of two portions, of different melting points, it is sometimes possible to melt or liquate out the more liquid portion. This is only possible under certain conditions, for reasons to be described later.

A very good example of this is in the case of copper and lead. These metals do not remain alloyed, but on solidification copper containing a little lead separates and rejects lead containing a little copper; but if the solidification be sufficiently rapid the two may remain intermixed. If the mixture be heated to just above the melting point of lead, the lead will melt and run out. Advantage was taken of this in the old Freiberg method of separating copper and silver, the silver dissolving in, and liquating out with, the lead.

In many cases, there is a tendency for the portion of an alloy of lowest melting point to "sweat" out on heating.

This is well seen in the case of highly-sulphurous pig iron, where globules of an iron and iron sulphide eutectic are often to be found on the surface of the pig, forced out by the pressure of the cooling and contracting metal on the still liquid material.

### SOLUTION OF GASES IN METAL.

Liquids always dissolve gases, but the conditions are somewhat different from those which hold in the case of solutions of solids or of other liquids. The amount of gas dissolved depends, of course, on the character of the gas and its solubility relation to the liquid, and it also depends on the temperature. There is always a temperature, or perhaps a range of temperatures, at which there is a maximum solubility, the solubility decreasing both at higher and lower temperatures, the gas being always—except in cases of chemical combination—expelled at the boiling point of the liquid, and also to a large extent, though frequently not completely, at the solidifying point. The solution of a gas usually causes expansion, so that the resulting solution has a lower specific gravity than that of the solvent.

The coefficient of solubility of gases in molten metals and alloys has not been determined, all experiments that have been made being on the solution of gases in water, saline solutions, and a few other liquids, so that the actual solubility of the gases in metals is not known.

The gases which are likely to be dissolved in molten metal are few in number. The metal may come in contact with oxygen or nitrogen from the air, hydrogen from the decomposition of water, carbon dioxide and carbon monoxide from the combustion of the fuel, and in certain cases also sulphur dioxide from the fuel. Oxygen is rarely likely to be present as such, but will probably be in the condition of dissolved metallic oxides, since most of the metals are easily oxidised at temperatures above their melting points. The gases in solution would be completely expelled if the metal were heated to near its boiling point, but this is not a practicable condition. If one constituent of the alloy be volatile at the temperature it may carry off with its vapour a considerable quantity of dissolved gas. Thus, in brass

making the volatilised zinc probably carries away with it much of the dissolved gas.

On freezing, most of the gas will probably be given off, and under certain conditions may lead to the formation of blowholes. The gas is separated much in the same way that solids are separated, but being much lighter than the liquid always tends to rise and thus escape. But bubbles of gas disengaged in a liquid are often very easily retained. They tend to adhere to a smooth surface, and thus may become enclosed in solidifying metal, and also as the solidification of the metal does not take the form of smooth surfaces, but of irregular growths projecting outwards into the liquid mass, gas bubbles may easily become entangled and surrounded by metal. Just as a fragment of solid matter in a solidifying solution tends to determine the solidification of the metal round about it, so a bubble of gas once formed tends to increase in size by the accumulation of more gas, the bubbles thus elongating and growing inwards.

The phenomena and results of gas evolution from cast metals may vary much—

(1) If the mass of metal or alloy be very fluid, *i.e.*, not pasty, and the solidification be very slow, a large portion of the gas may escape and thus do no harm to the casting. To ensure this, the upper parts of the casting must be kept liquid to the last, or if this be not possible, a head of liquid metal must be provided into which the escaping gas can rise, and the unsound portion thus produced can be cut off.

(2) If the mass be more or less pasty or the solidification be very rapid, or if the gas be not separated till solidification has gone on to a considerable extent, the gas may be retained in the form of bubbles, and thus produce blowholes. These will usually be more or less lenticular in form, with their long axes at right angles to the surface of solidification.

The formation of blowholes in steel has been more fully studied than in any other metal, but probably the same laws would hold good in all cases. The term blowholes should only be applied to these small bubbles, not to the larger masses of gas which accumulate in the upper part of the casting by the collection of gas which has

actually been given off, but is unable to escape, and which may produce larger or smaller gas cavities near the top of the casting.

(3) Under some conditions gas may actually be retained in solid solution, in which case of course it cannot cause blowholes.

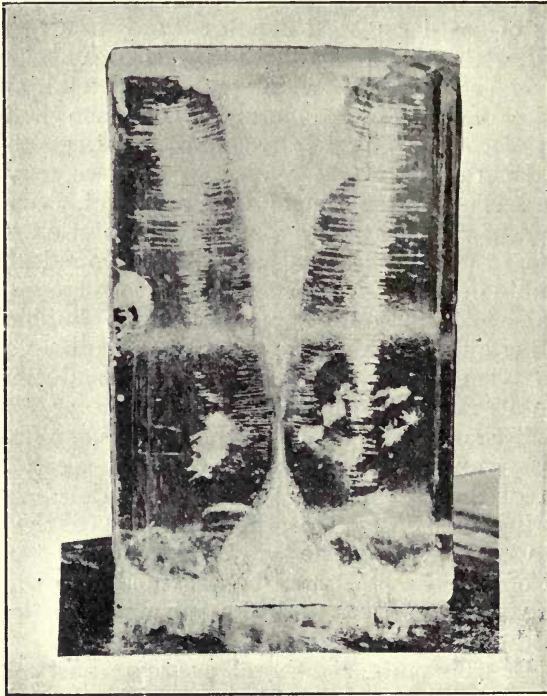


FIG. 19.—BLOCK OF ICE, SHOWING ARRANGEMENT OF AIR BUBBLES. THE OPACITY OF THE CONICAL PORTIONS IS DUE TO A MASS OF AIR BUBBLES. THE IRREGULAR WHITE PATCHES ARE WHERE THE SURFACE HAS BEEN DAMAGED BY THE DOGS USED FOR LIFTING.

**Prevention of Blowholes.**—The means of preventing unsoundness due to blowholes may be of three kinds :—

(1) The addition of substances which will destroy the gas in solution.

(2) Treatment of the metal so as to facilitate the escape of the gases.

(3) Treatment of the metal so as to retain the gas in solution.

The first method is rarely practicable, since if the gases are nitrogen, hydrogen, and the oxides of carbon they are not likely to be removed chemically by the addition of any reagent. The addition of easily oxidisable substances such as phosphorus or silicon may destroy the oxides of carbon, if present, but their action is probably mainly on solid dissolved oxides which may impair the strength of the metal, rather than on gases.

The second method is in general use. Agitation during solidification often has a good effect, but is in general impracticable. Slow cooling and keeping the upper portion of the metal liquid to the last, so as to allow free escape of gas, is usually all that can be done.

The third method may be carried out either by chemical or mechanical means. The addition of certain substances, usually metals, seems often to suddenly stop the evolution of gas, as it is unlikely, at least in most cases, that chemical changes have taken place by which the gas has been converted into a solid or liquid, the "quieting" can only be produced by a change which enables the gas to be retained in solution up to and after solidification. This is probably the action of silicon and aluminium on steel castings. As the solubility of gases in various alloys is not known, it is impossible to say which metals would increase the solubility in any particular case.

**Casting Under Pressure.**—Sound castings may very often be secured by casting under pressure, the pressure being obtained either by the use of a hydraulic press, gas pressure, or liquid pressure obtained by a head of metal.

The way in which pressure acts is somewhat uncertain. The action may be of three kinds, and probably all three may take place together.

Since pressure facilitates the solution of gases, the gas may actually be retained in solution, in which case casting under pressure would fall under the third division of methods above mentioned, and probably this action always takes place to some extent. On the other hand the pressure may actually squeeze the liberated gas out of the casting. This probably always happens to some extent, and in many cases the escape of gas can be dis-

tinctly noticed. In other cases, the pressure may simply compress the gas, and thus make the cavities which it forms so small as to be of little moment. As the volume of gas is inversely proportional to the pressure to which it is subjected, it will be reduced to one-half the volume which it would occupy under atmospheric pressure by a pressure of 15lbs. per square inch, and a pressure of 10 tons per square inch, which is often exceeded when steel is cast under hydraulic pressure, would diminish the volume of any separated bubbles to about  $\frac{1}{2900}$  of their normal volume, and under these conditions they might be so small as to be of little importance.

## CHAPTER IV.

### WHAT THE MICROSCOPE CAN TEACH.

#### I.—METHODS.

THE structure of metals as shown by a fracture has always been a factor in the judgment of the quality of the metal, but until recently only the appearance to the naked eye, or at anyrate as seen by a hand magnifier, could be taken into account.

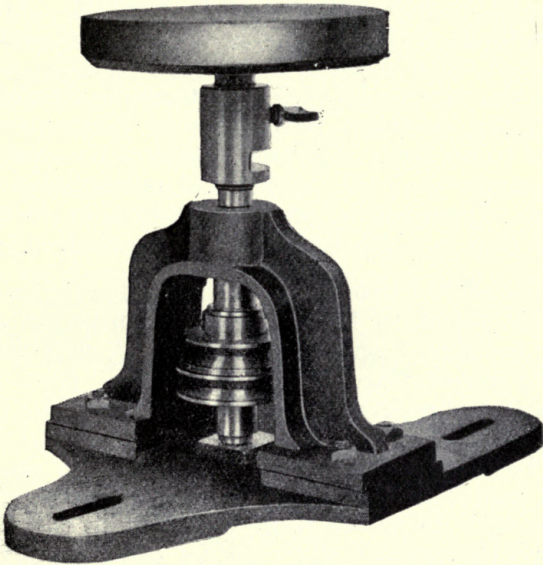


FIG. 20.—BAIRD & TATLOCK'S POLISHING MACHINE.

The fracture is of some importance, but for various reasons it is always an uncertain guide, the appearance depending as much on the way in which the fracture is obtained as on the structure of the metal itself, so that

it is always of limited value, except in certain special cases.

In 1864 Dr. Sorby suggested, and actually used the microscope for the examination of the structure of metals. He was, however, much before his time, and but little attention was paid to his work, and the wonderful results he obtained were almost completely overlooked. Slowly, however, the value of his work came to be understood, and other workers entered upon the field, and now the use of the microscope has become quite general for the examination of metals, and soon a metallographic laboratory will be regarded as being as essential as a chemical laboratory in a well-equipped works. There can be no doubt as to the real value of the results of microscopic investigation, but as is always the case with new methods, some workers over-rate its power and value, and expect far too much from it. Like all other methods of research, it has its own field, and there only is it of value.

For the microscopic examination of metals three things must be taken into account: The microscope which is to be used; the preparation of the sample for examination; and the methods of examination to be adopted. These will be briefly considered in the reverse order to that in which they have been named.

**Principle of the Methods Used.**—In all ordinary microscope work the object to be examined is transparent and is viewed by light transmitted through it, and reflected up by a mirror placed below the stage. Even in the examination of rocks and minerals the samples are ground so thin as to be transparent, and are examined in this way. With metals this is impossible, as they cannot be ground into such thin films as to be transparent, for however thin the metal, it is always quite opaque, and therefore the sample can only be examined by light reflected from the surface.

If the fractured surface of a piece of metal be examined with a microscope, nothing of the real structure can be made out, as appearance of the fracture depends on so many conditions that it throws but little light on the real structure, and, further, the surface is sure to be so



irregular that it is quite impossible to get more than a few points of it into focus, and the surface will often be covered with accidental markings which are of no importance.

To allow of focussing, the sample must have a perfectly plane surface, and this is obtained by polishing. A surface may seem perfectly smooth and bright to the eye, but when examined under the microscope even with a low power it is seen to be covered with scratches which look like deep grooves and effectually hide the real structure.

**Preparation of the Sample.**—The first thing to be done in the preparation of a sample is to obtain a surface perfectly smooth and free from scratches. This is done by means of a series of polishings, a finer polishing material being used at each stage than for the one before, so that at each polishing all the scratches are removed, and if the surface is not left perfectly smooth, the scratches left are much finer. This step-by-step polishing is essential because the abrading power of the polishing materials used for the last stages is so small that it would take a very long time and a large amount of labour, even if it were possible at all, to remove the amount of substance necessary to reach the bottom of the deep coarse scratches.

The polishing may be done by hand by carefully rubbing the sample on the polishing material mounted on suitable blocks, and excellent results can be obtained by this method, though it is laborious and somewhat tedious. Where very careful work is required it is still probably the best method which can be used. One of the conditions laid down by the Director of the National Physical Laboratory for an investigation into the structure of steel which is being undertaken by many independent observers is that the polishing shall be done entirely by hand.

Most workers, however, prefer the use of a machine of some kind, and there are several on the market. The machine consists of a disc of wood or metal suitably mounted so that it can be rotated at a very high speed by hand or foot, or by a small motor. On this disc the polishing material is mounted and the sample, held either in the hand or in a small holder, is kept in contact with it till the polishing is complete.

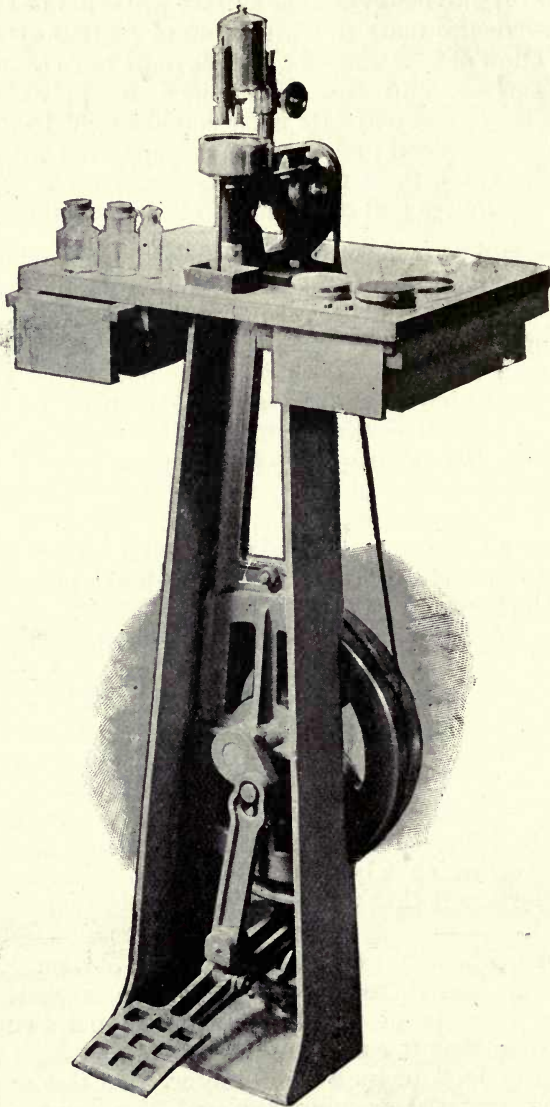


FIG. 21.—STEAD'S POLISHING MACHINE.  
(Made by Messrs. Carling & Co., Middlesbrough.)

Emery cloth and similar materials may either be glued to the disc or held in place by a metal ring, whilst the powdered polishing materials are spread on a piece of cloth, velveteen, or selvyt, stretched tightly on the disc, or for very fine polishing, a double layer of cloth may be used, the powder being put between the two layers, when enough works through to polish the specimen. As the sample is apt to get very hot during polishing it is kept wet, best by allowing water to drip on to the disc during the operation.

There is no difficulty in polishing hard substances, but soft metals are exceedingly troublesome, as the surface tends to flow rather than to be polished away. The original structure of the metal may thus be completely destroyed, and scratches and other marks may not be removed, but only covered by the surrounding metal being forced over them. Very brittle substances are apt to break away in minute fragments which, getting on the polishing disc, may produce deep scratches.

No two workers use exactly the same set of polishing materials or go through exactly the same routine. All that is necessary is that each polishing material should remove the scratches from the one before and that the last one should leave no scratches.

The following order is a convenient one for alloys: Very fine file, Nos. 0, 00, and 000 emery paper, the finest rouge, and lastly diamantine, a polishing agent consisting of pure alumina, which is specially prepared for this purpose.

When the polishing is complete, the surface will appear smooth and bright, but will show no structure, except in cases where some of the constituents are very soft, when these may be rubbed away and a structure shown. This is well seen in the case of pig iron containing large flakes of graphite. Use is made of this occasionally under the name of the "polish attack."

**Etching.**—In order to "develop" or rather to reveal the structure, the surface must be etched, that is, it is treated with some reagent which will attack the surface. If the metal be perfectly homogeneous no structure will be revealed, but if it be heterogeneous the constituents

will be attacked at different rates by the etching agent, some portions being dissolved away much more quickly than the rest, so that the portions least attacked are left standing in slight relief, the relief of course being so slight that both portions can be in focus under the microscope at the same time. Sometimes the different constituents are differently coloured by a reagent, and thus can be distinguished the one from the other.

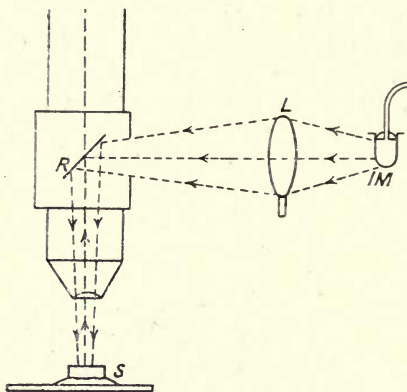


FIG. 23.—METHOD OF OBTAINING VERTICAL ILLUMINATION.

S, specimen for examination; R, reflector inclined at 45°; L, condensing lens; IM, incandescent mantle.

The etching agent must necessarily be selected so as to suit the peculiarities of the metal under examination. A reagent which will develop a structure in one metal may be quite useless for another, thus a reagent that is suitable for iron and steel may be quite unsuitable for brass or other alloys.

In some cases structure may be brought up by gentle heating, the constituents being differently oxidised and therefore rendered visible. This is called heat tinting.

**The Microscope.**—The microscope is, of course, the most important item in a metallographer's outfit. Good work may be done with an ordinary microscope, if it be of fair quality, but one specially made for and therefore adapted to metallographic work is much better. The makers of microscopes are now competing with each

other in the production of instruments suitable for metallographic work. Those of Messrs. Beck, Watson, Ross, and Swift, in this country, and of Messrs. Reichart, Zeiss, and other firms on the Continent leave little to be desired, and are made at various prices.

In all ordinary microscopes the object to be examined is transparent, and the light is reflected up from below ; for metallographic work this cannot be done, and the stage is best made solid. The samples to be examined may be of considerable size, so that a much larger motion of the stage or tube is necessary than in ordinary biological microscopes. Messrs. Swift make a stand so constructed that the stage can be dispensed with if necessary, the microscope standing on the article to be examined, so that large articles can be examined without the removal of specimens.

For a reason which will be seen directly, the coarse adjustments should be attached to the stage, and not to the tube, and the stage should be provided with transverse motions in two directions, and should be capable of being accurately levelled. The light must obviously be thrown upon the surface to be examined, and reflected upwards into the objective. With low powers,  $\frac{2}{3}$  in. and upwards, there is no difficulty—the light can be thrown upon the sample by means of a bull's-eye condenser. This is usually called natural or oblique illumination. With high powers this method of illumination is impracticable, as the sample is so near the objective that the light cannot reach it, and some other method of illumination must be devised, and vertical illumination by means of a reflector within the tube of the microscope is therefore used. This method of illumination can be used for low powers as well as for high, but it is often undesirable for the former.

The simplest form of vertical illumination is that of Messrs. Beck. At the lower end of the microscope tube, just above the objective or at some other convenient place, is fixed a short tube which contains a small mirror of very thin unsilvered glass so arranged that it can be rotated into any required position, and opposite this a circular hole is made in the tube. A horizontal beam of light is sent into the tube through the opening, and if

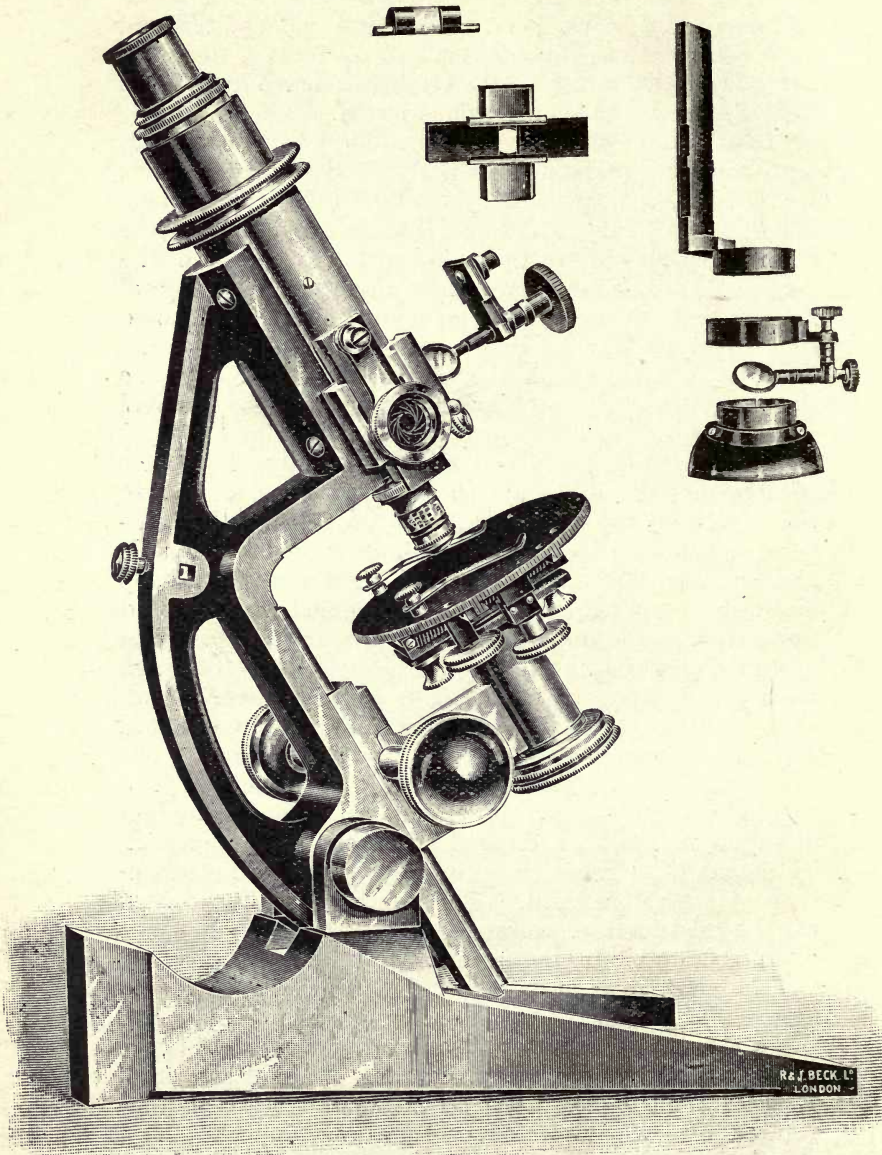


FIG. 22.—ROSENHAIN MICROSCOPE. MADE BY MESSRS. BECK & CO.

the mirror be placed at an angle of  $45^\circ$  the light will be partly reflected downwards and partly transmitted, the latter part being lost. The light which passes downwards passes through the objective, illuminates the object, and is reflected back again; the upward beam striking the mirror is partly transmitted and partly reflected, the portion transmitted passes upwards and reaches the eyepiece.

It is quite obvious that by this arrangement there is a considerable loss of light by the various reflections and transmissions, but enough reaches the eyepiece for the purpose.

In place of this simple mirror, a prism may be used, and Messrs. Beck have recently introduced a new form of mirror, the one half of which is silvered to act as a reflector, whilst the other half is clear to transmit the image.

**Appearance of the Object.**—The appearance of the object varies very much with the character of the illumination, a surface which appears bright with an oblique illumination often appearing dull by vertical illumination, and vice versa, so that when a specimen is described as being bright or dull, the character of the illumination should always be specified. Suppose a perfectly smooth surface to be examined by oblique illumination, it

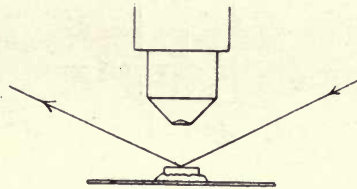


FIG. 24.—BRIGHT SURFACE, OBLIQUE ILLUMINATION.

will appear dull, or almost black, whilst on the other hand by vertical illumination it will appear brilliantly bright. The explanation of this is quite simple. A beam of light falling obliquely on a bright surface is reflected according to the law of reflection, and none of the light enters the object glass which is vertically above it, and thus the surface appears dull.

On the other hand, when the light is sent down vertically on to the bright surface, nearly the whole of it is reflected back and thus the surface appears bright.

[ ] If the surface be dull the oblique ray will not be regularly reflected, but will be scattered, so that a fair

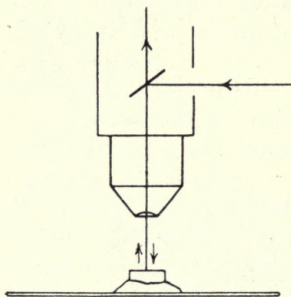


FIG. 25.—BRIGHT SURFACE,  
VERTICAL ILLUMINATION.

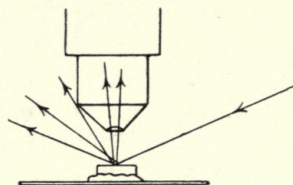


FIG. 26.—DULL SURFACE,  
OBLIQUE ILLUMINATION.

portion will enter the object glass and the object will appear bright; on the other hand, if the light is sent down vertically upon the surface, but a small proportion will be directly returned, so that the surface will appear dull.

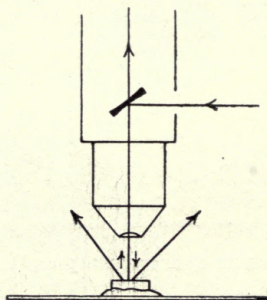


FIG. 27.—DULL SURFACE,  
VERTICAL ILLUMINATION.

As already remarked, on the etched sample portions stand up in relief, the surrounding portions having been dissolved away, and with oblique illumination a distinct shadow will be cast, which will make the distinction



between the two constituents much more pronounced than by vertical illumination, where there can be no shadow. Similarly, a small hole or depression will be much more strongly marked by oblique than by vertical illumination, since in the former case it will be in shadow.

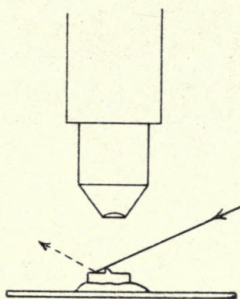


FIG. 28.—SHADOW CAST IN OBLIQUE ILLUMINATION.

It very frequently happens therefore that a change from oblique to vertical illumination quite alters the appearance of the specimen—the surfaces which before were bright become dull, and those which were dull become bright, and holes or scratches become much less strongly marked.

In order to preserve the results of an examination, a photograph should always be taken if possible. The magnification should be given thus,  $\times 30$ , meaning that the photograph is 30 times linear larger than the sample, and the illumination should always be marked, *o* for oblique illumination, and *v* vertical illumination.

Great judgment and experience is required for the correct interpretation of the meaning of the structure seen.

### RESULTS.

THE microscope can give very valuable information as to the structure of alloys, but like every other instrument it has its limitations, and to expect of it more than it can do is to court disappointment. Its field of usefulness is strictly limited to the detection of differences in physical structure, and more than this it cannot show. It can in

no way replace chemical analysis, though it is a very valuable adjunct to it; for it can give no hint of the presence of combined or dissolved impurities unless these give rise to differences of structure or colour. Its usefulness depends on the fact that the differences in structure on which the properties of an alloy depend are on such a small scale that the unaided eye is not able to detect them.

The methods of microscopic examination have been described, but it may be added that the difficulties in the application of microscopic research lie not so much in the observations themselves as in the interpretation of what is seen.

It has been already mentioned that there are three cases in which a metallic substance, or, indeed, any other substance, will solidify at a fixed temperature: (1) when it is an element, (2) when it is a definite chemical compound, (3) when it is an alloy of eutectic composition.

An alloy which solidifies at a definite temperature has a sort of identity or individuality which cannot be claimed for one which solidifies in several parts at different temperatures. It may be well, therefore, to see what information the microscope can give as to the structure of such substances.

(1) **Pure Metals.**—When a pure metal solidifies from fusion it is obvious that the solid substance must be chemically homogeneous; it must, that is, have the same composition in all parts, and any lack of homogeneity can only be due to the formation of holes, by contraction during solidification, or perhaps from the giving off of dissolved gas, if the term pure metal be not held to exclude metals holding gas in solution. As the metal solidifies, it will always crystallise, and will therefore yield a crystalline mass, and the form and size of the crystals will depend on the metal solidifying and on the rate of solidification.

The crystallisation may take place in various ways. Very frequently when cooling takes place at the outer surfaces it is by the growing inwards of crystals into the still liquid interior, the liquid mass subsequently solidifying between them, and thus forming a solid

mass. In the case of metals which yield large crystals a feathery crystalline structure is often seen on the surface. The crystals being in slight relief from the contraction of

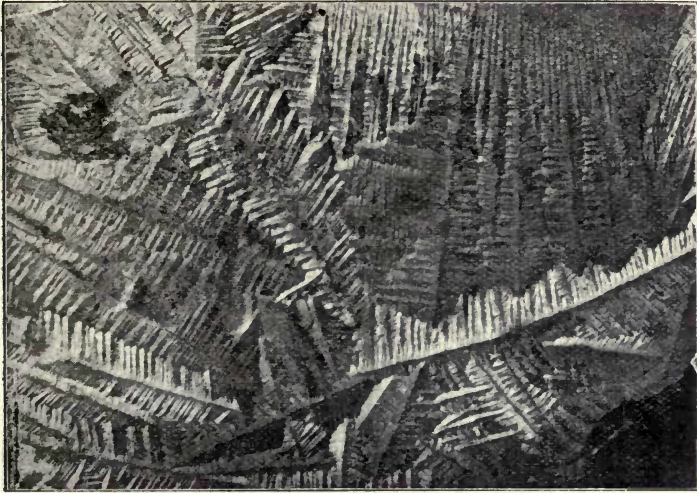


FIG. 29.—SURFACE OF AN INGOT OF ANTIMONY (NATURAL SIZE)

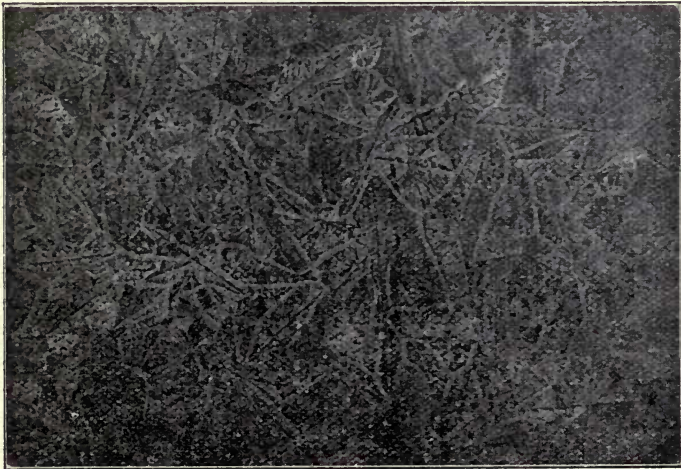


FIG. 30.—CRYSTALLINE SURFACE OF TIN (NATURAL SIZE).

the last solidified portions, can often be seen with the naked eye, and in other cases the structure can be brought up by etching. Antimony and tin are very good examples of this. When a section of such a metal is made, the structure is often difficult to make out, as there is little to differentiate the first-formed crystal from the subsequently solidified material. With soft metals, it is very difficult to secure a surface smooth enough for etching, except by casting on a surface of some very smooth substance, such as mica.

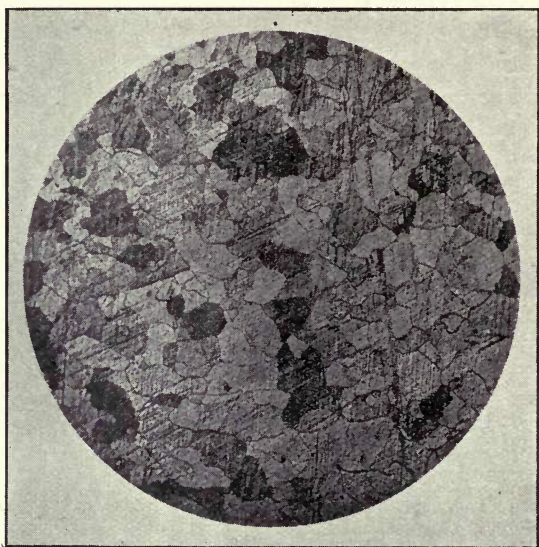


FIG. 31.—A PURE METAL, NEARLY PURE IRON. FERRITE V 50 $\times$ .

In the normal case of the solidification of a metal crystallisation begins at a large number of centres, the crystals growing outward in all directions into the mother liquor, the space between them therefore gradually becomes less and less, and at last they press one upon another, so that the sharpness of the edges and the regular crystalline form is completely lost, an irregular polygonal structure only remaining. When such a metal is polished and etched, these polygonal grains, which are distorted crystals, can often be made out. The boundary line is an optical phenomena, and does not indicate a real

line of separation between the crystals. Such structures are spoken of as "allotriomorphic" crystals, because they do not show the true crystal form; and sometimes they are called crystal grains. It may happen in some

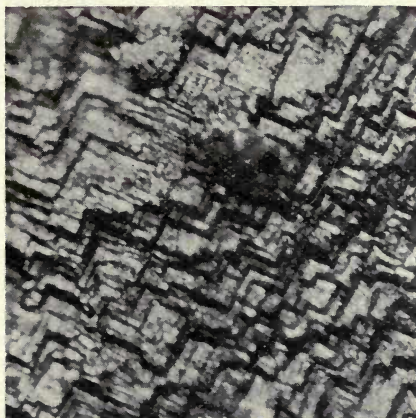


FIG. 32.—A CRYSTALLINE METAL. IRON WITH 4 PER CENT. SILICON. (STEAD.)

cases that the crystals retain their natural crystal forms, and it sometimes happens that distinct lines indicating cleavage planes can be distinguished.

The appearance of the fracture to the naked eye usually depends on how the planes of fracture are related to these crystals. If the fracture takes place along lines between the crystals a granular structure will usually be produced, whilst if owing to the presence of cleavage planes the fracture takes place across the crystals brilliant cleavage faces are often visible. When the metal is very malleable, so that it draws out before fracture, a fibrous fracture may be obtained.

It is obvious that the information which the microscope can give as to the structure of pure metals is not of much value.

**Definite Chemical Compounds.**—None of the definite compounds of one metal with another are of much practical importance. A chemical compound is just as much a unit as an element, and on solidification it behaves

exactly in the same way, showing usually a definite crystalline structure, exactly similar to that shown by a pure metal; indeed, the microscope would give no indication whether a substance under examination was a pure metal or a chemical compound.

**Solid Solution.**—A solution of one metal in another of such composition that the metals remain in solution in the solid condition may not show under the microscope any sign of variation in composition, the solid will be distinctly a unity, and no structure except that due to crystallisation will be detectable. It does not follow, of course, that the presence of the foreign metal may not alter the structure of the whole, but simply that the separate constituents will not be distinguishable.

**Eutectics.**—When the two constituents are present in the eutectic proportion, the mass solidifies at a definite temperature, but the conditions are very different from those already considered, for whilst, in the liquid condition, the mass is a solution at the moment of solidification the two constituents separate completely, so as to remain only as a mechanical mixture; and as the two constituents of any mixture will certainly be differently acted on by some etching reagent, a structure can easily be brought up.

As the two portions of the eutectic solidify at the same time, it might be expected that the separated portions would be so small as to be indistinguishable, even if not of molecular dimensions. This, however, is not the case; molecular attraction comes into play and the separated molecules aggregate into masses of sensible size,—at least, in most cases, though there are cases in which the constituents remain mixed in such minute portions as not to be distinguishable, forming what has been called a eutectic emulsion. The actual amount of differentiation in the constituents will depend, among other things, on the rate of cooling.

The arrangement of the separated portions will also vary very much. What may be called the normal eutectic structure consists of a series of more or less parallel plates of minute size, the parallelism, however, only extending over small areas, the whole surface being frequently broken up into series of eutectic areas in which

the orientation of the plates varies considerably, it often appearing as if incipient solidification has taken

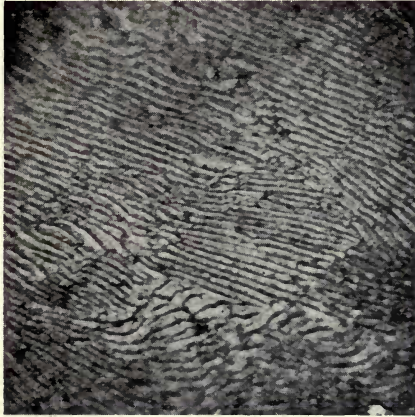


FIG. 33.—A TYPICAL EUTECTIC STRUCTURE, PEARLITE. (IRON AND  $\text{Fe}_3\text{C}$ .)

place to a sufficient extent to form a series of crystals, and then that independently within each of those areas the eutectic has been formed.

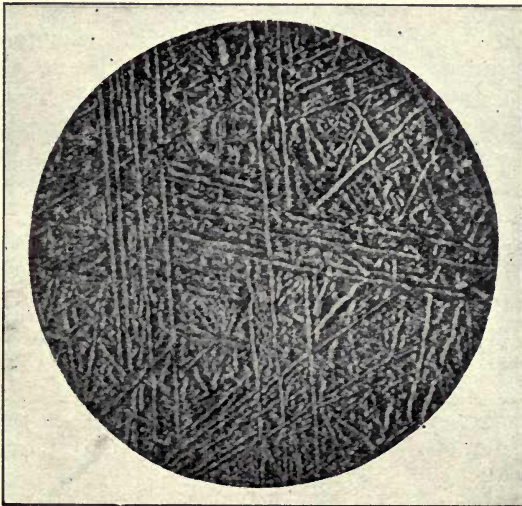


FIG. 34.—THE EUTECTIC OF SILVER AND LEAD. V-90, BY SAVILLE SHAW.

Mr. Stead has classified eutectics into three groups\* :—

- (1) The curviplanar, in which the constituents consist of curved plates in juxtaposition. Examples of this structure are to be found in the alloys of silver and copper, and in slowly-cooled carbon steels.

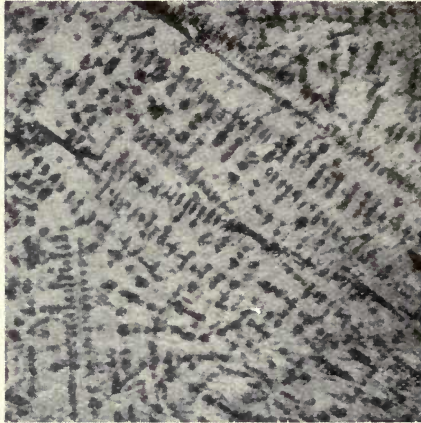


FIG. 35.—AN ALLOY OF TWO CONSTITUENTS. WHITE SWEDISH IRON  $\times 20$ .  
The dark parts are pearlite, the white parts the solidified eutectic.

- (2) The honeycombed or cellular, a very common variety. Gold and lead, bismuth and tin, and many other alloys yield eutectics of this type.
- (3) The rectiplanar, in which the two constituents separate in flat plates. Silver and lead eutectic is an example.

To these may be added :—

- (4) A spherulitic structure, usually produced when alloys are very rapidly solidified, the growth taking place from centres and forming a mass resembling the spherulitic structure in certain minerals.
- (5) An emulsion structure, in which the constituent particles are so small that they can only just be detected, or perhaps may not be detectable at all, and are apparently not arranged in any definite form.

\* Proceedings Cleveland Institution of Engineers, 1900-1, p. 36.



No doubt other forms of structure also exist, but these include all those commonly met with.



FIG. 36.—CRYSTALS OF GRAPHITE SEPARATED IN A GROUND MASS OF FERRITE.

**Micro-structure of Alloys.**—Most alloys are more complex in structure, and two or more of the structures described may be present.



FIG. 37.—INGOT CONTAINING 10·17 PER CENT. PHOSPHORUS AND 88·9 PER CENT. IRON, SHOWING SECTIONS OF RHOMBIC OR OBLIQUE IDIOMORPHIC CRYSTALS OF  $Fe_3P$  EMBEDDED IN A GROUND MASS OF EUTECTIC.  $V \times 60$  (STEAD).

In an ordinary alloy, as cooling goes on, one constituent—usually a solid solution—separates, and then the mother liquor solidifies, forming the eutectic, or there may be more than one stage of solidification before the eutectic point is reached. The visible structure of the alloy will

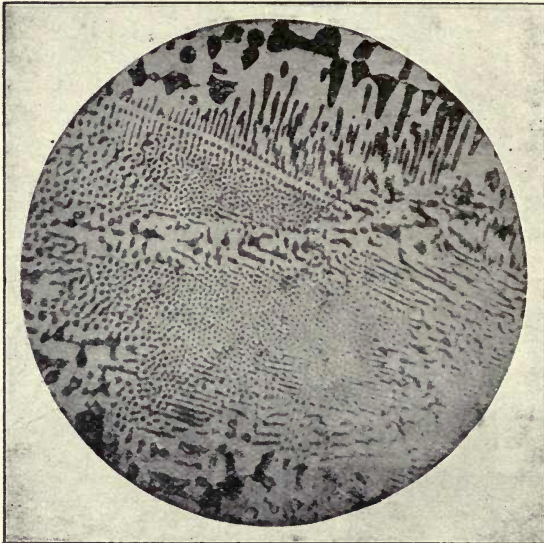


FIG. 38.—INGOT CONTAINING 10.2 PER CENT. PHOSPHORUS AND 89.8 PER CENT. IRON (STEAD).

It is the eutectic of phosphorus and iron. It has only one critical point, at about 980° C. Etched with nitric acid.  $\times 350$ .

vary very much, according to the relative quantities of the constituents.

If the quantity of the eutectic be small, the crystals first formed may go on growing and, of course, ejecting the mother liquor, till when the eutectic point is reached it may be reduced to mere threads separating the crystals, or to isolated patches distributed through the mass. On the other hand, if the composition approaches the eutectic point the substance first solidified may form only a network, in the meshes of which the eutectic will solidify, or it may be more or less definite crystals which will be embedded in the subsequently solidified eutectic. If the conditions be favourable the crystals may assume their true form.

The structure of alloys may, however, vary so much according to the way in which the constituents crystallise, the proportions in which they are present, and the conditions of solidification, that at this stage only one or two typical examples can be given. Others will be considered in connection with the various groups of alloys.

## CHAPTER V.

### CHANGES IN THE STRUCTURE OF ALLOYS IN THE SOLID CONDITION.

WHEN an alloy has solidified it by no means follows that it has reached a perfectly definite and stable condition, for changes in structure and in proximate composition may still take place. A solid is not by any means the fixed rigid thing that is sometimes imagined, for the molecules retain some freedom and therefore can to a certain extent, though often very slowly, undergo re-arrangement. The higher the temperature the greater is the molecular mobility and therefore as a rule the greater the ease with which changes can take place, but it must by no means be assumed that such changes do not take place to an important extent at atmospheric temperature, and the structure may be greatly modified by various causes.

**Internal Changes During Cooling.**—When a mass of an alloy has solidified it will be in a distinctly crystalline condition, the crystals in the inner part of the casting being probably much larger than those near the outside, owing to the slower solidification; but even after solidification has taken place changes may continue, and the rate of cooling after solidification may considerably modify the structure.

The molecules are still in a condition of comparative freedom, and therefore can redistribute themselves, and just as in a solidifying solution the crystals tend to grow round a nucleus, so in the solid the crystals tend to grow round another crystal, the larger crystals growing and absorbing and thus obliterating the smaller ones. Very slow cooling, as distinguished from slow solidification, therefore tends to produce a largely crystalline structure, with the comparative weakness usually following from it. As a rule, therefore, as far as structure is concerned, the

more rapidly an alloy is cooled after it has solidified the better.

In a casting which is irregular in section so that the different portions cool at different rates, the crystalline structure and therefore the strength may vary very much in different parts. In many cases where a tensile or other test is specified, but where the casting itself cannot be tested nor a portion cut from it to test, a fin of some kind is cast on it which can be cut off and shaped into a test piece for testing. As this fin will usually cool much more quickly than the bulk of the casting,

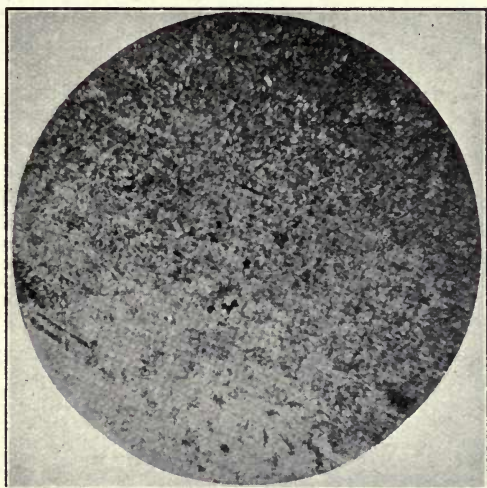


FIG. 29.—INGOT BRASS ROLLED DEAD HARD. (MAGNIFICATION 58 DIAMETERS.)

it will often show a much finer grain and be considerably stronger than a test piece cut from the casting itself. This is frequently seen in the case of propeller blades and similar castings. In all such cases the conditions under which the test piece is to be cast should be carefully specified, and the strength required must only be that of the test piece, as a guarantee of the quality of the metal, and not as a criterion of the strength of the casting itself.

No doubt in the case of an alloy a temperature is soon reached at which the molecular mobility becomes

too small to produce any serious and rapid change, and such a point, which in this connection might be called a critical point, has considerable practical importance, though in most cases it is not known with any great degree of

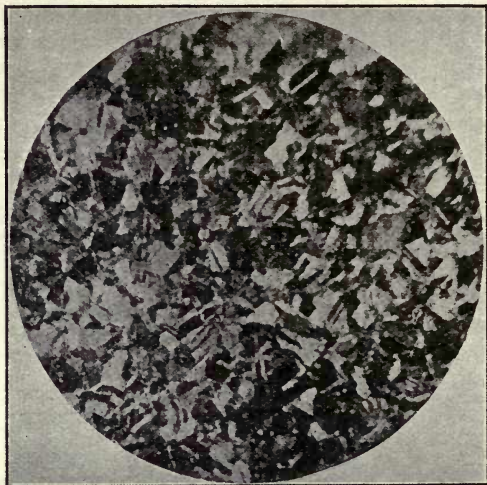


FIG. 40.—BRASS AFTER HEATING TO 500° C. (MAGNIFICATION 58 DIAMETERS.)



FIG. 41.—BRASS AFTER HEATING TO 600° C. (MAGNIFICATION 58 DIAMETERS.)

accuracy. It must not be assumed, however, that this is the actual limiting point of crystal growth, because the

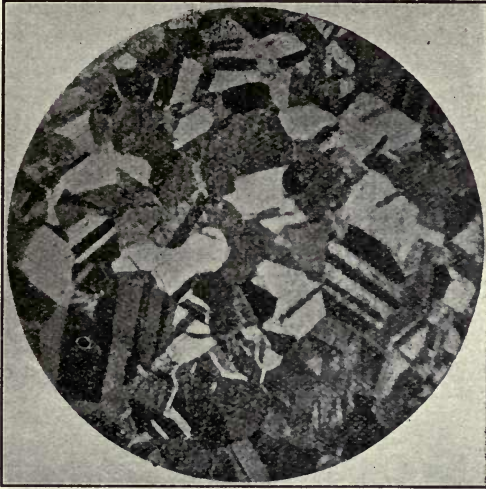


FIG. 42.—BRASS AFTER HEATING TO 750° C. (MAGNIFICATION 58 DIAMETERS.)

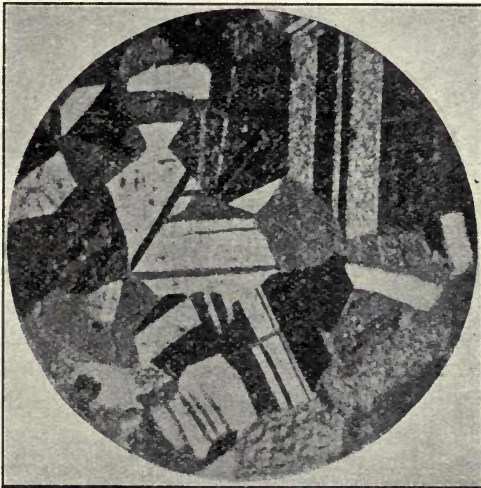


FIG. 43.—BRASS AFTER HEATING TO 800° C. (MAGNIFICATION 58 DIAMETERS.)

growth may go on, though probably very slowly, at considerably lower temperatures, especially under the influence of vibration or other mechanical stimulus.

It is obvious that this crystal growth at high temperatures may take place just as readily in the case of a metal heated from a low temperature to above the critical point as with one cooled from fusion, so that continuous heating at a high temperature is very apt to induce coarse crystallisation and subsequent brittleness in an alloy. This is well shown in the series of illustrations Figs. 39 to 45, which show the effect of heating to a high temperature on the structure of brass. The illustrations

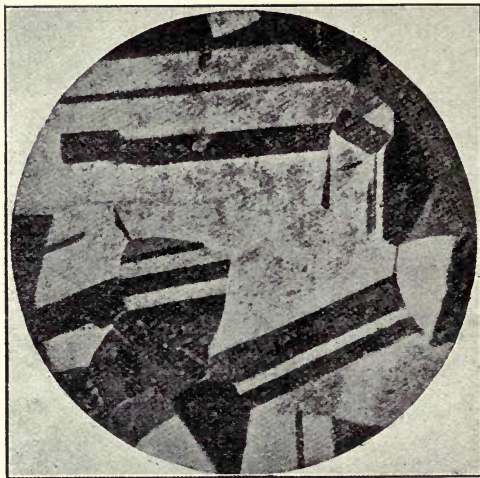


FIG. 44.—BRASS AFTER HEATING TO 900° C. (MAGNIFICATION 58 DIAMETERS.)

are reproduced from "Technics," by the kind permission of Messrs. Newnes & Co., Ltd. When brittleness is produced by overheating, the metal is usually said to be burnt. This is, however, not correct; it should be called overheating, and the term burning should be restricted to those cases in which there is decided oxidation or other chemical change.

**Annealing.**—By annealing is understood the heating of a metal or alloy to a high temperature, so as to allow of a molecular rearrangement or re-crystallisation, and



thus the removal of stress which may have been induced by work. The change produced is almost entirely one of crystal growth. The crystal structure of the metal has been broken down more or less completely by the work which has been put upon it, and a hardness thereby produced. When the metal is heated above the critical point the molecular forces are able to come into play and by restoring a normal crystal structure to restore the properties of the metal. It is quite obvious that the change must not be allowed to go too far, or the crystal structure may become too coarse and thus again injure the properties of the metal.

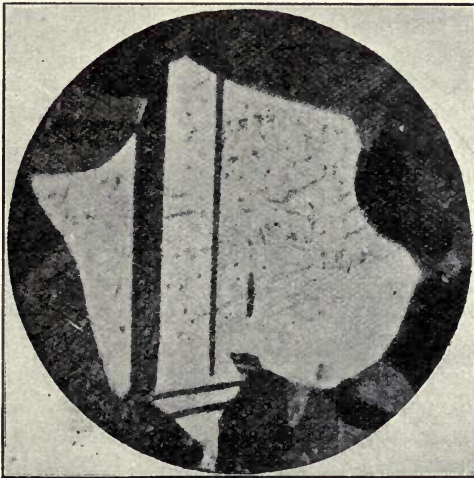


FIG. 45.—BRASS AFTER HEATING TO 1,000° C. (MAGNIFICATION 58 DIAMETERS.)

Annealing is usually looked upon as a very simple operation, and so, in fact, it is; but there is no operation in the whole range of metallurgy which requires greater care, so as to conform strictly to the conditions of success, and there is probably no operation in which failures are more frequent.

In all cases there are the two conditions to be considered—the temperature and the time of heating; whilst, as is pointed out below, the nature of the atmosphere in which the heating takes place may have a profound effect.

If the temperature be too low, the molecules will not have sufficient freedom to allow of re-arrangement, whilst if it be too high the change may be too rapid and the crystals may become unduly large and be so separated as to greatly impair the strength of the metal. On the other hand, even if the temperature be correct, if the metal be exposed to it for too long a time, the crystal growth may go on beyond the required point, and brittleness may be produced.

It is very important that the annealing range of temperature for various alloys should be carefully determined, and this can only be done by those who have control of works in which experiments can be made on a large scale and extending over a considerable time.

It is quite obvious that the perfect annealing of a large casting must be a matter of extreme difficulty since the heat can only slowly reach the interior, and therefore perfectly uniform heating becomes impossible.

In some cases the changes produced by heat treatment may be much more complex. This has been clearly made out in the case of steel, and there is reason to believe that similar phenomena take place in certain alloys. It is well known that in the case of steel, finishing rolling at a high temperature or heating to a high temperature may produce a very coarse structure with corresponding loss of strength, but that if the coarse-grained steel be then heated up to a temperature of about  $900^{\circ}$  C., but which varies according to the percentage of carbon in the steel, the whole structure is completely changed, the large grains breaking down and giving a fine-grained structure.

In the case of iron and steel also the internal changes are much more complex, owing to changes in the form of combination of the carbon present, and perhaps to changes in the allotropic condition of the iron itself, so that the metal can be hardened and tempered. It is impossible, however, to reason from the changes which take place in steel to those which may take place in other alloys, because the conditions are in many respects so different, but the occurrence of these phenomena, in the case of steel at least, warn us to be carefully on the watch for similar phenomena in the case of other alloys.

**Diffusion.**—It is well known that gases, however different their specific gravity, rapidly diffuse one into the other so as to produce a homogeneous mixture, and that with liquids diffusion takes place quite as surely, though nothing like so rapidly as in the case of gases. If pure water be placed above a saturated solution of sugar or copper sulphate, the dissolved substance will gradually diffuse through the liquid till the solution becomes of uniform composition. There is thus as far as diffusion is concerned a continuity between the liquid and the gaseous state, the difference being one of degree and not of kind. It is now known that solids behave in the same way, and that one solid will diffuse into another so as to tend towards uniformity of distribution. With most solids at ordinary temperatures the molecular mobility is so small that the diffusion is inappreciable, but if the temperature be raised to the point at which the molecules have any considerable amount of freedom, the diffusion may become recognisable or even well marked. The only case in which diffusion of solids at ordinary temperatures has been determined is that of gold into lead, in connection with which experiments were made by the late Sir W. Roberts-Austen. The diffusion was well marked, though of course, it was slow.

Solid diffusion may, and in some cases does, produce changes in metals which are kept at a high temperature for some time.

In the case of the growth of crystals in an alloy considered above, it was assumed that the alloy was homogeneous, *i.e.*, that it consisted of definite crystals, of one substance only, a condition only met with in a few of the alloys of commercial importance. How will the influence of high temperature or long heating be modified, if instead of an alloy consisting of one constituent, one be taken consisting of, say, two constituents, either a eutectic, or a eutectic together with an excess constituent ?

The cause of change, if any, will of course be molecular mobility as in the case already considered, but in this case the molecular mobility may act in two directions.

The tendency to segregate, which is the same thing as the tendency to grow into larger crystals, will tend to cause a more complete separation of the constituents.

The molecules of the excess substance will tend to grow together, thus ejecting the eutectic into well-marked areas, and the constituents of this eutectic will tend to aggregate into well-marked plates. When an alloy is slowly cooled this is the structure which is usually seen in the case of a eutectic alloy, whilst if the cooling (not only the solidification) be very rapid, the constituents of the eutectic may remain in the semi-emulsified or unsegregated form in which they are hardly distinguishable. Slow cooling in such a case will tend to produce a heterogeneous and coarse structure, in which not only are the crystals of each constituent large, but the segregated masses are also large, a condition necessarily tending to weakness and brittleness.

If, on the other hand, diffusion is the predominating influence, these conditions will tend to be reversed. Instead of the constituents tending to separate or segregate, they will tend to diffuse one into the other so as to produce a more or less homogeneous mass. It is quite evident that the influence of slow cooling on the properties of a heterogeneous alloy will depend on which of the two tendencies is the more powerful, and until this be known no idea can be formed as to what the influence will be, and no doubt the difference in the properties of alloys produced by similar treatment is to some extent due to this difference in behaviour.

If the phenomena during the two stages of solidification and subsequent cooling be considered, it will be found that in each case there is the double influence, *i.e.*, an influence in two directions, and the actual result will be the algebraic sum of the two actions :—

- (1) Slow solidification tends to increase segregation, and thus to produce a less homogeneous alloy by allowing more complete separation of the constituents, whilst rapid solidification has the reverse effect.
- (2) The effect of slow cooling after solidification will vary with the nature of the alloy. If the constituents are mutually insoluble, slow cooling may produce crystal growth and increased separation of the constituents, but if the con-

stituents are soluble one in the other their diffusion will come into play, the separated constituents may re-dissolve, and the alloy thus become more homogeneous. As a rule rapid solidification will be best, and the cooling after solidification should be slow or rapid, according to the character of the alloy.

It will be seen, therefore, that the structure of an alloy may be very considerably modified by the rate of solidification and of subsequent cooling, and that once the behaviour of the alloy is known, its properties may be controlled by the rate of solidification and cooling. As a rule, the rate of cooling can be much more easily modified than the rate of solidification.

Much further work is necessary on the behaviour of alloys during heating and cooling before much practical use can be made of these facts, but many workers are engaged on the subject, and no doubt much will be done in the near future.

**Effect of Work.**—When an alloy is subjected to work by hammering, rolling, or otherwise, the structure may be much modified, and the results will vary according as the work is done hot or cold; by hot work being understood work done above the temperature at which there is considerable molecular mobility, and by cold work that done at temperatures at which molecular mobility has ceased.

The result of work done at high temperatures is as a rule to increase the strength of the metal. The structure is more or less broken down by the work put upon the metal, but the molecules are free enough to re-arrange themselves, so that they are not left permanently in a condition of stress; the result is therefore usually a finely crystalline structure.

When the work is done cold, the result is somewhat different. As the pressure is put upon the metal it reaches momentarily the flow point, *i.e.*, the metal behaves as if it were plastic or fluid, and the crystals break up into a more or less fluid mass. The passage from this stage to the solid is so rapid, the whole change being almost instantaneous, that the metal has no time to re-form definite crystals, and it is therefore left in such a con-

dition that no crystalline structure can be made out. As the change of condition is so sudden the molecules, or particles perhaps would be more correct, have no time to adjust themselves to the condition normal to the cooled state and the metal is left hard and brittle, the particles being in a condition of stress which is relieved by annealing, when, as already explained, the metal is heated to a temperature at which there is a certain amount of molecular freedom.

**Burning.**—Certain metals, when heated to a high temperature or when heated for a considerable time in a particular atmosphere, are liable to a change which is called burning. The crystals become large, more or less distinctly separated, and the metal becomes very brittle, often indeed quite friable, and the plasticity and strength cannot be restored by annealing.

The cause of burning is not always the same, but it is probably always a chemical change. The most common cause of burning is oxidation. Plastic metals are usually more or less permeable to gases, and if air finds its way in, usually following the lines of separation of the crystal grains, films of oxide may be formed which break up the continuity of the metal, and thus make it brittle.

Copper, however, is burnt by being heated in a reducing atmosphere, probably by the removal of the last trace of oxygen.

## CHAPTER VI.

### THE METALS USED IN THE PREPARATION OF ALLOYS.

THE number of alloys in use is very large, but they may be conveniently classed into a few groups.

- (1) Brasses. Alloys of copper and zinc with or without the addition of small quantities of other metals.
- (2) Bronzes. Alloys of copper and tin with or without the addition of small quantities of other metals.
- (3) Machinery brasses or bronzes. Alloys of copper with tin and zinc, and sometimes with other metals.
- (4) Aluminium alloys.
- (5) White bearing metal alloys.
- (6) Soft alloys, such as pewters, type metal, &c.
- (7) Nickel alloys. German silvers.
- (8) Alloys of the precious metals.
- (9) Amalgams, or mercury alloys.
- (10) Alloys of iron and steel. This group will not be considered in this book.

The constituent metals used in the manufacture of alloys, excluding those used only in small quantity, are copper, zinc, tin, lead, antimony, nickel, aluminium, gold, silver, platinum, mercury. Whilst it is not necessary to discuss the metallurgy of these metals, it may be advisable to describe briefly the forms in which they are obtainable in commerce, and therefore in which they can be used in the preparation of alloys.

**Copper.**—Copper is distinguished by its characteristic red colour, and if present in large quantity it imparts a colour to alloys containing it, though the colour produced does not seem to be in any way related—at least in most cases—to the colour of the copper itself. It melts at about  $1,090^{\circ}$  C., and is slightly volatile, sufficiently to impart a green colour to a flame in which it is placed, but not sufficiently for there to be any loss when it is melted. It is malleable and ductile, and so can be obtained in thin sheets or in fine wire. Its specific gravity is about 8.9, but the figures obtained vary with the condition of

the metal examined, castings as a rule having a lower specific gravity than metal which has been wrought. The tensile strength of copper is not high, and varies considerably, according to the condition of the metal, being higher in the case of metal rendered hard by working than when the metal has been annealed, and much less in the case of castings than in the case of the wrought metal. Thurston states that when copper is to be used for structural purposes the strength specified should be not less than 25,000 lbs. (11·16 tons) per square inch for castings, 35,000lbs. (15·62 tons) for bars, and 60,000lbs. (26·8 tons) for wire. Dr. Watson\* quotes some samples of electrotype copper unworked as having a tensile strength of 16 tons, with an elongation of 20 per cent. on 4in., whilst when annealed the same copper gave 13·6 tons with an elongation of 42 per cent. Other samples of copper, pure copper deoxidised by phosphorus and rolled down to  $\frac{1}{2}$ in. thick without annealing gave the following figures:—

	Per Cent.	Tensile Strength.	Elongation. in 2in.
Pure copper	.. .. .	.. 14·38	.. 62·5
Copper containing arsenic	·050 =	.. 14·29	.. 60·0
"   "   "	188 =	.. 14·39	.. 61·0
"   "   antimony	·025 =	.. 14·50	.. 56·5
"   "   "	200 =	.. 14·777	.. 60·0
"   "   lead	200 =	.. 14·36	.. 58·0

Copper does not cast well, as in the molten condition it absorbs a considerable quantity of gas which is given out as the metal cools, and thus produces unsoundness. The addition of a small quantity of phosphorus, to a large extent, overcomes this defect.

Copper is a good conductor of heat and electricity, and the electric conductivity is considerably reduced by the presence of small quantities of impurities, quantities of certain metals which would escape detection by the ordinary chemical analysis having a marked effect on the electric conductivity.

Copper combines very readily with most metals and non-metals, and therefore may contain considerable quantities of impurities. How far these impurities will interfere with the use of the metal by the maker of alloys

\* Proceedings Inst. Mech. Engineers, 1893, p. 169.



will depend on the nature of the alloy being made and the purposes for which it is to be used. It by no means follows that an impurity which has little influence on the properties of the copper itself will therefore be equally uninjurious in an alloy, or that an impurity which has a marked influence on the properties of the copper will have an equally important influence on the properties of an alloy. Arsenic, for instance, is always considered to be a most objectionable impurity in copper, and yet for some purposes  $\cdot 5$  per cent. is not only not injurious, but seems to improve the quality of the metal. It would probably not be objectionable in copper to be used for preparing yellow brass which is to be cast, but it would render the metal quite unfit for the manufacture of a brass which had to be drawn cold.

Copper oxidises very readily on exposure to the air at high temperatures, black flakes of copper oxide or copper scale (a mixture of the two oxides  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ ) being formed. If the metal be in a liquid condition, probably only  $\text{Cu}_2\text{O}$  is formed, and this is rapidly dissolved, making the copper "dry," in which condition it is extremely brittle, and breaks with a brick-red granular fracture instead of the fibrous fracture of tough-pitch copper. The amount of oxygen present in copper as dissolved oxide varies very much. It is extremely difficult to estimate accurately, and many of the published figures are unreliable. In a series of analyses of copper fire-box plates, published in the Proceedings of the Institution of Mechanical Engineers for 1873, the amount of oxygen in combination is given as varying in the 11 samples analysed from  $\cdot 019$  to  $\cdot 248$  per cent. It is doubtful whether the presence of a small quantity of oxygen is any serious objection in the case of copper to be used for making alloys, since the other metal, zinc or tin, is so much more easily oxidisable that it would probably decompose the copper oxide forming zinc or tin oxide, which would not dissolve but which would pass into the slag.

The removal of the oxide of copper which is formed during the process of refining, and the presence of which in excess is necessary for the complete removal of sulphur and other easily oxidisable impurities, is brought about by the process of "poling," which consists as is well

known of immersing a pole of wood in the molten copper. The wood undergoes decomposition, and the reducing gases given off reduce the copper oxide and carry away the oxygen. If the poling be carried too far the metal passes beyond the tough stage, and becomes over-poled. It is then brittle, but the fracture is quite different from that of dry copper. The cause of over-poling has not yet been completely made out, but it seems that in presence of small quantities of certain impurities, especially arsenic and antimony, the presence also of a small quantity of oxygen in combination is essential to keep the metal in its "tough" form, and if this be removed it becomes brittle. Over-poling is closely related to the burning produced when copper is heated in a strongly reducing atmosphere. When copper is heated in an oxidising atmosphere, it is rendered brittle by the formation of oxide of copper along the planes separating the constituent crystals.

Commercial copper may contain arsenic, antimony, lead, bismuth, iron, nickel, cobalt, oxygen, sulphur, and in rare cases perhaps other metals.

Many alloy makers in order to secure the best results use the purest, and therefore the most costly, copper for the manufacture of their alloys. Where the brass is to be worked cold, as, for instance, where it is to be used for the manufacture of boiler or other tubes, it is essential to use a fairly pure metal, but even in this case it is doubtful whether metal of extreme purity is of much, if any advantage. For alloys which are to be cast it does not seem that metals of great purity have any advantage over the ordinary commercial forms, but at present the influence of small quantities of impurities on the quality of alloys has not been thoroughly worked out.

The purest copper obtainable is that known as electrotype copper, which is obtained by electro-deposition. This is almost chemically pure, and is now used on a large scale for the manufacture of brass condenser and other similar tubes.

Lake Superior copper made from the native copper of the Michigan copper district is also extremely pure.

The purest form of copper usually used is that known as B.S. (Best Selected) so-called because it was at one time

made in Swansea from metal containing a considerable quantity of arsenic and other impurities by a process known as the Best Selecting process. Now it is almost always made from materials so pure that that selecting is not necessary. It should not contain more than .05 per cent. of arsenic and a trace of antimony.

A test used by the Admiralty can be made use of to ascertain whether a copper is of the B.S. quality or not. Three pounds of the copper is melted in a crucible in the ordinary way and 2lbs. of zinc is added, so as to make an alloy of approximately the composition of 60 per cent. copper and 40 per cent. zinc. The metal is then cast into an iron mould about 4in. square and 1in. deep, and is allowed to cool slowly; the ingot is then nicked across the top with a swage and is broken either under the steam hammer or by means of a sledge. If the metal is B.S. quality the fracture will be dull, granular, and of a buff colour, and there will be few if any bright, brassy streaks crossing it. If it contains a considerable quantity of arsenic or antimony the whole fracture will be columnar, and will have a bright yellow colour and metallic lustre.

The following is a scale of qualities as indicated by this test:—

1. Very good. The fracture is of a uniform, dull buff tint.

2. Good. The fracture is mostly as in 1, but shows a few bright, brassy looking streaks.

3. Tolerably good. The number of bright streaks is greater.

4. Not good. The bright streaks are numerous, but cover not more than about one-third of the area.

5. Bad. The bright streaks predominate.

6. Very bad. The fracture is entirely, or almost entirely, bright and brassy.

Nos. 1, 2, and 3 would be passed as B.S.

The ingot must be allowed to cool naturally; sudden cooling considerably modifies the fracture.

Tough copper is the ordinary commercial copper. It may be very impure and may contain .5 per cent. or even more of arsenic. The name, of course, carries with it no guarantee as to quality.

It is perhaps hardly necessary to mention "Chili bar," though cases have occurred in which founders, seeing this quoted at lower prices than other varieties of copper, have purchased it for alloy making, with not very satisfactory results. It is an impure unrefined copper imported from Chili and may contain up to 2 per cent. or even more of sulphur.

Copper can be obtained in many forms, and it is needless to say that any quality can be prepared in any form. The usual form is that of ingots weighing about 14lbs., cast with one or two nicks at the bottom, so as to facilitate breaking. Ingots are, however, now cast of any form and size that the user may require. Slabs are of larger size and are usually used for rolling. Roller ends are often used for alloy making; they are the ends cut off a calico-printer's rollers, and then broken into pieces under a hammer. They are usually high in arsenic. Bean shot and similar varieties are obtained by pouring the molten copper into water.

No judgment can be formed as to the quality of a copper by the appearance of the ingot, or by the fracture, except that by the latter it can be seen if the metal is tough, dry, or over-poled. The surface and colour of the ingot depend largely on the way it is cast and cooled. Ingots cast in copper moulds are much smoother than those cast in iron moulds, and the red colour so often seen on the surface of the ingot is due to quenching in water immediately it has solidified. The sooner the ingot is turned into the water the better colour it will be. The red colour is best shown in rosette copper, which is solidified by throwing water on the surface of the liquid metal, or in Japanese copper, which is cast under water.

The following analyses will indicate the general composition of commercial coppers.

1. Electrotypes.
2. Lake Superior (Eggleston.)
3. B.S.
4. B.S.
5. Tough copper.
6. Copper fire-box plate.

	1	2	3	4	5	6
Arsenic . . . .	.01	Nil	.03	.025	.32	.373
Antimony ..	Trace	Nil	Trace	Trace	Trace	.035
Lead . . . . .	Trace	.016	—	.024	.07	.408
Bismuth . . . .	Trace	—	.05	.011	.01	.036
Iron . . . . .	Nil	—	Trace	.006	.01	.007
Nickel . . . . .	Nil	—	—	.041	.06	.304
Silver . . . . .	—	.026	.03	—	—	.035
Oxygen . . . .	Nil	.15	—	.143	.12	.018
Phosphorus	Nil	—	—	—	—	—
Sulphur . . . .	Nil	—	—	—	—	.006

It should be noticed that refined copper never contains more than a minute trace of sulphur or lead, but that as lead is often added during rolling, rolled copper may contain up to about .5 per cent. lead.

**Zinc.**—Zinc is a bluish-white metal having a specific gravity of about 7.1. It melts at about 415° C., and boils at about 930° C., so that it can be readily distilled, and there is always a sensible loss when it is used in the manufacture of alloys. The metal in fine shavings or vapour burns readily with an intense bluish-white flame, forming dense clouds of white zinc oxide (philosophers' wool). It is malleable and ductile through a limited range of temperature only, and is largely used for rolling into sheets for roofing and other purposes. It oxidises only slightly on exposure to the air, with the formation of a basic carbonate.

Zinc comes into the market in the form of rolled sheets, and also in cast cakes of about lin. thick, in which form it is known as spelter. The cakes are very brittle, and break with a more or less crystalline fracture. If the metal be nearly pure the crystal faces are large, bright, and smooth; if there be a small quantity of iron present dull spots appear on the crystal faces, and if the quantity of iron rises to a few per cent., as in dross spelter, the fracture becomes granular. The amount of iron present can be fairly judged from the appearance of the fracture. Its tensile strength is low, but it is never used for structural purposes where it is subjected to great stress.

Zinc casts well and contracts but little on solidifying, and is largely used for the manufacture of statuettes and other ornamental castings which are usually coated with bronze or brass by electro-deposition.

Zinc is never pure. The principal impurities are iron, lead, tin, copper, arsenic, and cadmium. Iron is always present in spelter. It does not distil over with the zinc, for freshly distilled zinc hardly contains a trace, but it is dissolved from the iron vessels in which the metal is melted, and rods with which it is stirred. When zinc is used for galvanising a hard zinc which contains several per cent. of iron accumulates in the vats. Good commercial spelter should not contain more than .05 per cent. of iron, and this is about the maximum allowable for alloy making.

Lead is invariably present in spelter in larger or smaller quantity as it distils over with the zinc during the process of manufacture. Lead is only slightly soluble in zinc and in the solid condition zinc cannot retain more than about 1.5 per cent. It sometimes happens that from rapid cooling a sample may contain more, but in that case some of the lead will almost always be found to be distributed in minute shots or fragments through the mass, and if the metal be melted and slowly cooled it will separate. For making brass or other alloys, a spelter containing more than 1.5 per cent. of lead should be rejected. When spelter is redistilled, even if the redistillation be repeated, about .2 per cent. of lead passes over, so that it is almost impossible to obtain a spelter containing less lead than this.

Cadmium is rarely present except in minute quantity, and is so like zinc in all its properties that it does not seem to be objectionable, at any rate in any quantity likely to be present in commercial zinc.

Copper is rarely present in any but the minutest quantities, and is quite unobjectionable for the preparation of alloys.

Tin is often present in minute quantities, but rarely in sufficient quantity to be objectionable.

Arsenic is rarely present except in quantities too small to be of any importance for practical purposes, whilst antimony and sulphur are sometimes present in minute traces.

**Tin.**—This is a silver-white metal having a specific gravity of about 7·3. It is soft and very malleable. It melts at about 232° C., and boils at a white heat. It does not tarnish rapidly on exposure to the air, but at a red heat it is readily oxidised, forming the oxide SnO<sub>2</sub>.

Commercial tin is never pure, though the quantity of impurity present is always small. The following analysis of Queensland tin by Thurston will give an idea of the composition of a good commercial tin :—

Lead	..	..	..	..	..	0·165
Iron	..	..	..	..	..	0·035
Manganese	..	..	..	..	..	0·006
Arsenic	..	..	..	..	..	Trace.
Copper	..	..	..	..	..	None.
Zinc	..	..	..	..	..	„
Antimony	..	..	..	..	..	„
Bismuth	..	..	..	..	..	„
Nickel	..	..	..	..	..	„
Tungsten	..	..	..	..	..	„
Molybdenum	..	..	..	..	..	„

Banca tin is said to be the purest obtainable. Mr. Parry states that Peruvian and Bolivian tin are the most impure, and contain lead and antimony, and that certain brands of Australian tin contain bismuth.

The impurities most likely to be present are lead, iron, and copper. The quantity of any of the elements should not exceed about ·1 per cent., and the total quantity of tin should be from 99·7 to 99·95.

Tin comes into the market cast in various forms, to suit the convenience of users. Block tin is in small bars, blocks, or cakes of various sizes. Stick tin is cast into small sticks. These sticks emit a peculiar crackling sound or “cry” when bent, and this sound is sometimes taken as being a test of the purity of the metal, because a small quantity of lead destroys it. Grain tin is made by casting a large block, heating it till it becomes brittle, and then breaking it up. Granulated tin is made by melting the metal and pouring it into water.

Tin foil is tin which has been rolled out into very thin sheets, often not more than  $\frac{1}{1000}$  in. in thickness.

Lead is an extremely soft metal of a bluish colour. Its specific gravity is 11.4, and therefore it is the heaviest of the metals used in making alloys. It has very little tenacity, is very malleable, but its low tenacity makes it difficult to draw it into fine wire. It melts at 327° C., and is sensibly volatile at high temperatures. It oxidises very slowly in air at ordinary temperatures, but rapidly at a red heat, forming the oxide  $PbO$  and finally, if the temperature be not too high, red lead  $Pb_3O_4$ .

Commercial lead is always very pure, the impurities present being in very small quantities and of no practical importance.

The following analysis by Thorpe will give an idea of the usual degree of purity :—

Silver	.. ..	0.00200	Antimony	.. ..	0.00173
Copper	.. ..	0.00228	Iron	.. ..	0.00035
Cadmium	.. ..	Trace.	Zinc	.. ..	0.00014
Bismuth	.. ..	0.00040	Sulphur	.. ..	0.00076

**Antimony.**—Antimony is a bluish-white crystalline metal, which melts at about 450° C. and is volatile at a white heat. It has a specific gravity of about 6.7 and is extremely brittle. When pure antimony solidifies slowly the surface assumes a fern-like crystalline appearance, and a structure called the antimony star is produced. To produce this appearance the solidifying surface must be kept covered with a layer of slag. Impure antimony does not give the star, but as it depends on the conditions of cooling pure antimony does not always show it. Commercial antimony usually contains sulphur, arsenic, lead, copper, and iron. The following analysis will indicate its composition :—

					Per Cent.
Arsenic	..	..	..	..	.06
Tin	..	..	..	..	—
Lead	..	..	..	..	.46
Copper	..	..	..	..	.07
Iron	..	..	..	..	.16
Zinc	..	..	..	..	.08
Sulphur	..	..	..	..	.20
Antimony (difference)	..	..	..	..	98.97
					<u>100.00</u>

The sample showed a well-crystallised surface.



**Bismuth.**—Bismuth is a pinkish-white metal having a specific gravity of 9.82. It melts at 266° C., and expands by over 2 per cent. on solidifying. It volatilises at high temperatures, its boiling point being between 1,000° C. and 1,500° C.

Metallic bismuth may contain silver, lead, copper, arsenic, iron, nickel, cobalt, and sulphur, and sometimes the rarer metals. The following analyses from the "Mineral Industry" for 1893, p. 72, will give an idea of the composition of commercial bismuth :—

	Saxon.	Peruvian.	Australian.
Bismuth.. ..	99.77	93.372	94.103
Antimony .. ..	Nil.	4.570	2.621
Arsenic .. ..	Nil.	Nil	0.290
Copper .. ..	0.08	2.058	1.944
Silver .. ..	0.05	—	—
Sulphur .. ..	0.01	—	.430
	<hr/>	<hr/>	<hr/>
	99.91	100.00	99.388

Bismuth is very little used, except for the preparation of very fusible alloys.

**Aluminium.**—Aluminium is metal of a brilliant silver-white colour. The most striking property of the metal is its extreme lightness, its specific gravity being only 2.7. It is soft, malleable, and ductile; when cast it has a tensile strength of about 6 or 7 tons per square inch, which by working may be increased to 16 tons or thereabouts. Its melting point is between 600° and 700° C., but owing to its very high specific heat, it melts, solidifies, and cools very slowly.

It does not oxidise readily in air, even at a red heat, unless finely divided, when it will burn with a brilliant, highly actinic flame; but it decomposes metallic oxides, alumina being formed.

Commercial aluminium, as now prepared by the electrolytic methods, is very pure, containing about 99.50 of the metal.

The properties of gold, silver, platinum, and mercury will be described as far as is necessary in connection with the alloys for which they are used.

## CHAPTER VII.

### THE BRASSES.

BRASS is an alloy of copper and zinc, and strictly speaking should contain no other added metal, the impurities present being only those present in the metals used in making the alloy or accidentally introduced in the process of manufacture. Brasses to which other metals are added in large or small quantity will be considered separately.

**Impurities in Brass.**—It is obvious from what has been said of the metals used in the manufacture of brass that the impurities present should be only in small quantity; indeed, if metals of good quality are used, a brass should not contain more than about—

Arsenic	..	..	..	..	..	.03
Lead	..	..	..	..	..	.50

and other impurities in still smaller quantity. As lead and arsenic cannot be accidentally introduced during manufacture, any larger proportion of these elements must be regarded as being due either to the use of impure materials or intentional addition. It must, of course, be remembered that it is only for certain purposes that a brass of high purity is necessary.

The quantity of iron present will usually exceed that due to the iron in the metals used, because iron tools are used for stirring, and some of the iron is always dissolved. About 15 per cent. is a fair amount to be present in a brass, but a slightly larger quantity is not usually objectionable.

Sulphur, which is one of the most objectionable impurities in brass, is never present in appreciable quantity in copper or zinc, and therefore is never present in brass made from fresh metal unless the brass has been melted under such conditions that sulphur can be absorbed either from the fuel or the products of combustion. Should coke fall into the crucible during melting, or

should the metal be melted in a reverberatory furnace with a fuel containing much sulphur, sulphur will almost certainly be taken up by the metal.

In actual practice, however, new metals are very rarely used alone, a portion of the charge being usually made up of scrap. If the scrap be new clean scrap, this will, of course, have no injurious effect, except to make the preparation of brass of definite composition more difficult, but if as is often the case the scrap is dirty, sulphur and other impurities may be introduced into the metal. Old boiler and condenser tubes returned as scrap are frequently used in the manufacture of brass, and these may contain deposit which consists partially, at any rate in the case of boiler tubes, of sulphur compounds. When such scrap is melted, the sulphur passes into the metal, and may seriously interfere with its quality. In some ingots of brass made by melting old boiler tubes the following percentages of sulphur were found.

						Per Cent.
No. 1	..	..	..	..	..	.018
No. 2	..	..	..	..	..	.020
No. 3	..	..	..	..	..	.020
No. 4	..	..	..	..	..	.107

As a rule the quantity will be less, as only a portion of the charge will be scrap.

**Range of Composition of the Brasses.**—The brasses used commercially range from about 95 per cent. copper and 5 per cent. zinc to 40 per cent. copper and 60 per cent. zinc, the most important, however, being those containing from 70 to 50 per cent. of copper. The brasses not only vary very much in composition, but necessarily vary very much in all the properties on which their usefulness depends. A large number of experiments have been made at different times for the purpose of tracing the connection between composition and these properties, but they have not until recently been attended with great success, for one reason among others that care has not always been taken that the alloys compared have been in the same physical condition or of the same degree of chemical purity, both of which conditions may have a marked influence on the properties. Few of the properties form a continuous series varying directly with the composition, but each

one rises or falls as the case may be to a maximum or minimum, and then decreases or rises again, and the only way of satisfactorily showing the variations is by the use of curves, and needless to say before these can be determined accurate data must be at hand.

Many tables have been published giving details of the results of the work of many observers; a very extensive table, for instance, which was drawn up by an American committee in 1881 is contained in most of the books on alloys. Such collections are of little scientific value because being the work of many observers, and the observations having been made under varying conditions, the results are not strictly comparable. If an attempt be made to plot a series of curves with the data given in the table mentioned above, it will be found that no curve can be drawn which will even approximately include all the observations. Such a table may, of course, be of general value as indicating the sort of variations that may be expected with alloys of very similar composition, but for little else.

The American committee above mentioned collected a large amount of useful information, and under the direction of Prof. Thurston many experiments of great interest and value were made. Later, the English Institution of Mechanical Engineers appointed an Alloys Research Committee, and under the direction of the late Sir W. Roberts Austen further research was made into the relationship existing between the composition and properties of alloys. The work of this committee is of special value, because it had at its command methods of research that were not available to the earlier workers. Much of our accurate knowledge of the alloys has been derived from the work of these two committees, but within the last few years the interest in alloys has greatly increased, and many competent workers have entered the field and published the results of their work.

Remembering that a brass is an alloy of copper and zinc in any proportion, and therefore the brasses form a series commencing with copper and ending with zinc, the simplest method of study will probably be to take the more important properties of the alloys and see how these vary with changes in composition.

**Colour of Brasses.**—The colour of brass is one of its striking properties, and brass yellow is a fairly descriptive term. Only certain members of the brass series, however, have a yellow colour, others being quite white.

The following is the colour series given by the American Committee,\* the observations having been made by Prof. A. R. Leeds.

The percentages of copper and zinc are those obtained by the actual analysis of the sample.

No.	Copper.	Zinc.	Colour.
0.	100	0	Red.
1.	96·07	3·79	Brilliant yellow-red.
2.	90 56	9·42	More nearly approaching yellow.
3.	89·80	10·06	Light yellow.
4.	81·91	17·99	Brass yellow.
5.	76·65	23·08	Full yellow.
6.	71·20	28·54	Dark yellow.
7.	66·27	33·50	Gold yellow.
8.	60·90	38·65	Orange yellow (tarnished).
9.	55·15	44·44	Surface tarnished, of dull reddish-yellow colour.
10.	49·66	50·14	Deep yellow.
11.	47·56	52·28	Reddish white.
12.	41·30	58·12	Nearly silver white, changed to yellow by oxidation.
13.	36·62	62·78	More silvery.
14.	32·94	66·23	Bluish white.
15.	25·77	73·45	Dull bluish white.
17.	20·81	77·63	„ „ „
18.	14·19	85·10	„ „ „
19.	10·30	88·88	„ „ „
20.	4·33	94·59	Bright bluish white.
21.	—	100	Bluish white.

The colours are those of a fractured ingot. From Nos. 10 to 14 the lustre is described as splendent or

\* Thurston's "Materials of Engineering," vol. 3, p. 373, second edition.

brilliant. It is, of course, impossible to give any numerical colour standard, and therefore the descriptions must necessarily be somewhat vague, but the general result is clear. The addition of a small quantity of zinc speedily destroys the red colour of the copper, producing first a reddish yellow and then a yellow alloy. The yellow colour varies much in shade, the exact shade seeming to have little relation to the percentage of copper, till this is reduced to about 40 per cent., when the yellow colour gives place to a white and white brass is produced.

In the United States Committee's report, the appearance of the fracture is also given, but this is of little importance, and it must be borne in mind that in some cases both the appearance and colour of the fracture may be very much modified by the presence of impurities even in small quantity.

**Specific Gravity.**—The specific gravity of copper being much greater than that of zinc, as might be expected the specific gravity of the alloy falls as the percentage of zinc is increased. The alloy always has a density greater than that which it would have if it were merely a mechanical mixture of the two metals.

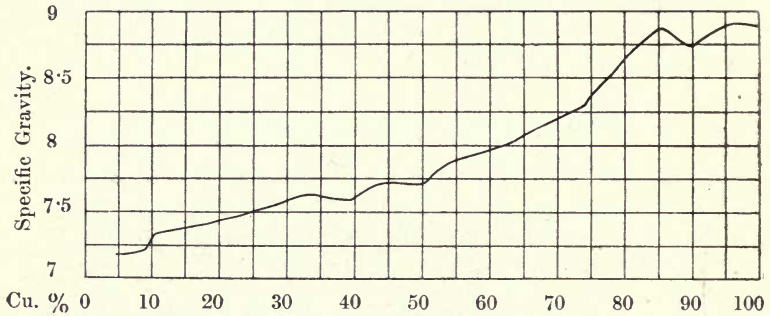
The following table gives the results of one series of experiments made by the U.S. Committee† which will be quite sufficient for general purposes :—

No.	Copper.	Zinc.	Sp. Gr.
1 ..	96·07 ..	3·79 ..	8·825
2 ..	90·56 ..	9·42 ..	8·773
3 ..	89·80 ..	10·06 ..	8·656
4 ..	81·91 ..	17·99 ..	8·598
5 ..	76·65 ..	23·08 ..	8·528
6 ..	71·20 ..	28·54 ..	8·444
7 ..	66·27 ..	33·50 ..	8·371
8 ..	60·94 ..	38·65 ..	8·405
9 ..	55·15 ..	44·44 ..	8·283
10 ..	49·66 ..	50·14 ..	8·291
11 ..	47·56 ..	52·28 ..	8·189
12 ..	41·30 ..	58·12 ..	8·061

† Thurston's "Materials of Engineering," vol. 3, p. 377, second edition.

No.	Copper.	Zinc.	Sp. G.
13	36.62	62.78	7.974
14	32.94	66.23	7.811
15	25.77	73.45	7.675
16	25.92	73.06	7.687
17	20.81	77.63	7.418
18	14.19	85.10	7.163
19	10.30	88.88	7.253
20	4.35	94.59	7.108
21	—	100.0	7.143

Fig. 46 gives these specific gravities plotted so as to give a specific-gravity curve.



Copper-zinc Alloys—Specific Gravity.

FIG. 46.

(It will be seen that the curve is not regular. Many of the variations may be due to differences in the condition of the samples.)

**Tenacity.**—The tenacity or tensile strength is, of course, one of the most important properties of alloys to be used for structural purposes, and many series of determinations have been made. Here again the American committee's results are of great value. The actual tensile strength of a brass will vary with the treatment to which it has been subjected, but if all the samples are treated in the same way, a series of figures will be obtained which will at least roughly indicate the relationship existing between the tenacity and the composition.

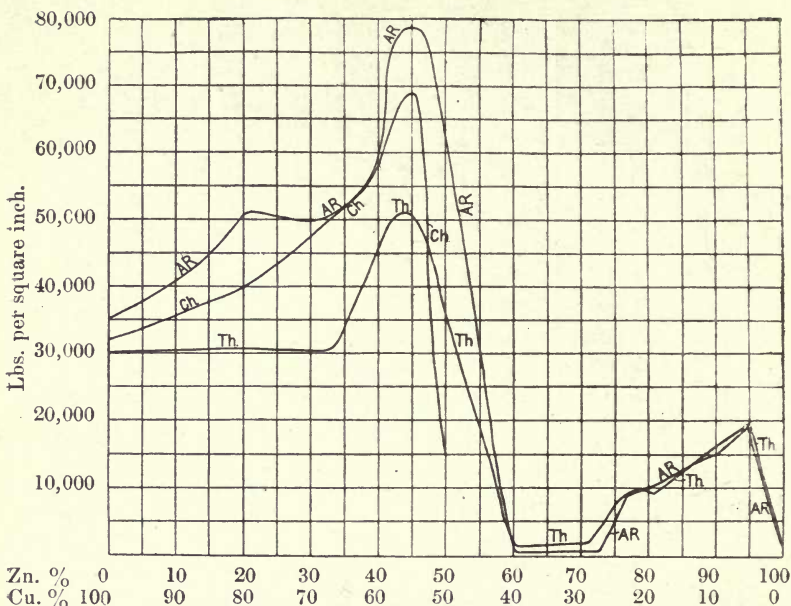


No	Copper.	Zinc.	Tensile Strength, lbs. per square inch of Original Section.	Elastic Limit per cent. of Breaking Load.	Total Elongation per cent.
0	100	—	27,800	51·8	6·47
22	97·83	1·81	27,240	—	—
25	82·93	16·98	32,600	26·1	26·7
4	81·91	17·99	32,670	30·6	31·4
5	76·65	23·08	30,520	24·6	35·8
6	71·20	28·54	30,510	29·5	29·2
7	66·27	33·50	37,800	25·1	37·7
8	60·94	38·65	41,065	40·1	20·67
9	55·15	44·44	44,280	44·0	15·31
10	49·66	50·14	30,990	54·5	4·97
11	47·56	52·28	24,150	100	·79
12	41·30	58·12	3,727	100	—
13	36·62	62·78	2,656	100	—
14	32·94	66·23	1,774	100	—
15	25·77	73·45	9,680	100	·35
16	25·92	73·06	7,931	100	—
17	20·81	77·63	9,000	100	·16
18	14·19	85·10	8,500	100	·31
19	10·30	88·88	14,450	100	·39
20	4·35	94·59	18,665	100	·49
21	—	100	5,400	75	·69

These figures are plotted in Fig. 47, and for comparison the curves obtained by the Alloys Research Committee and by M. Charpy are given.

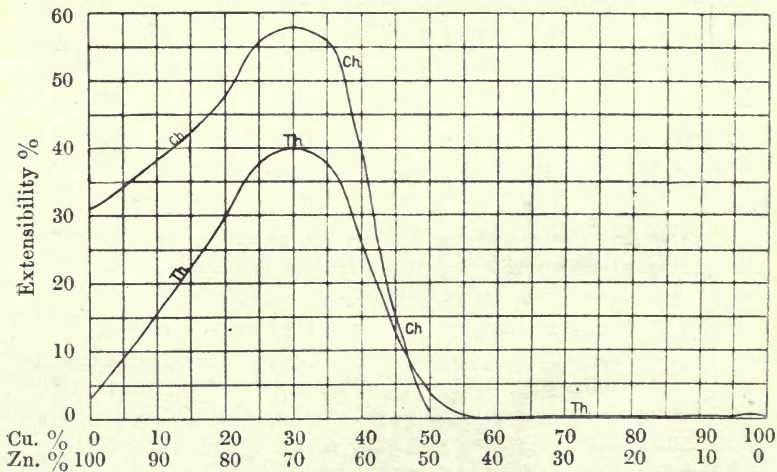
From these results it is possible at least to roughly summarise the influence of composition on the strength and other properties of a brass.

As zinc is added to copper the tensile strength increases, at first slowly, and then more rapidly till the maximum is reached with something between 55 to 60 per cent. of copper, the exact point being different in the three sets of determinations. As the amount of zinc is further increased the tensile strength falls off very rapidly, till when white brass is reached, with about 40 per cent. copper, the tenacity has become so small as to be negligible. The



Copper-zinc Alloys—Tenacity.  
 A.R.—Alloys Research Committee (worked rods). Th.—Thurston (castings).  
 Ch.—Charpy (annealed brass).

FIG. 47.



Copper-zinc Alloys—Extensibility.  
 Ch=Charpy. Th=Thurston.

FIG. 48.

maximum tenacity for cast brass is about 44,000lbs., or about 19 tons per square inch, whilst for worked rods it may reach about 80,000lbs., or nearly 36 tons.

**Extensibility.**—When the extensibility is considered, similar results are obtained. As zinc is added the alloy becomes more and more ductile, the ductility reaching its maximum when about 70 per cent. of copper is present. As the copper is diminished the ductility falls off very rapidly, and becomes negligible when the proportion of copper falls to about 50 per cent. It follows that where a brass is required for strength only, which, of course, may be accompanied by hardness and to some extent brittleness, it should contain about 60 per cent. of copper, but that where ductility and toughness are required, as is almost always the case, the percentage of copper must be about 70 per cent. On the whole, the alloy containing 70 per cent. of copper and 30 per cent. zinc is the strongest and most generally useful of the whole series. When the copper falls below 66 per cent. the alloy is difficult to work cold, though alloys poorer in copper may be readily worked hot.

**Hardness.**—The hardness of the alloy is greater than that of the copper, and like the other properties this reaches a maximum, then falls off. Hardness is a property which it is not easy to define or measure.

**Fusibility.**—The melting point of the brasses gradually falls as the quantity of zinc is increased. Reference should be made to what has been said on the meaning of the melting point of an alloy, because a study of the melting and freezing phenomena will throw much light on the structure of the alloys.

Fig. 49 is the freezing-point curve of the copper-zinc series of alloys as determined by the Alloys Research Committee.

It will be seen that copper melts at about  $1,082^{\circ}$  C., and that as zinc is added the solidifying or melting point of the alloy falls, the mass, however, solidifying as a whole until an alloy is reached which contains about 70 per cent. of copper, and which melts at

about  $950^{\circ}\text{C}$ . Beyond this the mass solidifies in two parts : Firstly, the copper containing zinc (which has a lower melting point as the percentage of zinc is increased), and, secondly, a eutectic solidifying at about  $890^{\circ}\text{C}$ ., or a little below. As the percentage of zinc is increased till there is about 55 per cent. of copper present, the mass solidifies as a whole at about  $890^{\circ}\text{C}$ ., the first eutectic temperature. As the amount of zinc is still further increased, the freezing point falls, but the alloy still

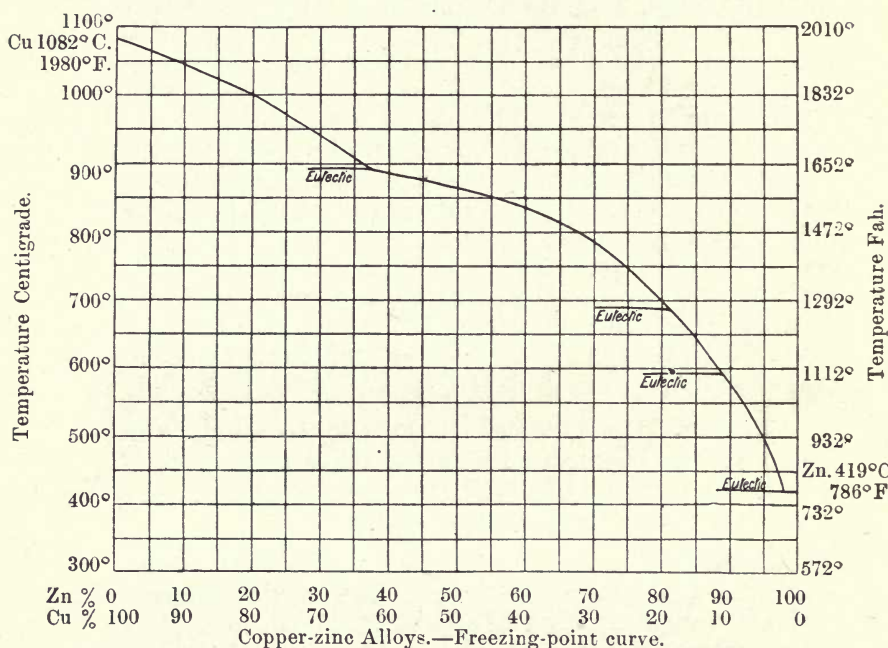


FIG. 49.

solidifies as a whole till a composition of about 45 per cent. of copper is reached, when, whilst the mass of the alloy solidifies at about  $860^{\circ}\text{C}$ ., a second eutectic separates which freezes at about  $840^{\circ}\text{C}$ .\* As the quantity of zinc is increased when it reaches about 72 per cent., whilst the freezing commences at about  $786^{\circ}\text{C}$ ., a third eutectic is formed which freezes at about  $680^{\circ}\text{C}$ ., and the alloy

\* The line of this eutectic is short and it was not noticed by the A.R.C., so is not shown in the diagram.

again solidifies as a whole, but immediately a fifth eutectic which has the freezing point of zinc begins to separate and continues until 100 per cent. of zinc is reached.

It will thus be seen that the freezing phenomena of the copper-zinc series are somewhat complex. On the whole the freezing point or melting point does fall steadily, though not uniformly, as the percentage of zinc is increased. For certain ranges, *e.g.*, from 100 per cent. to about 70 per cent. copper and through several other ranges of temperature, the alloy has only one freezing point and at certain (eutectic) points it solidifies as a whole, but for other ranges of composition it has always two freezing points, a definite eutectic being separated. All the useful alloys fall within the range of the compositions when the metal either solidifies as a whole or when the first eutectic separates.

It becomes of importance to see if any relationship can be traced between the physical properties of the alloy and the freezing temperatures. It will be seen that as zinc is added to copper, the whole retaining its homogeneity, the tensile strength and the ductility as measured by the extension gradually increase. When the eutectic begins to separate the ductility begins to fall, but the tensile strength continues to increase, and reaches its maximum at about the point when its whole mass is composed of the eutectic or a little beyond, after which the tensile strength also falls off very rapidly, soon becoming so small that the alloys are valueless for all practical purposes.

It will be seen, therefore, that the changes in physical properties are dependent on changes in the constitution of the alloy itself.

It is stated that several chemical compounds of copper and zinc exist, three at least having been described, *viz.* :

Cu. Zn.	49·3	per cent. copper,	50·7	per cent. zinc.
Cu. Zn <sub>2</sub>	32·7	„ „	67·3	„ „
Cu. Zn <sub>3</sub>	24·6	„ „	75·6	„ „

Mr. Campbell, however, states that no definite compounds occur, the six solid phases being all solid solutions which he indicates by the Greek letters  $\alpha$   $\beta$   $\gamma$   $\delta$   $\epsilon$   $\zeta$ .

Before the composition represented by the first of these is reached, the alloy has lost to a large extent the properties which render brass so valuable in the arts, except the yellow colour, and it may therefore be safely stated that none of the useful alloys of copper and zinc are definite chemical compounds.

**Microstructure.**—The microstructure of the brasses throws some light on the reasons for the change of character at the various critical points.

As will be seen from the cooling curve (p. 96) an alloy of copper and zinc containing more than 70 per cent. of copper solidifies as a whole, and is therefore probably a solid solution of zinc in excess of copper, and

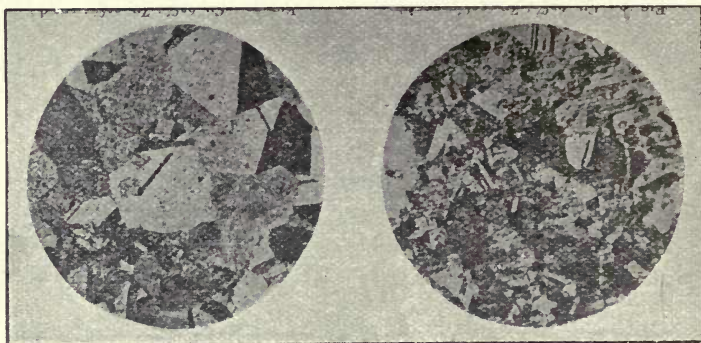


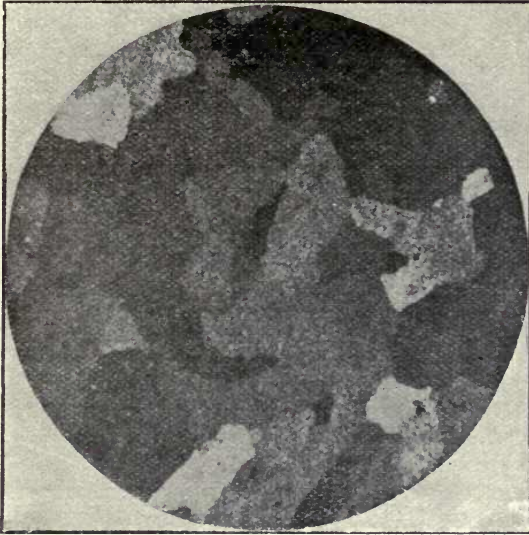
FIG. 50.

Brasses, 70 per cent. copper, 30 per cent. zinc. Crystals large in the one, small in the other. This is the normal structure of alloys containing 70 per cent. or more of copper after annealing, V, 100  $\times$ .

as might be expected, such alloys show a more or less uniform structure, the whole being made up of crystals variously oriented.

It must be remembered that a solid solution is not necessarily perfectly homogeneous, or, rather it should be said, is not normally homogeneous, for the solidification is always selective, the mother liquor growing stronger and stronger in the dissolved substance, and therefore if the cooling be slow, the mother liquor may be enriched up to the eutectic point, even though the mass of metal is not saturated. It therefore sometimes happens that distinct segregation takes place, and eutectic can be

detected even in alloys richer in copper than the proper eutectic. Such mixtures are, however, distinctly unstable, so that on annealing the eutectic diffuses, dissolves, and disappears. For this reason the structure is always better determined on the metal as annealed rather than as



A. 40 ×.

OBLIQUE ILLUMINATION.



B. FIG. 51. V, 100 ×.

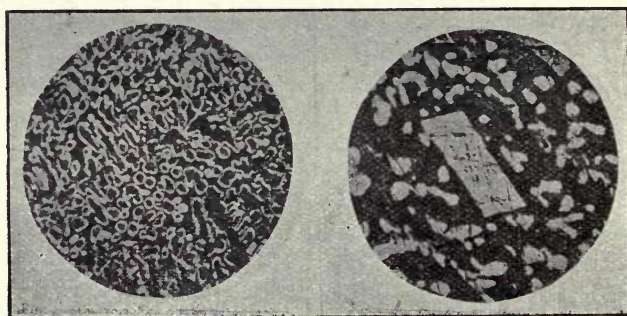
C.

- A. An alloy of 92 per cent. copper, 8 per cent. zinc.  
 B. An alloy of 67 per cent. copper, 33 per cent. zinc, as cast.  
 C. Alloy 59 per cent. copper, 41 per cent. zinc. This is the normal structure of alloys from 67 to 45 per cent. copper.

cast. The appearance of a brass containing about 70 per cent. copper is fairly uniform, but with higher copper it varies considerably with the circumstances, no doubt because the portion of the solution last solidified is richer in zinc than that first solidified, and therefore is different in colour.



A. FIG. 52. B.  
 A. Alloy, copper 23 per cent., zinc 77 per cent.  
 B. Alloy, copper 20·5 per cent., zinc 79·5 per cent.  
 V, 100 ×.



A. FIG. 53. B.  
 A. Alloy, copper 10·26 per cent., zinc 89·74 per cent.  
 B. Alloy, copper 6·65 per cent., zinc 93·40 per cent.  
 V, 100 ×.

As soon as the copper falls to about 67 per cent., the exact point varying somewhat according to the conditions of cooling, the whole character of the alloy changes, and it is seen to consist of irregular masses of a light yellow material (vertical illumination) embedded in a darker ground mass, and as the quantity of zinc is reduced the



ground mass increases in quantity. The yellow material seems to be the solution of zinc in copper which constitutes the whole mass of the higher alloys, whilst the ground mass is a eutectic probably made up of this solution and a solution much richer in zinc. As the composition of about 50 per cent. copper and 50 per cent. zinc is reached the structure again begins to change. The structure becomes more uniform, consisting only of crystals surrounded by a thin layer of the ground material. As the quantity of zinc is increased the quantity of ground mass increases, and other changes take place in the appearance; but these alloys, with such a large percentage of zinc, are of no commercial importance.

The constitution of these alloys is still somewhat uncertain, and the statements above may need revision. According to Mr. E. S. Shepherd:—\*

High copper alloys crystallise in more or less definite crystals which are a solid solution of zinc in copper (the  $\alpha$  solution). As the copper falls to about 67 per cent., the limit of saturation of solution  $\alpha$  is reached, and the brasses show two distinct constituents; as the percentage of copper falls, the  $\alpha$  crystals disappear and at 52.2 per cent. of copper the structure again becomes uniform, only one constituent, the solid solution  $\beta$ , being present. As the percentage of copper is still further reduced, a second constituent again makes its appearance, the solid solution  $\gamma$ , the crystals of which are white, and the alloy is homogeneous  $\gamma$  crystals from 40 to 31 per cent. copper. Below 36 per cent. a second constituent makes its appearance, the  $\delta$  solid solution, and then a third (the  $\epsilon$  solution), so that three constituents are detected, at 20 to 13 per cent. the alloy is again homogeneous, and is the  $\epsilon$  solution. Between 13 per cent. and 2.5 two constituents are visible and below this there is a solid solution of copper in zinc, the  $\eta$  solution.

The colour of the fracture is in some cases different from that of the filed surfaces when two constituents are present because the fracture is often determined along the crystals of one of the constituents, whilst the filed surface gives the average colour.

\* Journal of Physical Chemistry, Vol. 8, No. 6.

Mr. Shepherd gives the following table :—

Composition Per Cent. of Copper.	Crystals Present.	Colour of Filed Surface.	Colour of Fracture.
100-63	$\alpha + \beta$	Red, changing to pale yellow	Yellow
63-54	$\beta + \alpha$	Reddish yellow	Yellowish red
54-51	$\beta$	Reddish yellow	Yellowish red
51-43	$\beta + \gamma$	Reddish yellow	Yellowish red
42-40	$\gamma + \beta$	Yellowish red	Silvery, with pinkish tinge
40-30	$\gamma$	Silvery	Silvery, very bril- liant
30-20	$\gamma + \epsilon + \delta$	Silvery grey to bluish grey	Silvery grey, becom- ing duller
20-13	$\epsilon$	Bluish grey	Bluish grey
13-2.5	$\epsilon + \eta$	Bluish grey, becom- ing lighter	Zinc
2.5-0	$\eta$	Zinc	Zinc

It must be remembered also that the composition of the solid solutions varies with the temperature, as differences in stability are determined by the temperature, and where there are two or more constituents time is required for their separation, so that the structure may differ according as the alloy is slowly or quickly cooled, or annealed after cooling.

A reference to Prof. Roberts Austen's diagrams will show that the structure described is much what would be expected, there being four periods when two constituents separate out, and for the rest you would expect only one constituent. Mr. Shepherd says that one eutectic solidifying between  $800^{\circ}$  and  $900^{\circ}$  has been overlooked.

Mr. Shepherd gives the map, Fig. 54, which gives his idea as to how the constituents of a brass are arranged at different temperatures. The line A B C D E G represents the commencement of solidification, the dotted and full lines A  $b_1$   $b_1$   $c_1$  C  $d_1$   $e_1$   $f_1$  represent the completion of solidification, the part between these lines represents the condition during solidification, and the part below shows the condition of the solid. That some of the lines in this portion are curved indicates changes taking place in the solid alloy during cooling.

Mr. Shepherd states that there are no "definite compounds of copper and zinc," but that the six phases are all solid solutions.

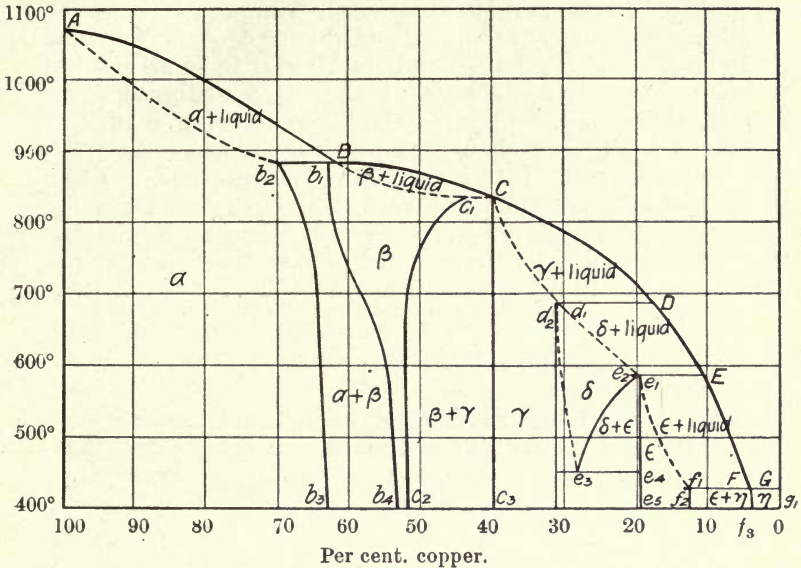


FIG. 54.—MAP OF THE CONSTITUTION OF THE BRASSES (Shepherd).

It is evident that if Mr. Shepherd's views are correct there should be five sets of brasses showing only one constituent, viz. :—

- (1) More than 67 per cent. of copper.
- (2) From 51–53 „ „
- (3) „ 30–40 „ „
- (4) „ 13–19 „ „
- (5) „ 0–2.5 „ „

and this seems to be borne out by microscopic examination of the alloys.

It will be noticed that the composition of the various solutions depends to some extent on the rate of cooling.

Figs. 51 to 53 are those given by M. Guillet in illustration, and are taken from the "Metallographist," vol. 9.

**Classification of Brasses.**—For practical purposes brasses may be divided into groups according to composition and use.

(1) Brasses containing 70 per cent. and upwards of copper.

This series includes the most useful of the brasses, as it includes those alloys of greatest tenacity and extensibility (see curves, p. 94). For all ordinary purposes the alloy of 70 per cent. copper and 30 per cent. zinc seems to be the most suitable, and nothing is to be gained by increasing the percentage of the more costly copper; but 70 per cent. copper may be taken as being about the lowest limit that should be touched on account of the possible separation of a eutectic when it is passed. All the brasses of this series will work well cold. Commercial names have been given to many of these alloys, but it would be well if all these names were discarded and the composition of the alloys always stated by the percentage of the metals present.

Among the more important alloys of this class may be mentioned :—

Tombac (Oréide, French gold)—

Copper, 90 per cent. Zinc, 10 per cent.

Pinchbeck varies very much, about—

Copper, 88 per cent. Zinc, 12 per cent.

Red brass—

Copper, 80 per cent. Zinc, 20 per cent.

Chiefly used for ornamental work. When pickled in acid it has a reddish colour.

Brazing metal—

Copper, 90 to 80 per cent. Zinc, 10 to 20 per cent.

The 80/20 alloy is known as quarter-metal and is largely used.

Dutch metals—

Copper, 80 to 85 per cent. Zinc, 20 to 15 per cent.

This alloy can be hammered into very thin leaves, and is used for Dutch metal gilding.

Standard English brass—

Copper, 70 per cent. Zinc, 30 per cent.

This is the alloy almost always specified for locomotive boiler and condenser tubes, and other purposes where a high-quality brass is required; it can be drawn into tubes cold or rolled into sheets, and it resists corrosion as well as the brasses richer in copper and better than those which are poorer.

(2) Brasses containing from 66 to 70 per cent. copper. These brasses are similar to the first class, but extensibility has begun to fall off, though the tensile strength has not diminished. As a result they do not work so well cold. They are just approaching the borderland, when a definite eutectic separates, and they do not resist corrosion so well as the members of group 1. They are, however, still ductile enough to be drawn cold into tubes or rolled into sheets.

Much ordinary brass has the composition of 67 per cent. copper and 33 per cent. zinc, and is therefore nearly a 2/1 alloy, which would give 66·67 and 33·33. The Admiralty brass used for boiler tubes for steamships has this composition.

The alloys used for rolling into sheets or drawing cold will necessarily belong to either series 1 or 2.

(3) Brasses containing from 55 to 66 per cent. of copper.

In these brasses the extensibility has fallen off very seriously, and they cannot be worked cold. They are still, however, malleable at a red heat, and can, therefore, be used when they are to be worked hot. Alloys of this series are often called yellow metal or Muntz metal, though the latter name should be restricted to the alloy containing 60 per cent. copper and 40 per cent. zinc, which was patented by Mr. G. F. Muntz in 1832, and which is largely used as a sheathing for wooden vessels. The metal is attacked fairly readily by sea water, and the poisonous zinc salts formed prevent the adhesion of the living organisms which so soon foul the bottoms of ships at sea. The same alloy is used for the manufacture of bolts and other ship's fittings. The alloy is rolled at a red heat. Hard-brass solder has about this composition.

(4) Brasses containing from about 48 to 56 per cent. of copper.

In these alloys the extensibility is so far reduced that they cannot be worked either hot or cold; but as they cast well, they are used for making brass castings of all sorts where great strength is not required. As the metal has a fine yellow colour, it is known as yellow brass. For ordinary castings a mixture of about 50 per cent. copper and 50 per cent. zinc is frequently used; but as a rule, since variations in the percentage are of

little moment, little trouble is taken to ensure a definite composition.

When an alloy of about this composition is heated to just visible redness, it becomes exceedingly brittle and can be readily powdered in an iron mortar with a heavy pestle. It then constitutes the yellow solder which is largely used for brazing purposes. In brazing or soldering it is, of course, essential that the brazing material should have a lower melting point than the materials being united.

(5) Brasses containing from 34 to 45 per cent. of copper.

As the copper falls below 50 per cent., the extensibility and the malleability almost disappear, the tensile strength rapidly falls off, and the colour of the alloy, which had previously been yellow, becomes whiter and whiter till, when the amount of copper falls to 40 per cent., the colour becomes silver-white, and the metal becomes very brittle. This alloy can be powdered in a mortar. It is known as white brass, and is used as a solder for brazing brass under the name of white solder. The composition of white solder varies from about 36 per cent. to 40 per cent. copper.

(6) Brasses below 34 per cent. of copper.

These alloys are of little commercial importance, as they are too brittle and weak to be of any use in the arts. Alloys of zinc with a small quantity of copper, up to about 10 per cent., are used for casting statuettes and other similar articles. The addition of the copper increases the strength of the alloy and destroys the very largely crystalline structure of pure zinc. Such statuettes are always bronzed by electro-deposition or otherwise, and are sold under the name of French bronze. They are of course much cheaper than true bronze, not only because the metals used in the composition of the alloy are much cheaper, but because the castings can be made more cheaply and at a lower temperature.

#### INFLUENCE OF FOREIGN CONSTITUENTS IN THE BRASSES.

As already remarked, a brass made from pure commercial materials should contain very small quantities of impurities. It sometimes happens, however, that the materials are not

pure. The copper may contain arsenic, antimony, and other elements, and the zinc may contain iron and lead, and in other cases small quantities of foreign metals may be added to modify the character of the brass. It therefore becomes important to study the influence of various impurities on the alloys.

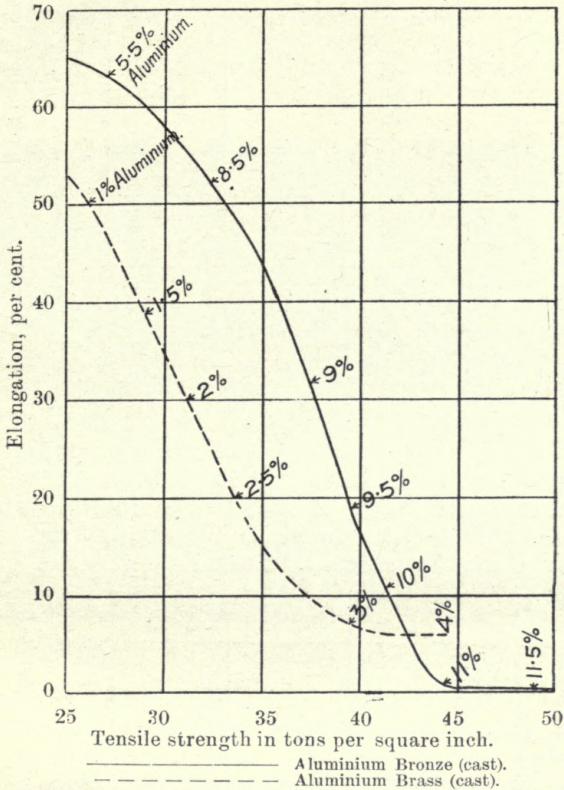


FIG. 55.—TENSILE STRENGTH OF ALUMINIUM BRASS AND ALUMINIUM BRONZE.

The data for many of the elements is very scanty, so that in many cases a full account cannot be given. The added elements will be considered alphabetically.

**Aluminium.**—Aluminium is never likely to be present as an accidental impurity, but is sometimes added in considerable quantity up to about 3 per cent., and such an alloy is known as aluminium brass. The copper is

usually from 60 to 71 per cent., so that the brass may be considered as an ordinary brass in which the zinc is partly replaced by aluminium. Such a brass has a fine yellow colour, has a high tensile strength, and elongation as is shown by the diagram Fig. 55. Figs.

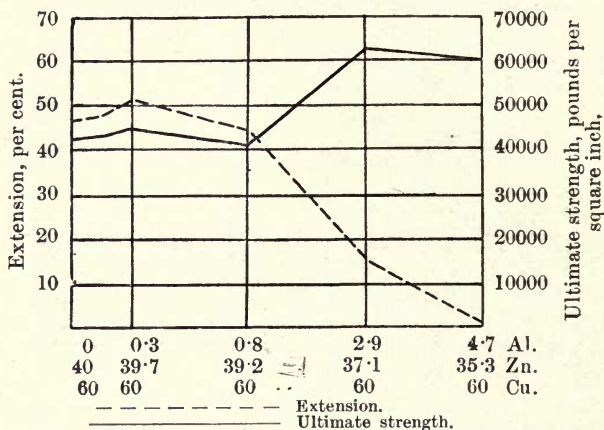


FIG. 56.—EFFECT OF ALUMINIUM ON 60/40 BRASS.

56 and 57 show the influence of aluminium in small quantities on brass containing 60 and 70 per cent. of copper. It casts well, and even when containing only 60 per cent. of copper can be forged readily at a dull red heat if it contains about 3 per cent. of aluminium. The forging

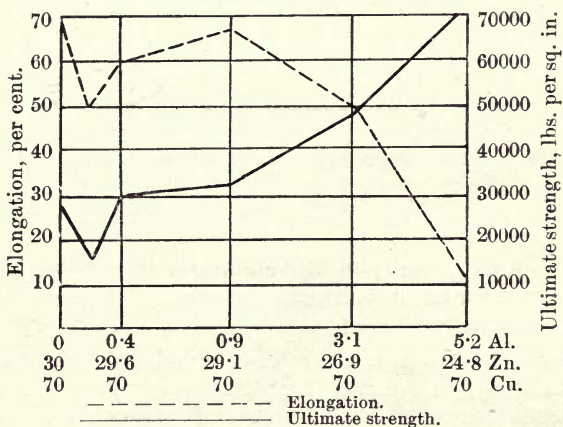


FIG. 57.—EFFECT OF ALUMINIUM ON 70/30 BRASS.



temperature is lower the less aluminium is present, so that with  $\frac{1}{2}$  per cent. it can only be forged cold. The alloy is easily made, and casts well, but the castings should always be allowed to cool slowly. Suddenly-cooled aluminium brass can be recognised by the deep gold colour and glittering lustre of the fracture.

**Antimony.**—Whilst aluminium is never likely to be present as an accidental constituent, but is always added, with antimony the reverse is the case; it is never added, but is always, when present, an accidental constituent,

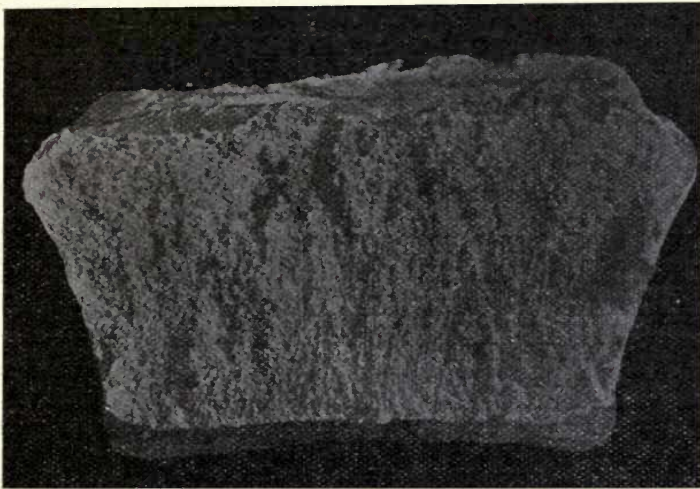


FIG. 58.—FRACTURE OF BRASS CONTAINING NO ANTIMONY.

and is derived from the copper. It is probably, with the exception of bismuth, the most injurious constituent that can be present in brass, the smallest quantity being objectionable. Antimony hardens the alloy and destroys its ductility, making it cold short, so that it will crack on rolling. For cold drawing brass tubes, or other similar purposes,  $\cdot 01$  per cent. of antimony renders the metal quite useless, and even  $\cdot 001$ , an amount which is sometimes present even in electrotype copper, is said to be objectionable. For rolling brass high in copper the maximum allowable is about  $0\cdot 01$ , and for safety less than  $0\cdot 005$  per cent. should be specified to be present in the copper to be used.

The presence of antimony produces a remarkable effect on the fracture of the alloy, which is best seen with an alloy containing about 60 per cent. of copper, and this, as already remarked, is sometimes used as a test for the quality of the copper.

The illustrations, Figs. 58, 59, 60, of the fracture of brasses containing antimony, from a paper by Mr. E. S. Sperry, read before the American Institution of Mining Engineers,\* will illustrate the effect of antimony on the structure of the metal.

The table below gives some of Mr. Sperry's results, the brass being approximately 60 and 40.

	60/40 Brass.	60/40 '01 Sb.	60/40 '02 Sb.	60/40 '05 Sb.
Tensile strength lbs. per square inch..	58,700	61,290	58,800	56,600
Elongation in 8in. per cent. ... ..	35	33·2	34·5	21
Reduction of area per cent. ... ..	43·9	43·7	45	27

With '01 per cent. the brass seemed to behave, on rolling, much like ordinary brass, but with 0·2 per cent. the metal rolled badly; the sheet could not be bent over to 45 degrees without cracking, but could be forged hot.

With even a very small percentage of antimony the presence of a dark-coloured constituent can be detected under the microscope distributed through the mass, and in larger quantities it forms a network through the mass.

**Arsenic.**—Arsenic is always present, at least in traces, in copper, even electrotype, and it is usually regarded as being a very objectionable constituent in brass. The maximum quantity allowable in brass which is to be used for cold drawing is about '05 per cent., and this is the amount which is usually specified for B.S. copper which is to be used for such purposes. The effect of arsenic is to harden the metal and render it brittle, but to a less degree than antimony.

\* Transactions. Vol. XXVIII., page 176.



FIG. 59.—FRACTURE OF BRASS CONTAINING .05 PER CENT. OF ANTIMONY.

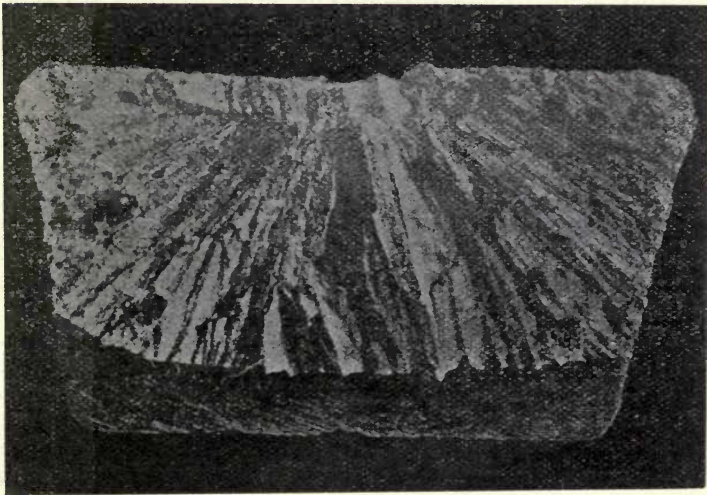


FIG. 60.—FRACTURE OF BRASS CONTAINING .1 PER CENT. OF ANTIMONY.

Mr. Sperry found that a 60/40 brass, with 0.50 of arsenic, would not roll at all, but "cracked to pieces" in "breaking down"; but it cast well, and "resembled phosphor-bronze in its limpid nature." With 0.25 of

arsenic the fracture showed traces of crystallisation. The bar was rolled from a thickness of lin. to .049in. with five annealings, and cracked badly during the rolling. With 0.10 per cent. of arsenic there were only slight traces of crystallisation visible on the fracture, but the bar cracked on "breaking down," and even with 0.05 per cent. the cracking was quite marked. With 0.02 per cent. of arsenic the qualities of the brass were better than most pure copper.

Mr. Sperry sums up his results :—

(1) Arsenic when present in brass to the extent of over 0.02 per cent. is injurious and causes it to crack on rolling.

(2) Arsenic produces great fluidity in melted brass.

(3) Brass containing arsenic makes a cleaner casting than when it is not present.

(4) When present in an amount not over 0.02 per cent., arsenic imparts ductility to brass, probably by a reduction of the oxide of copper formed during melting.

**Bismuth.**—This is probably the most objectionable constituent in brass, but fortunately it is very rarely present in any quantity. Mr. Sperry has investigated this subject, and the results of his experiments are published in the "Transactions" of the American Institution of Mining Engineers, Vol. XXVIII. He comes to the conclusion that as far as inducing cold shortness bismuth is less injurious than antimony, but that it produces very marked red shortness. An alloy containing 0.05 per cent. would forge on a thin edge, but if bent over cracked at the bend, whilst an alloy with 0.25 per cent. would not forge at any temperature. He also comes to the conclusion that bismuth is the cause of fire cracks, and that even when these are not actually visible they are present latent, not perhaps as actual cracks, but more likely as lines of inferior cohesion in an apparently homogeneous mass. Rolling develops them, and to all appearance they then partake of every character of true fire cracks. Mr. Sperry gives 0.01 per cent. as the maximum that should be allowed in brass for rolling, and even less than this will be injurious to the copper.

Brass containing bismuth breaks with a highly crystalline fracture, as is seen by the photograph of the brass containing 0.09 per cent. as from Mr. Sperry's paper. It will be seen that the crystalline structure is much less marked than in the case of antimony.

Under the microscope the separation of a substance containing bismuth can be seen.

**Iron.**—Iron is only likely to be present in very small quantities as an accidental impurity. The zinc may contain a small quantity, and the remainder can only

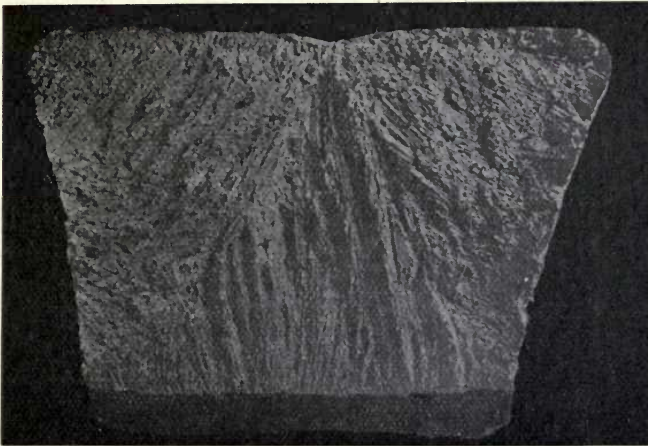


FIG. 61.—FRACTURE OF BRASS CONTAINING .5 PER CENT. OF BISMUTH.

be derived from the iron tools used to stir the alloy. It is considered as being objectionable, so that zinc which is to be used for the manufacture of high-quality brass is usually specified not to contain more than 0.05 per cent. of iron. It is sometimes added in considerable quantity, and produces somewhat remarkable alloys, which have been known for a long time as sterro-metal and Aich metal, and in more recent form as delta metal. Prof. Roberts Austen found that a brass having a tensile strength of about 20.7 tons at 20° C. had this increased to 25.6 tons by the addition of 1.5 per cent. of iron, and though both the alloys lost strength very considerably as the temperature was increased, the loss was less with

the alloy containing the iron than with that which was free from iron, so that the difference became greater as the temperature rose.

The reason for this difference is explained by Sir W. Roberts Austen as being due to the fact that iron raises the solidifying point of the alloy, and that it also prevents the formation of a eutectic which otherwise forms at a comparatively low temperature. Sterro-metal consists of copper, 60 per cent.; zinc, 38 to 38.5; and iron, 1.5 to 2. It is therefore as 60/30 of brass, in which a small part of the zinc is replaced by iron. Aich metal is almost if not quite the same. Delta metal contains varying quantities of iron according to the purpose for which it is to be used, and other metals, such as iron and manganese, may also be present, a little phosphorus being added to deoxidise the copper. The alloy has a brass-yellow colour, is strong, having a tensile strength up to from 25 to 35 tons, with an elongation of from 11 to 39 per cent. on an 8 in. test-piece. It is therefore very tough, and can be rolled and worked quite satisfactorily. It is also said to resist corrosion much better than ordinary brass.

**Lead.**—Lead is present in brass in small quantities derived from the spelter used in its manufacture, and is sometimes intentionally added. The amount of lead which brass will take up is not large, and it tends to separate on cooling. With 5 per cent. or over the tendency of the lead to separate is marked, and it may squeeze out during working, and even with much smaller quantities it can be detected as a separate constituent under the microscope. The presence of lead reduces both the tensile strength and the extension of the metal, the effect being very much more marked with cast brass than with that which had been drawn and annealed, probably on account of the segregation of the lead in the latter case. The presence of lead makes the metal softer for working, and for that reason it is sometimes added to brass, and its effects can be well seen by the difference in the turnings that are obtained, the turnings from the brass itself coming away in long curled pieces (Fig. 62), while those from the leaded brass come away in short chips (Fig. 63). The amount of lead added usually varies between 2 and 3 per cent. Mr. Sperry, in

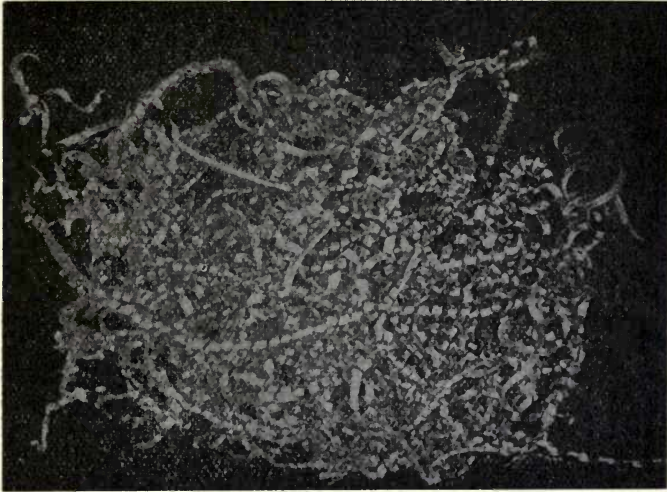


FIG. 62.—BRASS CHIPS FREE FROM LEAD.

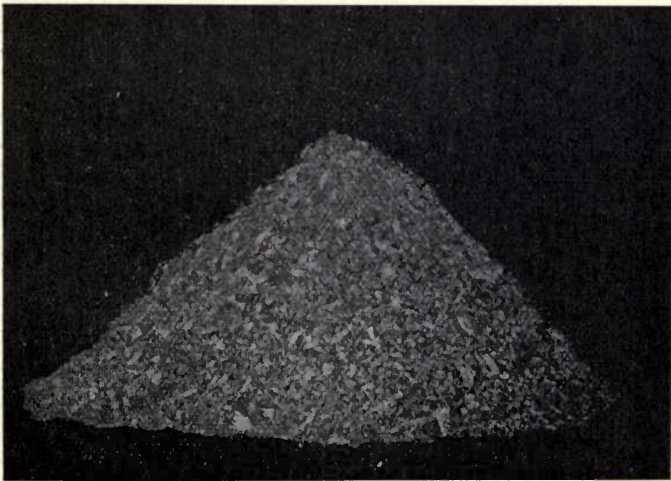


FIG. 63.—BRASS CHIPS CONTAINING 2 PER CENT. OF LEAD.

a paper read before the American Institute of Mining Engineers, in 1897, gives the analysis of a considerable number of brasses for various purposes containing lead,

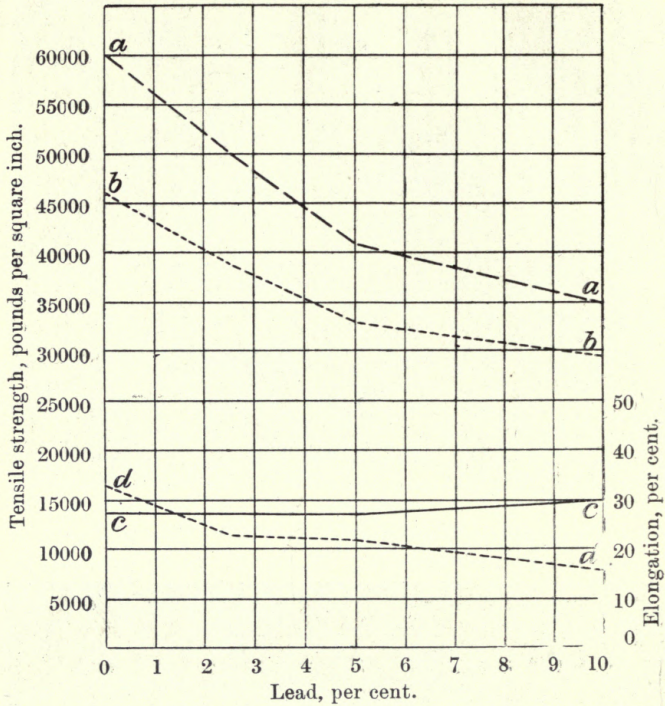


FIG. 64.—ALLOYS OF COPPER, ZINC, AND LEAD, CONTAINING 60 PER CENT. COPPER.

- a a* Tensile strength of annealed sheet.
- b b* " " cast metal.
- c c* Elongation " lin. of cast metal.
- d d* " " Sin. " "

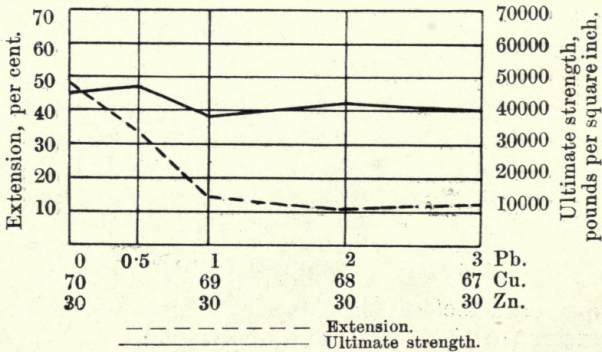


FIG. 65.—EFFECT OF LEAD ON 70/30 BRASS.



and discusses the influence of lead on brasses very fully. The diagram (Fig. 64) is from Mr. Sperry's paper.

**Manganese.**—Alloys are now largely made under the name of manganese bronze which are really nothing more than brasses, to which a small quantity of manganese has been added. The composition of the commercial manganese bronzes (or rather brasses) is very variable,

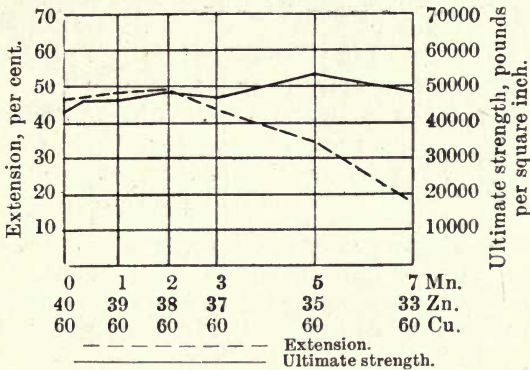


FIG. 66.—INFLUENCE OF MANGANESE ON 60/40 BRASS.

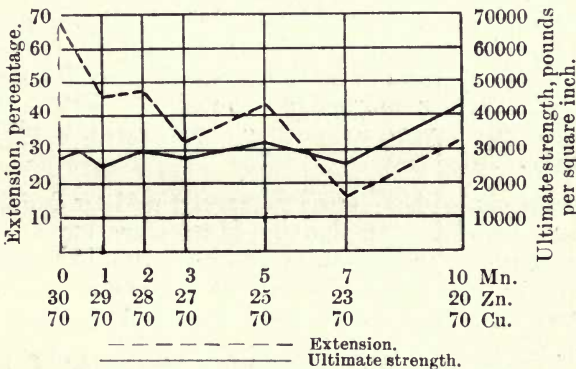


FIG. 67.—INFLUENCE OF MANGANESE ON 70/30 BRASS.

and sometimes they contain no manganese, the manganese having been all oxidised out, owing to its ready oxidisability. It does not, of course, follow that the manganese has been of no use because it will have acted as a deoxidising agent. Again, the manganese is usually added in the form of ferro manganese, so that even if the manganese is completely

oxidised out, the residual iron may have an influence on the properties of the resulting metal. The presence of manganese seems to harden the alloy, increase its strength, and at the same time diminish very considerably the extension before fracture. Figs. 66 and 67 show the influence of small quantities of manganese on brass.

Now that comparatively pure manganese can be obtained, it can be used as a deoxidiser in brass and bronze casting, and it has the advantage that an excess is not injurious, as in the case of phosphorus, but rather the reverse. The melting point of pure manganese is so high that the manganese should always be added in the form of a copper-manganese alloy.

Manganese bronze contracts very much on solidification, so that large gates and rising heads are essential.

**Nickel.**—When present in very small quantity nickel has no important influence on the properties of the alloy. Alloys containing a considerable proportion of nickel will be considered under the head of German silver.

**Oxygen.**—Copper dissolves oxygen very readily and becomes very brittle or dry. When such copper is used in the manufacture of brass it has been thought that it would produce an alloy of inferior quality. This, however, does not seem to be the case. The oxide of copper is apparently decomposed by the zinc. Whether brass contains any oxygen in solution is uncertain, but it seems unlikely.

**Phosphorus.**—Phosphorus is largely used for deoxidising copper, and has occasionally been used for a similar purpose in the manufacture of brass, whether with any real advantage or not the writer is unable to say. He has never come across a brass containing phosphorus.

**Tin.**—Tin is sometimes added to brass for various purposes. In the manufacture of condenser tubes and other articles 1 or 2 per cent. of tin is sometimes added. Naval brass, largely used for condenser tubes, contains—

Copper	...	...	...	...	...	70
Zinc	...	...	...	...	...	29
Tin	...	...	...	...	...	1

Whether the addition of this small quantity of tin is any real advantage is somewhat uncertain, but the author thinks not. The influence of tin is to harden the alloy, increase its strength, and diminish the extension before fracture. With 1 per cent. of tin the influence is not very great, but as the percentage is increased the

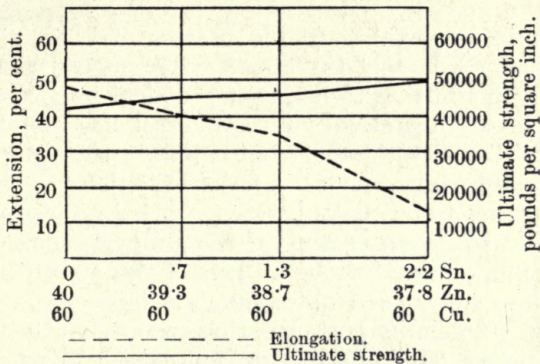


FIG. 68.\*

action becomes very marked. It is sometimes said that the brass containing tin is less liable to corrosion than brass; this, however, is not the case. The tin seems to dissolve in the alloy, and does not alter the micro-structure. Fig. 68 shows the influence of small quantities of tin on brass.

\* Figs. 64 to 68 are from an article by L. S. Austin in the "Mineral Industry," Vol. XIV., p. 151.

## CHAPTER VIII.

### THE COPPER-TIN SERIES.

NEXT in importance to the brasses may be placed the bronzes, or copper-tin alloys. For many reasons this series, in addition to its great practical importance, is of very great theoretical interest, and it has therefore been very fully investigated from a purely scientific point of view, and whilst much has been done there are still some obscurities to be cleared.

The influence of tin on the properties of copper is very marked, and though alloys of the metals in all proportions have been obtained it is only two series that are of practical importance, those properly called bronzes, containing 80 per cent. or more of copper, and the speculum metals, containing about 50 per cent. of copper, and these are used for quite different purposes.

Bronze has been known and used from times before the commencement of the historic period. In prehistoric times it was used for weapons and tools, and is generally supposed to have been in use for such purposes before the discovery of iron. In early-historic times it was used for the manufacture of coins, medals, and similar articles, the composition of the alloy used being almost identical with that used to-day.

**Range of Composition of the Bronzes.**—The range of composition is much less in the case of the bronzes than of the brasses, as all those of any importance for engineering purposes contain 80 per cent. of copper or over, the influence of tin in modifying the character of the alloys being much more marked than that of zinc. An immense amount of information has been collected as to the properties of bronze and the influence of its composition on its qualities.

The United States Board Committee on Alloys published an elaborate report in 1878, giving the composition and properties of a large number of bronzes used for various purposes, and this table, in whole or in part, has

been reproduced in most books on alloys. The Alloys Research Committee of the Institution of Mechanical Engineers took up the subject, and published very valuable material in its third Report in 1895, and since then the work has been carried on by many workers, and results have been obtained which may be of great practical importance.

**Freezing-point Curve.**—At the outset it may be advisable to describe the phenomena which are met with as an alloy of copper and tin is cooled, since the position of an alloy on the freezing-point curve seems largely to determine its properties.

As tin is added to copper (which melts at  $1,090^{\circ}$  C.) the melting point slowly falls, as usual, and the alloy solidifies as a whole, *i.e.*, is a solid solution, till the percentage of tin reaches about 5. As soon as the percentage of tin becomes larger a double freezing point occurs, exactly as in the case of brass, one portion solidifying at a temperature constantly falling as the percentage of tin increases till with about 25 per cent. of tin it reaches about  $790^{\circ}$ , whilst the other portion, the mother liquid, solidifies uniformly at about  $790^{\circ}$ , so far the alloy behaving exactly like an ordinary eutectic alloy. When the percentage of tin reaches about 10 per cent., however, another phenomenon makes its appearance. The solidification begins at about  $1,000^{\circ}$  C., the second freezing takes place at about  $790^{\circ}$  C. as before; but there is still some material left unsolidified which freezes at  $500^{\circ}$ , so that with the alloys containing from 10 to 20 per cent. of tin there are three distinct freezing points; that is, the alloy solidifies in three separate portions. Fig. 69 shows the freezing-point curve as determined for the Alloys Research Committee. It will be seen that it is very complex, that with alloys containing a little over 60 per cent. of copper there are no less than four distinct freezing points, that with 40 per cent. of copper these have fallen to three which persist till there is less than 10 per cent. of copper, and that up to about 97 per cent. of tin there are still two freezing points. Reference will be made to this freezing-point curve later, and explanation given of some of its peculiarities; but enough has been said to indicate its

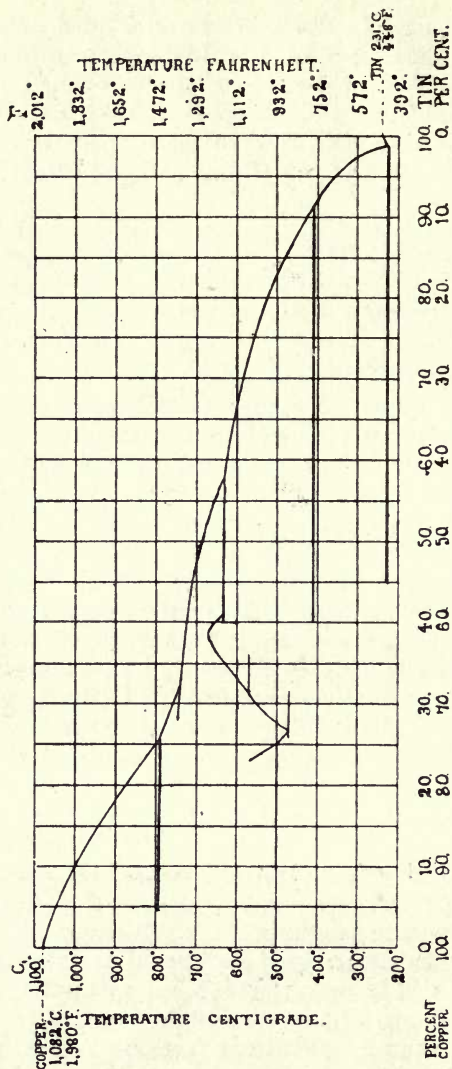


FIG. 69.—FREEZING-POINT CURVES OF COPPER-TIN ALLOYS.

general character. Other observers have worked on the subject, and have on the whole confirmed the results obtained by the Alloys Research Committee.

The properties of the alloys will now be studied in the light of this freezing-point curve.

**Colour.**—Tin very rapidly destroys the colour of copper, and imparts to the alloy a bronze-yellow colour. The following table of the influence of an increasing percentage of tin on the colour of the alloy is taken from the report of the American Committees :—

Copper.	Tin.
96·27 ..	3·73 reddish yellow.
90·00 ..	10·00 greyish yellow.
80·00 ..	20·00 yellowish red.
75·00 ..	25·00 reddish white.
70·00 ..	30·00 white.
60·00 ..	40·00 light grey.

All below this being shades of greyish white.

It will be seen therefore that generally all alloys below 75·00 per cent. of copper are white or grey in colour.

It will be seen from the cooling curve that in the alloys containing over 80 per cent. of copper there will be a considerable portion of the constituent which solidifies at the highest temperature, and this is apparently a solid solution of tin in copper, similar to the solution of zinc in copper described under the brasses, and which is yellow in colour. The eutectic, which solidifies at about 760° and contains only about 70 per cent. of copper, is white, so that it gradually dilutes the colour of the alloy, and when it becomes the predominating constituent the colour becomes white. It will be seen that for alloys containing a smaller percentage of copper the constituents will vary, and with this variation in composition there is a small change in the colour of the alloy.

When the alloy contains about 66·6 per cent. of copper, it has a fine silver-white colour, and it is then called speculum metal, because it was at one time used for making the mirrors or specula for reflecting telescopes.

**Specific Gravity.**—The specific gravity of the bronzes is greater than that of a mean of its constituents, the metals therefore contracting on mixing.

The following table from Thurston\* gives the specific gravity of the alloys :—

Copper.	Tin.	S. G. Actual.	S. G. Calculated.	Difference.
100	4	8·79	8·74	0·05
100	6	8·78	8·71	0·07
100	8	8·76	8·68	0·08
100	10	8·76	8·66	0·10
100	12	8·80	8·63	0·17
100	14	8·81	8·61	0·20
100	16	8·87	8·60	0·27
100	33	8·83	8·43	0·40
100	100	8·79	8·05	0·74

**Tenacity.**—Very many experiments have been made to determine the tensile strength and other mechanical properties of the bronzes.

The following figures are taken from the American report before quoted :—

Copper.	Tin.	Tenacity, lbs. per Square Inch.
96·27	..	3·73 .. 32,000
92·80	..	7·20 .. 28,560
90·91	..	9·09 .. 32,093
89·29	..	10·71 .. 37,688
85·71	..	14·29 .. 44,071
84·29	..	15·71 .. 36,004
81·10	..	18·90 .. 39,648
80·00	..	20·00 .. 32,980
76·29	..	23·71 .. 21,728
72·80	..	27·20 .. 10,976
70·00	..	30·00 .. 5,585
68·25	..	31·75 .. 1,620
61·71	..	38·29 .. 638
50·00	..	50·00 .. 725

These are only examples taken from the table. An examination of the whole table will show that the figures are extremely discrepant, and that no definite inference could be drawn from them except that of a general rise of tenacity up to about 80 per cent. of copper, then a fall which soon becomes very rapid, and the tenacity almost disappears, to increase somewhat as the tin end of the

\*"Materials of Engineering," part 3, p. 141



series is reached. Fig. 70 gives the curve for tensile strength and elongation as given by the Alloys Research Committee in its third report. A glance at that will show that tensile strength rises, but not uniformly, till it reaches a maximum of about 36,000lbs., with rather more than 80 per cent. of copper, and then it falls off very sharply.

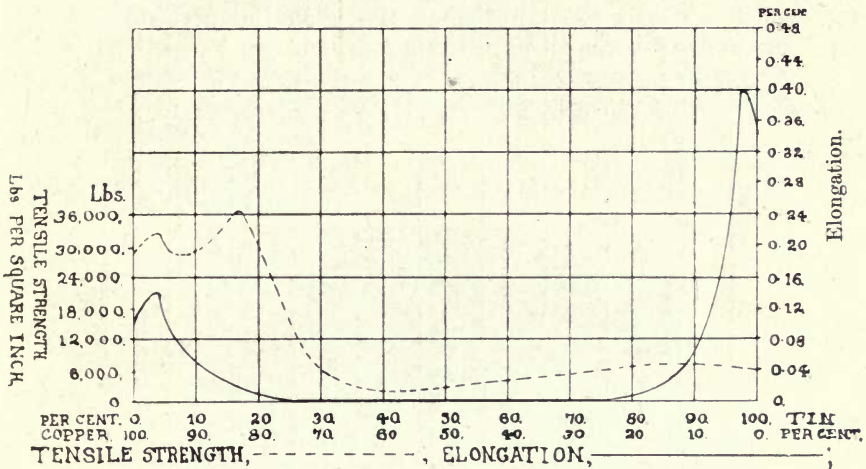


FIG. 70.—TENSILE STRENGTH AND ELONGATION OF COPPER-TIN ALLOYS.

**Ductility.**—The ductility which marks the toughness of the metal, and which is in many cases quite as important as actual tensile strength, is seen to reach a maximum when there is about 5 per cent. of copper, then to fall off and almost disappear, and then to reappear when about 80 per cent. of tin is present, and, as might be expected from the known softness and ductility of tin, to increase considerably as the tin approaches purity. As ductility is the reverse of brittleness it will be judged that those alloys which are devoid of ductility will be very brittle, and this is the case.

The passage from the strong to the weak condition is attended with a complete change in the character of the fracture. The strong alloys break with a more or less granular fracture, but the brittle ones are almost glassy, and the fracture is often distinctly conchoidal.

**Electric Conductivity.**—Fig. 71 gives the curves for electric and heat conductivity as determined by the Alloys Research Committee. It will be seen that as the percentage of tin increases the conductivity falls, becoming very small, then with about 9 per cent. of tin there is a sudden break and a continued fall at a slower rate till about 32 per cent. of tin is present, then a slight rise, and then a nearly-constant conductivity as the percentage of copper falls, until pure tin is reached.

**Heat Conductivity.**—The heat conductivity, as will be seen by reference to Fig. 71, varies very irregularly.

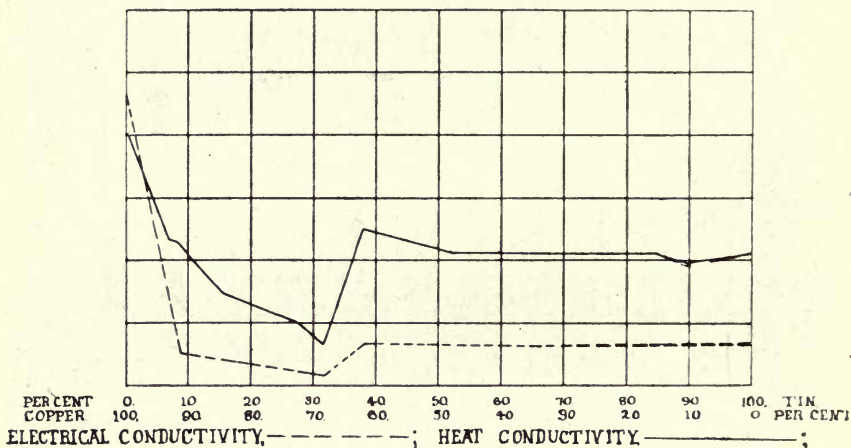


FIG. 71.—CONDUCTIVITY OF COPPER-TIN ALLOYS.

**Microscopic Structure.**—As might be expected, the microscope throws considerable light on the structure of the alloys of the copper-tin series; but, owing to their complexity and the great influence of the rate of cooling on the structure, it is not possible to give a clear outline of the results that have been obtained.

It may be simplest to take the classification and description of Dr. Campbell, who, in his paper read before the Society of Mechanical Engineers, as an appendix to the Reports of the Alloys Research Committee, has given a full account of his researches into the microstructure of the copper-tin alloys. He begins with tin, adding small percentages of copper. He classifies the alloys into groups.

(1) 0 to 1 per cent. copper. The mass consists of tin with a second constituent surrounding the grains of tin.

(2) 1 to 8 per cent. of copper. Crystals which are hollow rhombic crystals, which form groups, and which appear in section as three or six rayed stars. The more slow the cooling the larger and less numerous are the stars.

(3) 9 to 40 per cent. copper. A new constituent crystallises out, and as the copper reaches 40 per cent. "plate-like crystals are grouped in parallel bunches," and in the eutectic between them small bright, hollow crystals are seen.

(4) 41 to 61.7 per cent. copper. Dr. Campbell says "the difference between the alloy containing 40 per cent.

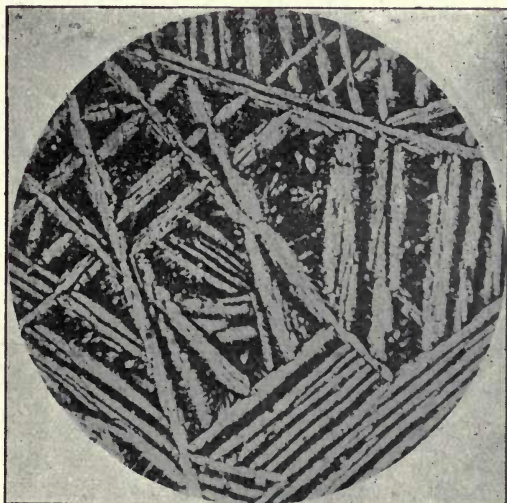


FIG. 72.—BRONZE. COPPER, 2 PER CENT.; TIN, 98 PER CENT.  $V \times 50$ .

This shows its constituents, but not the star-like crystals which the author has been unable to obtain with alloys of this composition.

and that containing 41 per cent. of copper is very marked. The crystals in the latter are small and lath-shaped, and arranged more or less in groups, and separated from one another by eutectic." With each addition of copper the groups of crystals become more and more compact, and the amount of eutectic diminishes till at 50 per cent. copper it disappears altogether.

The bright constituent of the crystals grows smaller and smaller; at 50 per cent. it takes the place of the eutectic and forms the ground mass in which the constituent containing the higher percentage of copper has solidified. "When 61.7 per cent. of copper is reached the bright constituent disappears, and we have a homogeneous mass, probably the definite compound  $\text{Sn Cu}_3$ ."

(5) 61.7 to 68.2 per cent. copper. Each addition of copper to  $\text{Sn Cu}_3$  brings out more and more of the bright

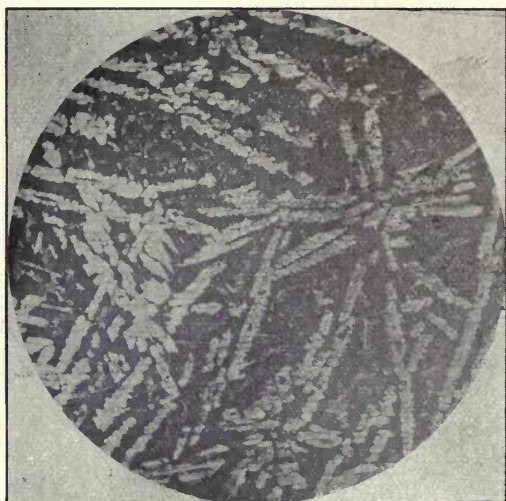


FIG. 73.—COPPER, 11; TIN, 89 V  $\times$  40.

constituent  $\text{Sn Cu}_4$ . "The alloys set as a whole at the first break, and tend to rearrange themselves subsequently in the solid."

(6) 68.2 to 74.5 per cent. copper. "A second eutectic makes its appearance, enveloping the grains of  $\text{Sn Cu}_4$ . As the copper increases the grains split up into veins and dendrites which attain their full development in the neighbourhood of 72 per cent. As the total copper increases the eutectic increases also, the veins of  $\text{Sn Cu}_4$  gradually disappear, and finally the dendrites go, leaving the mass entirely made up of the eutectic, about 75 per cent. copper."

(7) 75 to 100 per cent. copper. "With 76 per cent. of copper present two new constituents make their appearance, and the alloy assumes a yellow tint. It loses its brittleness. In section are found yellow grains surrounded by a bright white border set in the second eutectic, in which small bright white grains also occur." As the total copper is increased, the yellow grains increase, forming dendrites and skeleton crystals; the white borders and grains merge together, and the eutectic decreases till at about 90 per cent. it disappears. The yellow grains become darker

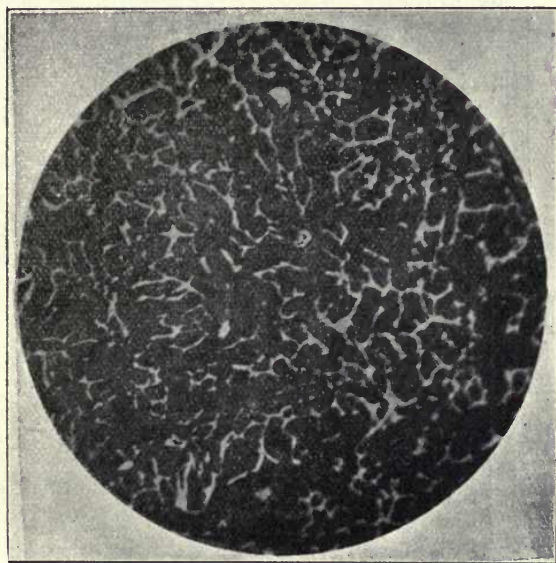
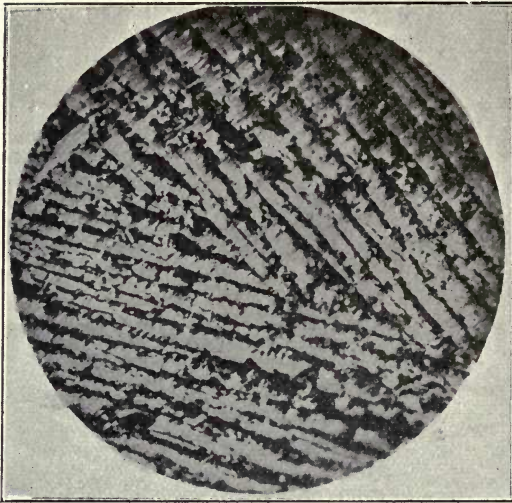
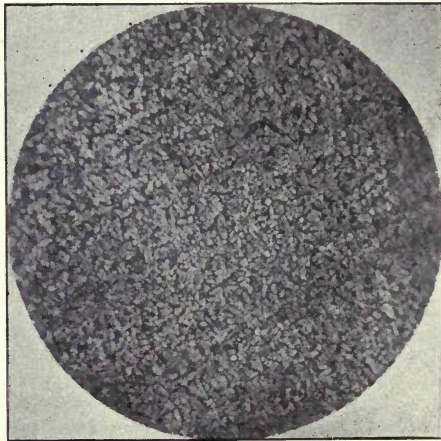


FIG. 74.—COPPER, 21; TIN, 79 V  $\times$  140.

and darker, containing less tin in solid solution, till they become copper colour. The light borders disappear, leaving only copper dendrites at 95 per cent.

It will thus be seen that the structure of these alloys is excessively complex, and that, as a rule, they are made up of copper containing tin in solid solution, probably the definite compounds  $\text{Sn Cu}_4$  or  $\text{Sn Cu}_3$  and  $\text{Sn Cu}_2$  with perhaps other compounds containing less copper, and eutectics made up a mixture of the two of these. The ordinary useful

FIG. 75.—BRONZE. COPPER, 38; TIN, 62 V  $\times$  20.FIG. 76.—BRONZE. COPPER, 65; TIN, 35 V  $\times$  140.

bronzes being composed mainly of copper containing tin in solution, and the eutectic of the copper-tin solution and the compound  $\text{Sn Cu}_4$ . The metal becoming brittle and ceasing to be of value as soon as the eutectic predominates.

The four known compounds of copper and tin which may be present in alloys are :—

	Per cent. Copper.	Per cent. Tin.
Sn Cu <sub>4</sub> .. ..	68·1 ..	31·9
Sn Cu <sub>3</sub> .. ..	61·6 ..	38·6
Sn Cu <sub>2</sub> .. ..	51·7 ..	48·3
Sn Cu .. ..	34·8 ..	65·2

It will be noticed that the two first-named are the only two which seem to exist as definite compounds in the copper-tin series of alloys.

From the complex character of the alloys it is to be expected that great changes would be produced by the rate of solidification ; and this is so, the structure of the alloy

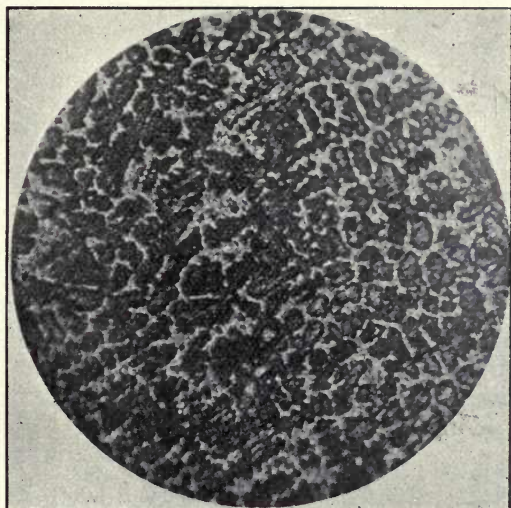


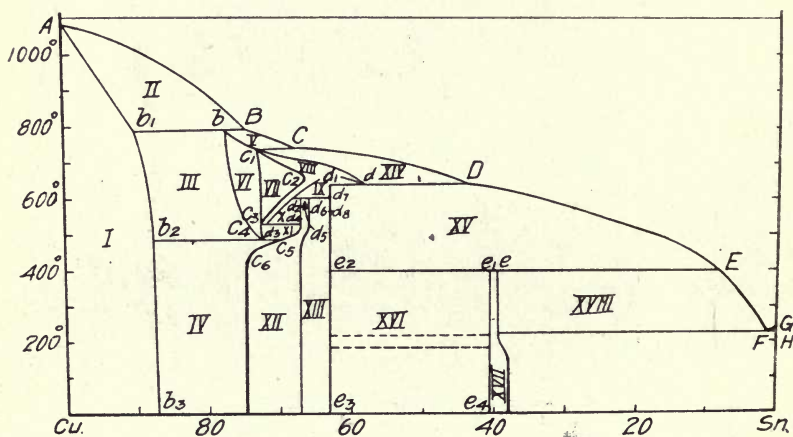
FIG. 77.—BRONZE. COPPER, 87; TIN, 13 V × 20.

suddenly solidified being in some cases quite different from that which has been allowed to solidify slowly. The reason for this is quite obvious. All the separations that take place during the solidification of an alloy require time, longer or shorter according to the nature of the change ; and if the solidification be very rapid, the constituents may not have time to separate, but may remain so mixed as to be indistinguishable. This is especially the

case where the constituents usually occur in more or less distinct crystals. On the other hand, very slow solidification allows of more complete separation.

Messrs. Shepherd and Blough have recently investigated the copper-tin series very completely in certain directions, and as a result they have somewhat modified the results previously obtained. They have replotted the cooling curve, and mapped out the constituents of these alloys. They find four solid solutions of copper and tin,  $\alpha$   $\beta$   $\gamma$   $\delta$  and  $\epsilon$  solutions,  $\text{Cu}_3\text{Sn}$  and the definite compound pure tin.

The map is shown in Fig. 77A. The line A B C D E represents the commencement of solidification, the line



- |                                |                                       |  |
|--------------------------------|---------------------------------------|--|
| I. = $\alpha$                  | VII. = $\beta + \gamma$               | XIII. = $\delta + \text{Cu}_3\text{Sn}$      |
| II. = $\alpha + \text{liquid}$ | VIII. = $\gamma$                      | XIV. = $\gamma + \text{liquid}$              |
| III. = $\alpha + \beta$        | IX. = $\gamma + \text{Cu}_3\text{Sn}$ | XV. = $\text{Cu}_3\text{Sn} + \text{liquid}$ |
| IV. = $\alpha + \delta$        | X. = $\gamma + \delta$                | XVI. = $\text{Cu}_3\text{Sn} + \epsilon$     |
| V. = $\beta + \text{liquid}$   | XI. = $\beta + \delta$                | XVII. = $\epsilon$                           |
| VI. = $\beta$                  | XII. = $\delta$                       | XVIII. = $\epsilon + \text{liquid}$          |

FIG. 77A.

$A b_1$  the completion of solidification, and the horizontal lines the eutectic solidification. It will be seen at once from the position of the lines that complex changes take place during solidification, and during cooling after solidification. The region I. is that in which solid solution  $\alpha$ , containing over 92 per cent. of copper, exists alone. In the region II.  $\alpha$  is solidifying and leaving a



liquid, and in the region III. there is a mixture of the two solid solutions  $\alpha$  and  $\beta$ , but at  $486^\circ$  the  $\beta$  solution breaks up, yielding another form  $\delta$ , so that the region III. consists of the two solid solutions  $\alpha$  and  $\delta$ , the latter containing from 68 to 75 per cent. of copper. The field V. is a small one, containing  $\beta$  crystals in contact with still liquid matters, which solidifying gives in region VI.  $\beta$  solution. Region XIV. contains  $\gamma$  solution in contact with liquid matter which solidifying gives in region VIII. pure  $\gamma$  solution. Its shape is very peculiar. Region VII. contains both  $\beta$  and  $\gamma$  solutions, the crystals of the former being yellow, those of the latter white. Region X. consists wholly of white crystals, but these are seen to consist of two constituents. In region XI. below the lines  $d_3$ ,  $d_4$ , the structure changes, and there is a mixture of brilliant yellow crystals in a white matrix. "The phase  $\delta$ , which is formed entirely through transformation in the solid, was for a long time considered to be the compound  $\text{Cu}_4\text{Sn}$ ." The components of this phase vary much with changing temperature. Region XIII. consists of a mixture of  $\delta$  and  $\text{Cu}_3\text{Sn}$ , resulting from the breaking down of the  $\gamma$  crystals along the line  $d_2$ ,  $d_5$ . Region XV. is  $\text{Cu}_3\text{Sn}$ , in presence of liquid matter passing over as it cools into XVI.,  $\text{Cu}_3\text{Sn} + \epsilon$ . XVII.  $\epsilon$ , and XVIII.  $\epsilon$ , with still liquid matter, after which pure tin or a solid solution, which is mostly tin, separates.

"In addition to the changes in the solid which have been recorded for the copper-rich alloys, we found two other heat changes in the alloys containing from 41 to 61.5 per cent. of copper. The first of these changes is at  $218^\circ$ , and occurs at the same temperature in all the above-mentioned concentrations. The second change is likewise one at a constant temperature, and is found at  $182^\circ$ ."\*

**Heat Treatment of Copper-Tin Alloys.**—Not only are there the changes due to sudden solidification, but a complex body like bronze may undergo changes after solidification, which may be altered very considerably by rapid or slow cooling, and which are in some respects similar to those

\* Shepherd and Blough. *Journal of Physical Chemistry*. Vol. 10 (1906), p. 651.

which steel undergoes, and therefore it might be expected that heat treatment would considerably modify its properties. Messrs. Heycock and Neville have shown that this is the case as far as the microscopic structure is concerned. The sudden cooling of the alloys under certain conditions almost obliterating the microscopic structure, much in the same way as does the quenching of steel, and they found, moreover, that the structure could be restored by heating the chilled specimen to below its melting point and allowing it to cool slowly, so that changes in the structure of bronzes may take place not only during but also after solidification. Mr. Campbell has also pointed out how greatly the microstructure of the bronzes varies according as the alloy is allowed to cool slowly or quickly—structures quite visible in the one case often being indistinguishable in the other.

M. Guillet, following up the work of Messrs. Heycock and Neville, thought that perhaps the useful properties of the alloys might be modified by heat treatment, and his experiments show that with some of the alloys the changes are well marked.

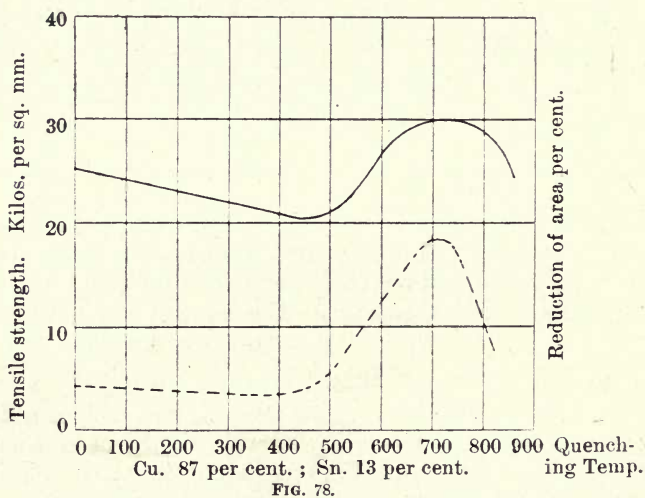


Fig. 78 shows diagrammatically the results obtained with a brass containing 87 per cent. copper and 13 per cent. tin.

With copper 84, tin 16, the results were :—

Quenching Temperature.	Tensile strength. Kilos. per sq. mm.	Elongation Per Cent.	Reduction of area Per Cent.
Not quenched	... 25	... 4.7	... 1.4
300 ...	... 22	... —	... 0
400 ...	... 24.4	... —	... 0
500 ...	... 19.4	... 5.6	... 1.4
550 ...	... 40.1	... 10.1	... 5.9
600 ...	... 42.6	... —	... 3.6
650 ...	... 36.3	... —	... 1.4
700 ...	... 34.4	... —	... 2.9
750 ...	... 29.6	... —	... 5.0

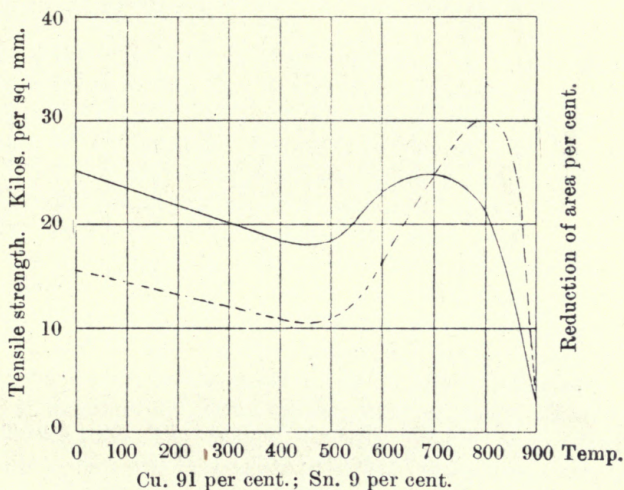


FIG. 79.

With copper 91, tin 9, the results were :—

Quenching Temperature.	Tensile Stress. Kilos. per sq. mm.	Elongation. Per Cent.	Reduction. Per Cent.
Not quenched	25.4	10.3	16.5
400 .....	18.4	10.5	14
500 .....	18.4	10.5	11.5
600 .....	25	9.2	23.5
700 .....	25	10.5	23.5
800 .....	20.7	7.1	30
900 .....	3.9	3.9	2

The results are shown diagrammatically in Fig. 79.

With copper 90, tin 5, the results were:—

Quenching Temperature.	Tensile Strength <sup>1</sup> Kilos. per sq. mm.	Elongation per Cent.	Reduction per Cent.
Not quenched.	19.2	—	20
300	24.0	10.2	27.5
450	24.6	11.1	27
550	23.4	6.8	28
600	21.0	—	27
650	19.3	6.1	25
700	19.3	6.8	20
750	19.2	7.5	22
800	6.7	—	3

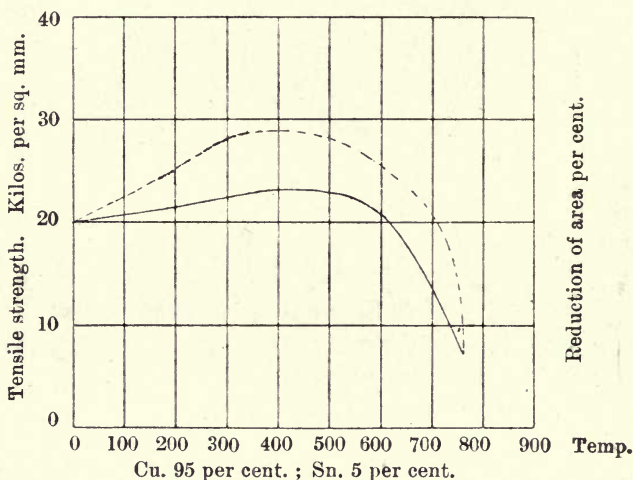


FIG. 80.

These results are shown diagrammatically in Fig. 80.

M. Guillet draws the following conclusions from the results of his experiments:—

(1) In the case of alloys containing over 92 per cent. of copper the tenacity is slightly increased by quenching between 400° and 600°, and the elongation is similarly affected.

(2) In the case of alloys containing less than 92 per cent. of copper the tenacity and the elongation increase decidedly as soon as the quenching temperature exceeds 500°.

(3) Maximum strength is reached, whatever the composition of the alloy at a quenching temperature of about 600°.

(4) Maximum elongation is reached by quenching from temperatures which vary with the composition of the alloy. With 91 per cent. copper, maximum elongation corresponds to a quenching temperature of 800°, while with 79 per cent. the maximum elongation corresponds to a quenching temperature of 600°.

(5) The difference between the tenacity of the cast alloy and that of the metal quenched at the most desirable temperature is the greater the less the percentage of copper.

The heat treatment of the bronzes opens up a wide field for research, and the influence of the temperature of annealing needs investigation.

**Segregation.**—Bronze is very subject to segregation during solidification, the segregation increasing as the percentage of copper falls. Of the bronzes within the range of those of commercial importance, those with 95 per cent. of copper and over seem to be solid solutions of a definite compound of tin and copper or of tin itself in copper; but it must be remembered that even in such cases the freezing is selective, the first-solidified metal being comparatively pure, and the mother liquor growing richer and richer in the second metal, as it falls in temperature, and if the mother liquor be lighter than the solidifying copper solution, as it will be, since it contains a larger proportion of the lighter metal, very distinct segregation may take place. With less copper than this there are one or two distinct eutectics. It is uncertain how far during annealing diffusion might restore uniformity of composition.

#### VARIETIES OF BRONZE.

**Gun Metal.**—This alloy is so-called because it was at one time largely used for casting guns. It contains about 90 per cent. of copper and 10 per cent. of tin, and, as will be seen by reference to the diagram Fig. 70, it is about the strongest of the copper-tin alloys. Like all bronzes, gun metal liquates considerably during slow solidification, and guns were therefore always cast mouth upwards, with a long, sinking head. The term gun metal should be restricted to alloys containing about 10 per cent. of copper, but it is now often loosely used as

a synonym for bronze, and sometimes even for triple alloys containing zinc as well as tin.

**Bell Metal.**—This alloy is largely used for bell founding, and consists approximately of 80 per cent. of copper and 20 per cent. of tin. It therefore approaches the lower level of the useful bronzes. It must not be supposed that this is the only alloy used for bells, as they are often cast in brass and in the triple alloys, but the name has come to be associated with alloys of this composition. Bell metal is hard and brittle, but is very resonant, whence its use for bells.

The addition of small quantities of other metals has sometimes been thought to improve the tone of bells, and silver has sometimes been added for this purpose. Foreign metals do not seem, however, to have any good effect, and the pure copper-tin alloy is probably the best that can be used. Brandt states that an alloy containing 78 per cent. of copper and 22 per cent. of tin gives the best results. Bell metal seems to lose its resonance if remelted several times, probably by the formation of oxides, which dissolve in the alloy.

Brandt gives the following as being the composition of alloys actually used in bell founding :—

	Copper	Tin.	Zinc.	Lead.	Silver.	Iron.	Anti- mony.
Normal metal ...	80	20	...	...	...	...	...
	78	22	...	...	...	...	...
Alarm bell at Rouen ...	76·1	22·3	1·6	...	1·6	...	...
„ at Darmstadt	73·94	21·67	...	1·19	·17	...	...
„ at Reichen- hall, 13th century	80	30	...	...	...	...	...
House bells ... ..	80	20	...	...	...	...	...
Small bells ... ..	75	25	...	...	...	...	...
Sleigh bells ... ..	84·5	15·42	...	...	...	...	...
Clock bells (Swiss) ...	74·5	25	·5	...	...	...	...

It will be seen that the composition of alloys used for bell founding may depart considerably from the standard bell metal.

**Coin or Medal Bronze.**—Bronze has been largely used for the manufacture of medals and coins, and as these are made by striking by means of a die the metal must be plastic in the cold. Copper is of course well suited for such a purpose, and so-called bronze medals are frequently

copper, electro-bronzed to give them the proper colour. For coins, however, which have to stand considerable wear copper has been almost altogether replaced by bronze, German silver, or some other alloy which is harder than copper.

As the ductility of bronze reaches its maximum with about 5 per cent. of tin, the best composition would be about 95 per cent. of copper and 5 per cent. of tin. This is the composition of British bronze coins, except that about 1 per cent. of the tin is replaced by zinc. Alloys with up to 8 per cent. of tin are used, sometimes even with more, but in that case the alloy is usually tempered by heating to redness and quenching in water.

When an impression has to be obtained by repeated blows of the die, the metal must be annealed from time to time, as it becomes very brittle under the influence of work. A small quantity of lead or zinc softens the alloy somewhat. Coins and small medals are stamped on blanks cut out of rolled sheet, but larger medals are stamped on cast discs.

A bronze specially suited for medals is given by Brandt as containing: Copper, 97 per cent.; tin, 2 per cent.; lead, 1 per cent. Greek and Roman coin bronzes often contain about 97 parts of copper to 3 parts of tin.

**Statuary Bronzes.**—For casting statuary a metal is required that will flow freely and cast well. A bronze containing about 94 per cent. of copper and 6 per cent. of tin answers the purpose best, and is largely used for small castings. For large castings triple alloys containing zinc are more usually used.

The following analyses of bronzes will show the composition of some alloys used for various purposes:—

	Copper.	Tin.	Zinc.	Lead.	Iron.
Macedonian Coin ...	87.95	11.44	...	...	...
Coin of Alexander the Great .. ...	95.96	3.28	...	0.76	...
Coin of Alexander Severus ... ..	89.0	10.2	...	0.80	...
Celtic Weapon... ..	92.00	6.70	...	0.69	0.29 N <sub>2</sub>
Egyptian Dagger ...	85.00	14.00	...	...	...
Small Statue found at Oldenburg ...	92.58	6.33	...	...	0.99
Column, Place de Vendome ... ..	89.16	10.24	0.49	0.10	...
French Coin ... ..	95.00	4.00	1.00	...	0.56

Only alloys are included here in which the quantity of foreign metal is small. Obviously in most cases what is present is due to accidental impurities in the metal used.

**Speculum Metal.**—Before perfection was attained in the manufacturing of glass and the silvering of glass reflectors the specula for reflecting telescopes were always made of metal. For this purpose an alloy was required of a white colour, which should be hard enough to take a good polish. Such a material was found in an alloy containing about 66 per cent. of copper and 34 per cent. of tin, which was manufactured for the purpose and came to be called speculum metal. The composition is very near that of the definite compound,  $\text{Sn Cu}_4$ , which would contain 68.1 per cent. of copper.

In practice, the composition of the alloy may vary a little, up or down, without alteration in the properties, and various makers have a composition to which they adhere very closely. Either the proportions of 2 of copper to 1 of tin, or those given by the formula  $\text{Cu}_4 \text{ Sn}$ , being usually used. Increase in the quantity of copper tends to give the alloy a yellowish colour, whilst increase in the percentage of tin tends to give it a bluish tinge and at the same time to make it so brittle that it will not polish.

Some makers add small quantities of foreign metals such as arsenic, antimony, or nickel, but as a rule the pure alloy of copper and tin is best.

The following analysis of specula, from Brandt, will show the variations:—

	Copper.	Tin.	Zinc.	Arsenic.	Nickel.
Standard alloys, $\text{Cu}_4 \text{ Sn}$ ...	68.1	36.9	...	...	...
Otto's ... ..	68.5	31.5	...	...	...
Richardson's ... ..	65.3	30.0	0.7	2.0	...
Little's ... ..	65	30.8	2.3	1.9	...
Sallit's ... ..	64.6	31.3	...	...	4.1

**Oxides in Bronze.**—One great difficulty in the casting and working of bronzes is the tendency which the metal has to retain oxide, either in solution or in admixture, and this very seriously interferes



with the useful properties of the alloy. To overcome this difficulty, good results have been obtained by the addition to the alloy of some powerfully reducing substance which decomposes the oxide of tin, and at the same time the oxide of which is insoluble in the alloy and light enough to rise readily to the surface.

**Phosphor Bronze.**—This is bronze to which a small quantity of phosphorus has been added. The phosphorus may be added in the free condition, since phosphorus combines readily both with tin and copper, but this

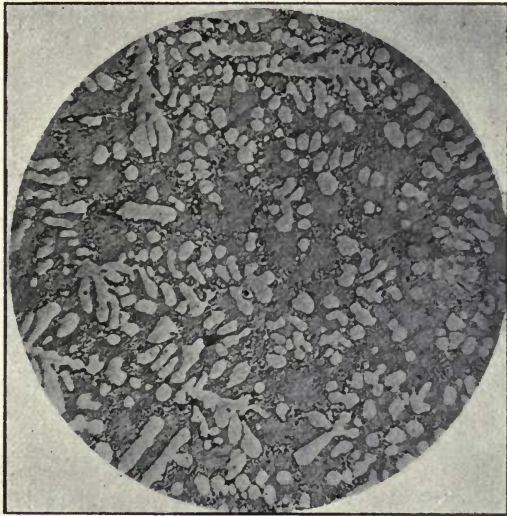


FIG. 81.—PHOSPHOR COPPER, 879 PER CENT. PHOSPHORUS.  
MAGNIFIED 40 DIAMETERS. VERTICAL ILLUMINATION.

method of adding it is inconvenient, and the composition of the resulting alloy is uncertain, as a considerable quantity of phosphorus may be lost. The phosphorus is usually, therefore, combined either with copper or tin to form phosphor copper or phosphor tin, the compound being then used in the manufacture of the alloy, a certain weight of it being used to replace some of the metal.

**Phosphor Copper.**—This is an alloy of copper made by melting together copper and phosphorus under suitable conditions. It is a hard brittle substance with a white metallic fracture, and may be obtained up to about 16 per

cent. of phosphorus. Under the microscope it is seen to consist of two constituents. (Fig. 81.)

**Phosphor Tin.**—This is an alloy of tin and phosphorus made by melting the two elements together under suitable conditions. It has a white colour and a metallic lustre, and is extremely brittle, breaking with a largely crystalline fracture. Under the microscope it is seen to be composed of two constituents, a ground mass of metallic tin through which are scattered plate-like crystals of a phosphide of tin (Fig. 82). When the quantity



FIG. 82.—PHOSPHOR TIN, 9.78 PER CENT. PHOSPHORUS.  
MAGNIFIED 40 DIAMETERS. VERTICAL ILLUMINATION.

of tin is very small the crystals are merely isolated plates, but when the amount of phosphorus reaches 9 per cent. the mass is made up almost entirely of the interlacing crystals of the phosphide. The proportion of copper to tin in bronzes is usually about 8 : 2, and an alloy of the metals in these proportions containing about 6 per cent. of phosphorus is made commercially under the name of hardener.

## PHOSPHOR BRONZE.

The addition of phosphorus to bronze has a remarkable effect upon its properties. The tensile strength is increased, the limit of elasticity is enormously raised, and the power of resisting repeated stresses is also largely increased.

Many figures of tests made have been published. The following, issued by the Phosphor Bronze Company, will be sufficient to indicate the character of the metal.

Two samples of rolled phosphor bronze, tested by Mr. Harry Stringer, M.Inst.C.E., of Westminster, gave :—

Diam. of Test.	Area of Test.	Reduction of Area.	Extension per cent. on 2in.	Elastic Limit.		Breaking Stress.	
				Pounds per sq. inch.	Tons per sq. in.	Pounds per sq. in.	Tons per sq. in.
·757	·4501	58·1	24	Not perceptible		75,577	33·74
·747	·438	22·6	9	90·360	40·34	90,360	40·34

These were, of course, of different composition.

Another series of tests of cold-rolled phosphor bronze by M. E. G. Izod gave :—

Area in Square Inch.	Breaking Load. Pounds per sq. inch.	Breaking Load. Tons per sq. inch.	Elongation per cent. on 4in.
·6235	54,900	39·6	10·75
·625	55,200	39·4	10
·614	54,420	39·5	11
	Mean.	39·5	10·58

The resistance to repeated pulls is shown by the following figures from tests made in the Royal Berlin Academy of Industry, by order of the Prussian Government. The tests were of cast phosphor bronze, and they were compared with similar tests on ordinary cast gun metal.

(a) Trials by repeated pulls :—

Phosphor bronze. Highest pulling stress per square inch.	Number of pulls before rupture.	Cast gun metal. Highest pulling stress per square inch.	Number of pulls before rupture.
Tons. 1. 10	408,350	Tons. 10	Broke before this stress was reached.
2. $12\frac{1}{2}$	147,850	10	4,200
3. $7\frac{1}{2}$	3,100,000	$7\frac{1}{2}$	6,300

## (b) Trials by repeated one-sided bends :—

10	862,980	} Not broken	10	102,650
9	4,000,000		9	150,000
7½	3,000,000		7½	837,760
6	2,000,000			

## (c) Trials made by repeated double twists :—

A bar of forged phosphor bronze has resisted without rupture 2,500,000 twists at a strain of 12 tons, whilst a bar of Krupp's cast steel under a 12-ton strain broke after 879,700 twists.

It is obvious, therefore, that the properties of phosphor bronze are so different from those of ordinary bronze that it may almost be regarded as a new metal. Indeed it may be said that phosphor bronze has all the good qualities of the same bronze without the phosphorus, very greatly extended.

As, however, phosphorus can be added to bronzes of any composition, the term phosphor bronze is very vague, and any comparison should be between a bronze and another of the same composition but containing phosphorus. The data for such comparisons in detail is not available.

Phosphor bronze of suitable composition can be rolled and drawn cold, forged, and cast. Hence its uses are very numerous. It seems to resist the corrosion of sea water better than most alloys, and therefore is often used for propeller blades and other purposes where it will be exposed to the influence of sea water.

The phosphorus in most cases seems to have little direct action, but to exert its influence mainly as a deoxidising agent, and the quantity of phosphorus left in the alloy is often very small, so that the appearance of the metal and its structure as seen under the microscope is not changed. Most phosphor bronzes contain about 1 per cent. of residual phosphorus, present as phosphide dissolved in the alloy, but in some cases where hardness is required there may be as much as 1 per cent., the phosphorus then apparently exerting a distinctly hardening influence. With 4 per cent. the alloy becomes useless.

## SILICON BRONZE.

If the action of phosphorus in phosphor bronze is as is generally believed merely one of deoxidation, then similar results should be obtained by the use of other easily oxidisable non-metals, or metals, and this has been found to be, to a large extent, the case.

Silicon bronze, for instance, is a bronze to which a small quantity of the element silicon has been added for the purpose.

Silicon bronze has great tenacity, resists atmospheric corrosion very strongly, and at the same time is a much better conductor of electricity than is phosphor bronze, the presence of a small quantity of phosphorus greatly diminishing the electric conductivity of the alloy. For that reason wires of silicon bronze are used for telephone and other wires. The quantity of silicon left in the alloy is very small.

The following tests of silicon bronze sheet are published by the Phosphor Bronze Company :—

Dimensions.	Area. Sq. in.	Reduction of Area at Fracture. Per cent.	Extensions.		Elastic Limits Tons. Per sq. in.	Breaking Stress. Tons. Per sq. in.
			Per cent. on 12in.	On 2in. at Fracture.		
lin. × 0·06in.	0·06	52·3	5·3	19·7	23·33	26 unannealed
lin. × 0·06in.	0·06	67·7	39·0	51·5	5·83	20 annealed

## MANGANESE BRONZE.

Manganese, as is well known, is added to steel in the process of manufacture for the purpose of removing the oxygen which has been dissolved in the metal, and it may be used for a similar purpose in the manufacture of alloys ; but, also, as manganese and copper alloy readily, the resulting alloys may contain a considerable quantity of manganese. It is only recently that manganese was obtainable in anything like purity, so that the manganese alloys have usually been made by the addition of ferro-manganese to the alloy, or sometimes a copper-ferro manganese was prepared, and this was then used for making the alloy. Manganese oxidises so readily when the alloy is melted that there is often considerable loss, and it often happened, especially in manganese bronzes where the manganese was only intended

for deoxidation, and, therefore, where the quantity added was small, that the whole of it was oxidised out, but part of the iron from the ferro-manganese remained, so that the alloy was rather an iron bronze than a manganese bronze. Now that nearly pure manganese can be obtained the presence of iron is not so likely.

Many of the so-called manganese bronzes contain a large quantity of zinc, and are thus rather manganese brasses than bronzes, and these have been described under the brasses.

The manganese bronze which does not contain zinc usually contains about 80 per cent. of copper, and a very small quantity of manganese. It can be cast in the usual way, has a high tensile strength, and resists the corrosion of sea water strongly.

Ferro-manganese is an alloy of manganese and iron, often containing 80 per cent. manganese, about 7 per cent. carbon, and small quantities of other impurities.

Mr. Parsons states that a bar of manganese bronze cast in sand in the ordinary way, and of one square inch section, placed on supports 12in. apart, requires upwards of 4,200lbs. to break it, and before breaking will bend to a right angle, and it will sustain from 1,700lbs. to 1,800lbs. before taking a permanent set. Manganese bronze is used for gearing wheels, many parts of machinery, and largely for screw propellers.

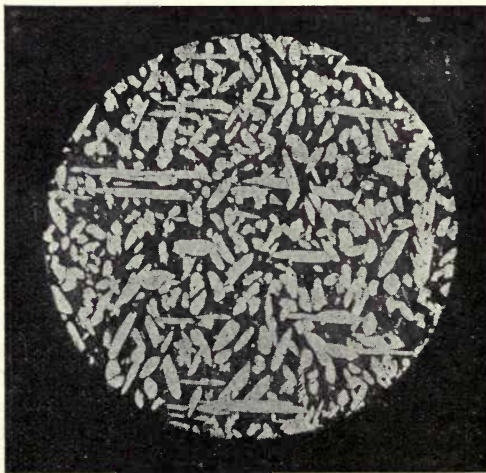


FIG. 82A—MANGANESE BRONZE, '8 PER CENT. MN. V  $\times 70$  X

## CHAPTER IX.

### MACHINERY BRASSES AND BRONZES, BEARING BRONZES, AND OTHER COPPER ALLOYS.

As already remarked, brass should contain only copper and zinc, and bronze should contain only copper and tin ; but there are a large number of alloys which consist of copper alloyed with both zinc and tin and sometimes with other metals also, and which are largely used in engineering. For want of a better term these may be called machinery brasses or machinery bronzes, the names being used almost indiscriminately. Prof. Thurston has suggested the name kalchoids for the series, but this has not been generally adopted.

These alloys are used for various purposes, but in general either for castings or for bearings.

#### CASTINGS.

The addition of zinc to bronze makes it cast better, and for that reason a large proportion of the so-called bronzes contain a little zinc. The British coin bronze, which contains 1 per cent. of zinc, has been already mentioned. A very common bronze alloy is one containing 8 per cent. of tin and 2 per cent. of zinc, the object of the addition of zinc being, at least partly, to improve the colour. The quantity of zinc may be very largely increased, sometimes to nearly 10 per cent., the alloy still retaining the name of bronze. On the other hand, a considerable amount of tin may be added to brasses, an alloy of copper 58, zinc 25, tin 17, being said by Thurston to be excellent for general castings and for casting statues. An alloy of copper 90 per cent., tin 6 per cent., and zinc 4 per cent. has a fine golden colour, and is used as an imitation gold.

Other metals are often added to these alloys for various purposes.

No complete investigation has been made as to the strength and qualities of these alloys as depending on their chemical composition. Much has been published, but as a

rule the alloys are only indicated by their names, and no data are given as to the actual percentages of the metals present; they are usually of little value.

It will probably therefore be sufficient to give a table of the composition of alloys which have been used for various purposes.

Alloy.	Copper.	Tin.	Zinc.	Lead.	Use.
Gun metal ... ..	84	14	2	—	Valves, screws, &c.
Hard brass ... ..	77·93	16·3	6·4	—	—
Statuary bronze ... ..	91·4	1·4	5·5	1·7	—
French Tombac ... ..	80·0	3·0	17·0	—	—
Statue of Napoleon I. Paris	75·0	3·0	20·0	2·0	—
Column Vendome, Paris .	89·2	·5	10·2	·1	—
Brass wire... ..	70·29	9·28	29·39	·17	—
Brass leaf ... ..	66·80	2·0	32·80	·40	—
White alloy ... ..	57·9	5·3	36·8	—	For buttons
„ ... ..	63·88	5·55	30·55	—	—
Sheathing nails ... ..	63·60	2·60	25·00	8·80	—
Yellow solder, hard ... ..	53·30	1·30	43·0	·30	—
White „ soft... ..	44·00	3·30	49·90	1·20	—
Lafond's alloys ... ..	88·00	10·00	2·00	—	Castings for pumps

#### BEARINGS.

Copper alloys are largely used for bearing metals, *i.e.*, for metals on which iron and steel shafts are to revolve. In modern practice, the bearing metal is always made of a softer material than that of the shaft which is to revolve on it. The conditions which are required for a good bearing metal are to some extent incompatible, so that all that can be done is to try and get the most useful mean. The metal should be hard because, as a rule, the harder the metal the lower will be the coefficient of friction; and at the same time it should be soft enough to allow it readily to adapt itself to the form of the running surface, so that the bearing may be uniform over the whole surface; whilst in order that the metal may be durable both conditions must come into play.

It is found in general that alloys which give the best results are those which are made up of hard portions embedded in a softer matrix.

The bearing metals in general use may be divided into two classes, those in which copper is the principal constituent, which may be called bearing bronzes, and those which



consist principally of tin or lead, with other metals, which may be called white bearing metals; the former only will be considered here, the latter are dealt with in Chapter XI.

Owing to its hardness and plasticity, bronze with 5 to 10 per cent. or even 15 per cent. of tin has been used, but the higher the tin the harder is the alloy, and, therefore, whilst it fulfils the former condition better, it at the same

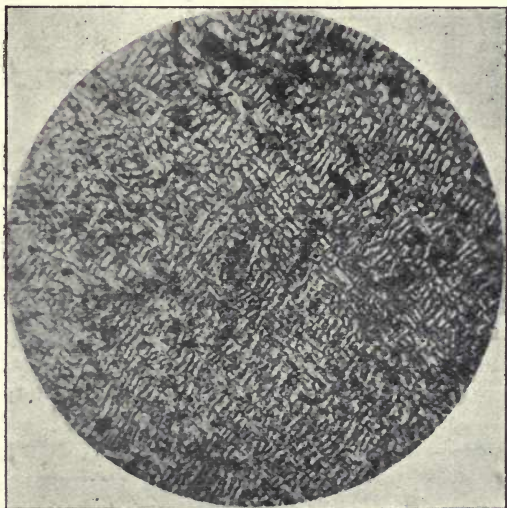


FIG. 83.—BEARING BRONZE.  
Copper 85, tin 5, lead 10,  $V \times 90$  diameters.  
The lead is seen scattered through the mass.

time fails to fulfil the latter, so that hard bronzes cannot be considered to be suitable for this purpose, and with such alloys the wear is always unduly great.

Mr. G. H. Clamer has made a large series of experiments on bearing metals of this class, and his results were published in a paper read before the Franklin Institute in 1903. He experimented with three bronzes, (1) containing copper 85 per cent., tin 15 per cent.; (2) copper 90 per cent., tin 10 per cent.; and (3) copper 95 per cent., tin 5 per cent. Of these, of course, No. 1 was by far the hardest. The two first named have a duplex

structure consisting of copper, or a solution of tin in copper, and a separated eutectic, the hard eutectic being less in quantity in No. 1 than in No. 2. The results obtained in one set of experiments in which both the frictional resistance and the amounts of the metal worn away were determined, were :—

	Friction in Pounds.		Wear in Grammes.	
No. 1 ... ..	...	13	...	·2800
No. 2 ... ..	...	13	...	·1768
No. 3 ... ..	...	14	...	·0776

The experiments were conducted in such a way that the results could be directly compared. It will be seen that the loss of the hardest alloy was much the greatest, but that the friction was the least.

Bearing in mind the structure of an alloy that would be likely to give the best result, it will be seen that the addition of lead would probably be beneficial, for lead only dissolves to a small extent in copper or copper-tin alloys, and therefore it might be expected that lead or a soft alloy of tin and lead would separate so that the resulting alloy would consist of the copper containing some tin in solution, and a copper-tin eutectic, and the softer constituent would be mechanically intermixed through it. It is, of course, essential that the alloy should not be of such a character that extensive liquation would take place, or it might be too irregular in composition.

When lead is added to bronze, a eutectic of lead and tin separates on solidification, and in general the larger the amount of this soft eutectic the better will the metal be for bearing purposes. Mr. Clamer found that with 5 per cent. of tin the alloy could take up as much as 30 per cent. of lead without the lead separating during solidification, but that as the tin was increased the amount of lead that could be taken up diminished. With 7 per cent. of tin not more than 20 per cent. of lead could be taken up. The explanation which Mr. Clamer gives of this phenomena is as follows: The copper-tin alloy is made up of dendrites of copper, a chemically constituted alloy of copper and tin and a eutectic, the eutectic being made up of laminæ of Sn Cu<sub>3</sub> and laminæ of copper, and is found by analysis to contain 73 parts of copper and

27 parts of tin, and to have a solidifying point of approximately  $930^{\circ}$  Fah., whilst the copper solidifies above  $1,800^{\circ}$  Fah. As the tin is increased, the eutectic is increased, and one can readily imagine that when a large bulk of the alloy must cool down from the casting temperature above the melting point of copper to  $930^{\circ}$  it must necessarily remain a long while in the liquid state in the mould. The lead is but mechanically held by the network of copper and tin, and having a solidifying

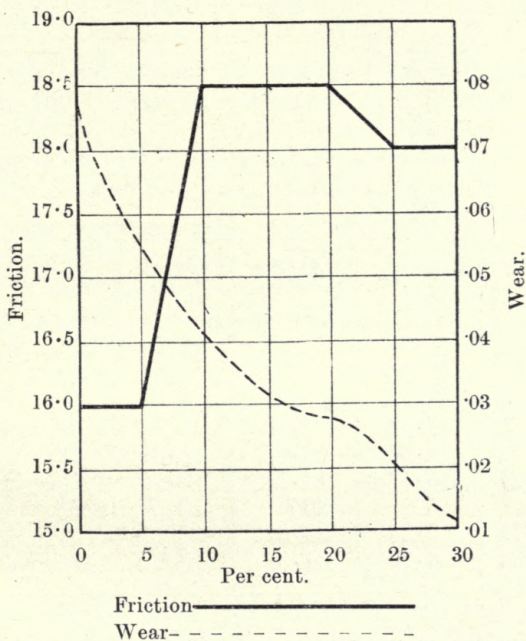


FIG. 84.—VARIATION OF FRICTION AND WEAR IN A BEARING ALLOY, WITH THE PERCENTAGE OF LEAD.

point more than  $300^{\circ}$  below the eutectic, owing to its higher specific gravity, has abundant opportunity to liquefy to the bottom of the casting, and this, in fact, is exactly what happens; but in the absence of eutectic or the presence of only a small amount of it, solidification takes place soon after the metal enters the mould, and a copper-tin network is formed which envelops and upholds the still-liquid lead.

The following are the results of the tests made with bronzes containing lead :—

Composition.			Friction in lbs.	Wear in Grammes.
Copper.	Tin.	Lead.		
90	5	5	16	.0542
85	5	10	18½	.0308
80	5	15	18½	.0327
75	5	20	18½	.0277
70	5	25	18	.0204
65	5	30	18	.0130

It will be seen, therefore, that as the lead is increased, the friction is not materially increased, but the wear becomes less and less.

The following table, from Mr. Clamer's paper, gives the actual results obtained, and the composition of the samples used, by analysis.

Copper per Cent.	Tin per Cent.	Lead per Cent.	Friction in lbs.	Temperature above Room.	Wear in Grammes.
1—85.76	14.90	...	13	50	.2800
2—90.67	9.45	...	13	51	.1768
3—95.01	4.95	...	16	52	.0776
4—90.82	4.62	4.82	14	53	.0542
5—85.12	4.64	10.65	18.5	56	.0380
6—81.27	5.17	14.14	18.5	58	.0327
7—75?	5?	20?	18.5	58	.0277
8—68.71	5.24	26.67	18	58	.0204
9—64.34	4.70	31.32	18	44	.0130

The addition of nickel was found by Mr. Clamer to greatly improve the alloy by diminishing the segregation, probably by causing more rapid solidification of the metal. An alloy of copper and tin containing lead and about 1 per cent. of nickel is known commercially as plastic bronze, and is made by the Ajax Metal Company, Philadelphia.

Many other bronzes are used for bearing metals. Ordinary bronzes are sometimes used, but as a rule lead is added.

The following figures, from Mr. Clamer's paper, show the results with some other alloys tested exactly in the same way as those described above.

Copper.	Tin.	Lead.	Zinc.	Friction in lbs.	Temperature above Room.	Wear in Grammes.
85·12	4·64	10·64	—	18·5	56	·0380
82·27	5·28	10·25	2·07	18·5	68	·0415
79·84	4·71	10·30	5·44	18·5	66	·0466
77·38	5·62	11·42	6·54	18·5	68	·0672
74·28	4·68	10·61	11·04	18·5	69	·0848

An analysis of Ajax plastic metal by Mr. C. N. Forest gave:—

				Per Cent.
Copper	..	..	..	65·26
Tin	..	..	..	5·18
Lead	..	..	..	28·75
Nickel	..	..	..	0·78
				99·97

Ajax standard metal contains:—

Copper .. 77·0    Lead .. 11·5    Tin .. 11·5

but alloys with much larger quantities of lead are made.

The following experiments illustrate the influence of a large percentage of lead:—

	Friction in lbs.	Temp. above Room Temp.	Actual Wear in Grains 1,000,000 revolutions.
Phosphor bronze ... (Composition not given)	16½	50	10·5
Ajax standard metal	18½	32½	7·2
„ 21 % lead ...	18	44	6·7
„ 30 % „ ...	16	40	3·0
„ 47 % „ ...	13½	34	1·65

Another series of alloys tested by the Pennsylvania Railway Company gave:—

	Composition.					Relative Wear.
	Copper.	Tin.	Lead.	Phos.	Arsenic.	
Phosphor bronze...	79·70	10·0	9·6	·80	—	1·00
Ordinary bronze ...	87·50	12·50	—	—	—	1·49
Arsenic bronze ...	79·70	10·0	9·50	—	·8	1·01
Bronze K ...	77·00	10·50	12·50	—	—	·92
	77·00	8·0	12·50	—	—	·86



## OTHER COPPER ALLOYS.

## ALUMINIUM BRONZE.

An alloy of copper and aluminium containing 10 per cent. or less of the latter metal is known as aluminium bronze, or aluminium gold, and is largely used in the arts. As it contains no tin it is not a bronze, but the name being in general use must be adhered to. The aluminium bronzes generally used contain from 5 to 10 per cent. of aluminium, though those with less than 5 per cent. have some valuable properties, but with much above 10 per cent. they cease to be of any value. The higher limit might probably be put at about 11 per cent.

**Colour.**—The addition of a small percentage of aluminium to copper destroys the red colour, and 1 per cent. is sufficient to change this to yellow. The 5 per cent. alloy has a fine yellow colour, very closely resembling that of pure gold, whilst the 10 per cent. alloy is a little darker and resembles ordinary 22-carat gold, this alloy being, therefore, very largely used for the manufacture of jewellery. As the percentage of aluminium is increased beyond 10 per cent. the colour becomes paler, with 15 per cent. it is yellowish-white, and with a little more it becomes white. The addition of a small quantity of copper to aluminium has but little influence on its colour.

**Specific Gravity.**—Aluminium is a very light metal, and it might be expected therefore that the alloys would be lighter than copper. They are so to a small extent, but contraction takes place when the metals mix, so that the resulting alloy has a density greater than that of a mean of its constituents, the contraction being greatest with an alloy containing 7.5 per cent. of aluminium, when it, according to Richards, amounts to about 5 per cent. The following table of the specific gravity of aluminium alloys may be of use. The figures marked \* are from a table given by Richards † from determinations made by Saarburger and given by Messrs. Cowles & Bell Bros.; the rest are from the recently published report of the Alloys Research Committee of the Institution of Mechanical Engineers. ‡

† Aluminium, page 553.

‡ This exhaustive Report of Researches made under the direction of its Committee by Professor Carpenter and Mr. C. A. Edwards, is referred to in what follows by the letters A.R.C. It should be carefully studied by all who are interested in the aluminium-copper alloys.

The metal used by the Committee was in the form of bars rolled down to  $\frac{1}{8}$  in. diam.

Aluminium. Per Cent.	Specific Gravity Determined.	Specific Gravity Calculated.	Contraction. Per Cent.
.1	8.92	—	—
1.06	8.73	—	—
2.10	8.62	—	—
*2.5	8.60	8.40	2.3
2.99	8.47	—	—
*3.00	8.69	8.33	4.1
*4.00	8.62	8.13	5.7
4.05	8.31	8.0	{ 4.4 2.4
*5	{ 8.37 8.20	— —	— —
5.07	8.18	—	—
5.76	8.07	—	—
6.73	7.95	—	—
7.35	7.85	—	—
7.50	8.00	7.60	5.0
8.12	7.78	—	—
8.67	7.69	—	—
9.38	7.61	—	—
9.90	7.56	—	—
*10	{ 7.69 7.56	7.25 7.25	5.5 4.1
10.78	7.45	—	—
*11	7.23	7.10	1.8
11.78	7.35	—	—
13.62	7.25	—	—

The figures of the A.R.C. may be taken as being accurate.

The specific gravity of chilled castings is sensibly the same as that of the worked bars, and that of sand castings is a little lower.

**Hardness.**—Hardness is a property very difficult to estimate. The A.R.C. used the method of Brinell, which consists in pressing a ball of steel of known diameter by a known weight into the alloy, and measuring the size of the concavity produced. The hardness number



being obtained from the formula of Benedicks, viz.,  
$$n = \frac{L}{S} \times \sqrt[5]{\rho}$$
 where  $L$  = the load in kilogrammes,  $S$  the superficies of the cavity, ( $\text{mm}^2$ ) and  $\rho$  the radius of the ball. Obviously if a ball of uniform size be used, a series of numbers could be obtained which would give the relative hardnesses without the use of the last factor. This method of determining the hardness is the best that has yet been proposed, but so far it has been little used except for testing steel, and the ordinary determinations, or perhaps it should rather be said statements as to the hardness of alloys, are very uncertain and often misleading.

The hardness of the alloys was found to increase continuously but not quite regularly as the aluminium was increased, the alloy with 15 per cent. of aluminium being harder than the lower members of the series. The hardness of a 15 per cent. alloy is just about that of a .45 per cent. carbon steel quenched at  $20^\circ \text{C}$ . Work hardens the alloys and they are softened by annealing; the presence of impurities, especially silicon, which is often present, is said to harden the alloy very considerably.

**Tensile Strength.**—The high tensile strength is one of the most marked properties of the aluminium bronzes. Many determinations of the tensile strength have been made, but those of the A.R.C. on account of their completeness and the care with which they have been made should supersede all others. In most results that have been published, either the composition of the alloy is not stated or no full account is given of the treatment to which it has been subjected, and either of these omissions renders results of very little value. The A.R.C. examined the alloys under various conditions, (1) sand castings, (2) chilled castings, and (3) rolled bars. The castings were examined under various conditions of cooling, and the properties measured were ultimate tensile strength (ultimate stress) and ductility as measured by the extension on a 2in. test piece.

It was found that the tensile strength increased with the percentage of aluminium till a maximum was reached, after which it fell considerably. The increase of strength.

was gradual till about 7.5 per cent. of aluminium was reached, after which it rose more quickly, and then when the maximum was passed fell away again very rapidly.

The maximum tensile stress and the composition of the alloy which gave it varied with the treatment. In slowly-cooled castings, made in sand moulds, the strongest alloy contained 10.78 per cent. of aluminium, and gave a tensile strength of 29.52 tons per square inch; when the casting was cooled in water from 800° C. the strongest alloy was that with 10 per cent. of aluminium, which had a tensile strength of 50 tons per square inch; with chill

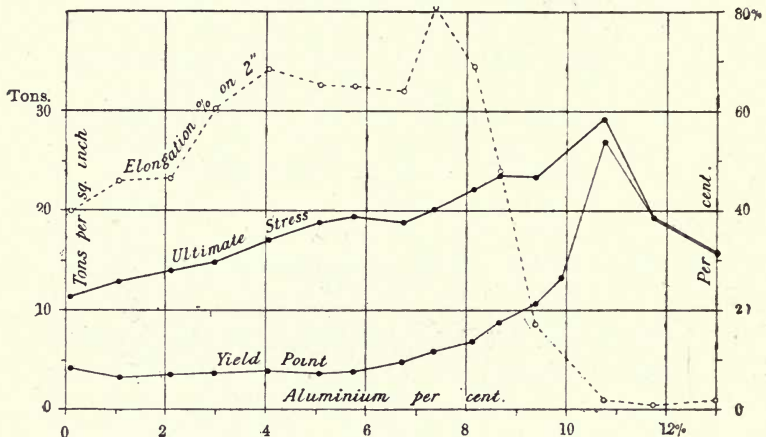


FIG. 85.

Tensile strength, yield point, and elongation of aluminium bronzes.  
Sand castings slowly cooled from 800° C. (A.R.C.)

castings the strongest alloy was that containing 10 per cent. of aluminium, which under those conditions gave a tensile strength of 36.93 tons, which, however, was reduced to 27.72 tons when the alloy was slowly cooled. With rolled bars also the strongest alloy was that containing about 10 per cent. of aluminium, with a maximum tensile strength of about 38 tons. In some experiments made at Zurich on aluminium bronze made by the Heroult process, and quoted by Richards, the 10 per cent. alloy was found to have a strength of 88,325lbs. (39 tons), and the 10½ per cent. alloy 83,915lbs. (37 tons) and 91,000lbs. (40 tons).

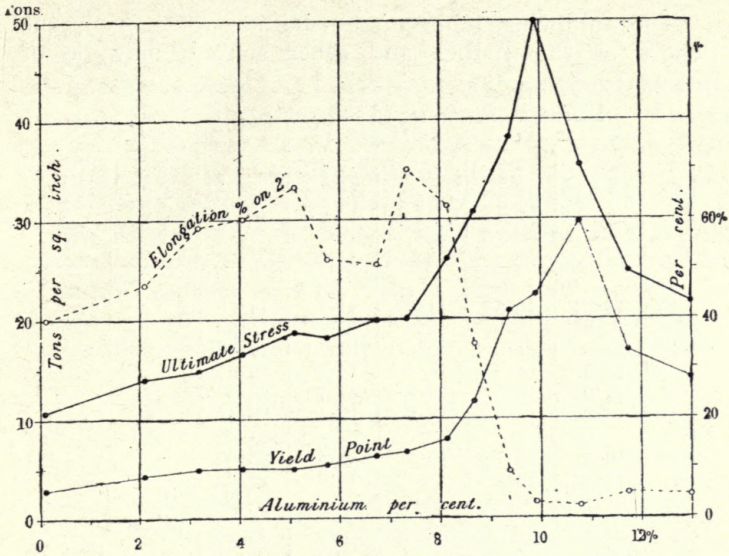


FIG. 86.  
Tensile strength, yield point, and elongation of aluminium bronzes.  
Sand castings quenched from 800° C. (A.R.C.)

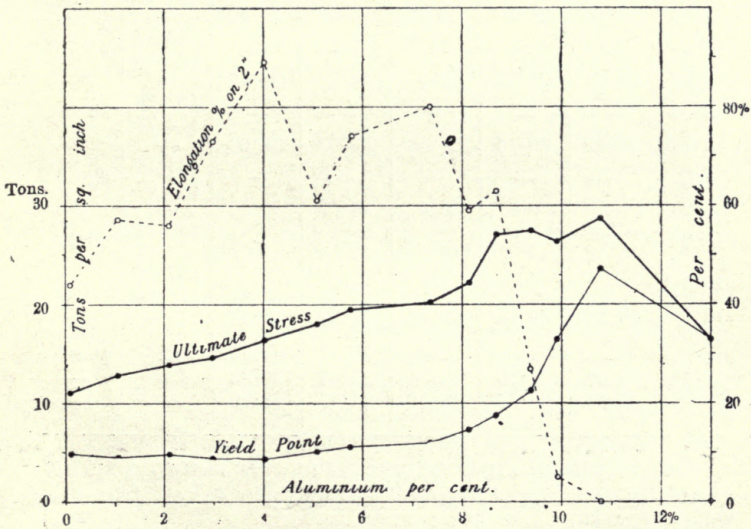


FIG. 87.  
Tensile strength, yield point, and elongation of aluminium bronzes.  
Chill castings slowly cooled from 800° C. (A.R.C.)

The following table of tensile strengths from the Report of the A.R.C. and other sources may be of interest:—

*Ultimate Strength (Tons per square inch).*

Alumin. Per Cent.	Sand Castings Slowly Cooled from 800°.	Sand Castings Quenched from 800°.	Chill Castings Slowly Cooled from 800°.	Chill Castings Quenched from 800°.	Bars Rolled to 1½.	Neuhausen Figures.	Tetmayer's Results.
.10	11.34	10.67	11.07	11.30	14.50	—	—
1.06	12.9	—	12.9	12.60	15.88	—	—
2.10	14.0	14.0	13.9	13.90	17.46	—	—
2.99	14.8	14.8	14.6	14.9	19.97	—	—
4.05	17.0	16.5	16.4	17.7	23.80	—	—
5.07	18.8	18.6	18.0	19.1	26.41	—	—
*5.5	—	—	—	—	—	—	27.95
5.76	19.4	18.1	19.5	20.5	28.60	—	—
6.73	18.82	19.9	—	18.9	28.85	—	—
7.00	—	—	—	—	—	{ 21.97	—
7.35	20.1	20.0	20.2	19.8	29.68	{ 24.59	—
7.50	—	—	—	—	—	{ 24.38	—
8.00	—	—	—	—	—	{ 25.98	—
8.12	22.15	26.0	22.23	24.94	33.22	{ 23.11	—
8.5	—	—	—	—	—	{ 28.58	—
8.67	23.5	30.7	27.1	29.8	36.67	{ 29.44	31.76
9.00	—	—	—	—	—	{ 30.48	—
9.38	23.41	38.16	27.46	35.59	38.00	{ 32.25	36.51
9.50	—	—	—	—	—	{ 32.76	—
9.90	—	50.6	26.4	35.57	38.10	{ 33.14	39.88
10.0	—	—	—	—	—	{ 35.56	—
10.5	—	—	—	—	—	{ 37.67	40.12
10.78	29.21	35.45	28.72	32.26	38.62	{ 40.62	—
11.00	—	—	—	—	—	—	—
11.5	—	—	—	—	—	—	43.18
11.73	19.37	24.79	—	25.04	33.85	—	50.76
13.02	15.83	23.18	16.51	25.97	37.16	—	—

The results in the first five columns are shown diagrammatically in Figs. 85 to 89, which are taken from the Report of the A.R.C.

It will be seen that work considerably increases the strength of the alloy, and that as regards tensile strength

the alloys may be divided into two groups—those containing less than 7.5 per cent. of aluminium, which are very little affected by heat treatment, and those containing more than 7.5 per cent., in which the heat treatment greatly modifies the strength of the alloy, sudden cooling raising and slow cooling lowering it.

The ductility also varies much in the same way, but the variations are much less regular. The extension was measured on 2in., the test pieces being turned down parallel and of uniform size for 2¼in. With slowly cooled sand castings an extension of 81 per cent. was obtained with the alloy containing 6.73 per cent. of aluminium, when the

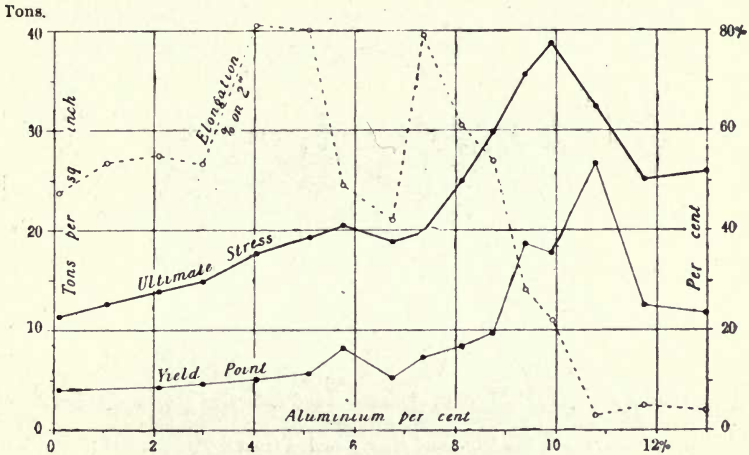


FIG. 88.  
Tensile strength, yield point, and elongation of aluminium bronzes.  
Chill castings quenched from 800° C. (A.R.C.)

casting was quenched from 800° C. and an extension of 70 per cent. with an alloy containing 7.35 per cent. of aluminium. With a chill casting slowly cooled an elongation of 89 per cent. was obtained with an alloy containing 4.05 per cent. of aluminium and the same casting quenched from 800° C. gave an elongation of 81 per cent. Prof. Tetmayer's experiments, quoted by Richards, give a maximum elongation of 64.0 per cent. for an alloy containing 5.5 per cent. of aluminium.

The yield point of all the alloys is very low, and does not vary much till the alloy contains about 7.5 per cent.

of aluminium, after which it rises rapidly till in some cases it coincides with the ultimate breaking stress.

A 10 per cent. aluminium bronze tested by Le Chatelier at various temperatures was found to lose

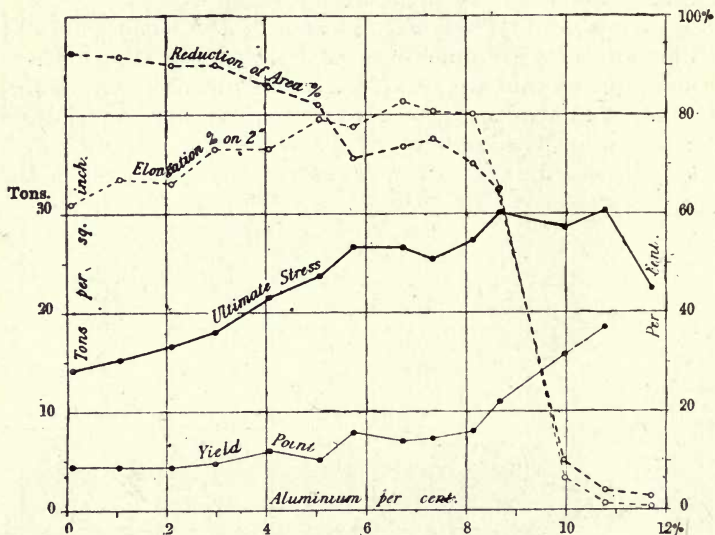


FIG. 89.

Tensile strength, yield point, elongation, and reduction of area of aluminium bronze.

Bars rolled to  $\frac{1}{16}$  in., and slowly cooled from 800° C. (A.R.C.)

strength very slowly at first, then very rapidly. Richards gives his results as being:—

Temperature.	Tensile Strength. Tons per sq. in.	Elongation. per cent.
15° C. ...	3.4	19
100 ...	33.4	22
150 ...	32.5	21
200 ...	31.3	22
250 ...	29.9	21
300 ...	28.1	19
350 ...	23.6	15
400 ...	14.7	21
450 ...	6.4	23

The A.R.C. made many tests on other properties of the alloys, some of which should be noted. For torsional strength it was found that the alloys containing from 0·10 to 2·10 per cent. of aluminium gave results "far higher than those of either pure copper or any of its alloys of which the authors have found mention in literature."\* "Alloys containing up to 7½ per cent. behave extremely well, but beyond this percentage there is a rapid deterioration of properties."†

Tests were also made as to the influence of alternating stress both in the National Physical Laboratory and by Professor Arnold in the University of Sheffield. "The alloys containing 0 to 10 per cent. of aluminium behaved very satisfactorily in their tests, but the most valuable range is from 5 to 10 per cent."

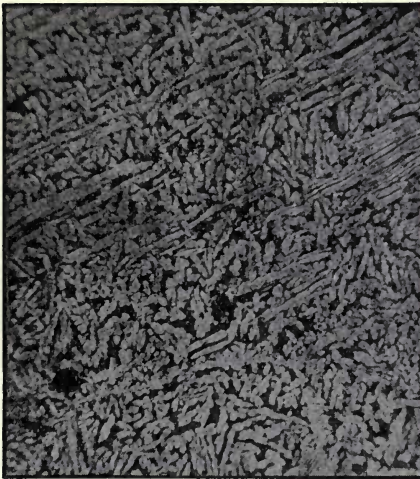


FIG. 90.

Aluminium bronze, 10 per cent. aluminium V  $\times$  75

**Cooling Phenomena.**—As the percentage of aluminium in the alloy is increased the solidifying point of the alloy slowly falls, till it contains 7·8 per cent. of aluminium, then it rises slightly and then falls till there is 67 per

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\* Report of the A.R.C. p. 133. † p. 134.

cent. of aluminium, after which it rises again. The solidifying points of the alloys already given are:—

	°C.	°Fah.
0.00 Pure Copper	1,085	1,985
2.99 per cent. Aluminium	1,070	1,958
5.76	1,051	1,923
7.35	1,035	1,895
8.12	1,032	1,889
8.67	1,034	1,893
9.90	1,041	1,906
10.78	1,043	1,909
11.73	1,044	1,911
13.02	1,042	1,908



FIG. 91.  
Aluminium bronze, 10 per cent. aluminium.  
Heated to 900°C. and quenched  $\times 75$ .

The evolution of heat in each case being very considerable. All the alloys containing less than 13 per cent. of aluminium seem to solidify as a whole, there being only one solidification point. With alloys containing larger proportions of aluminium there are two or more temperatures at which heat is evolved, either on account of the solidification taking place in stages or of changes occurring in the mass after solidification, but with alloys containing from 7 to 13 per cent. a small evolution of heat was noticed at a temperature below 500° C.



**Microscopic Structure.**—The microstructure of the alloys shows nothing of very great importance as far as the alloys within the range of the aluminium bronzes is concerned. The structure of alloys with less than 7.35 per cent. of aluminium is distinctly and uniformly crystallised, and only one constituent seems to be present, with alloys containing more than this two constituents seem to be present. With the alloy containing 8.12 per cent. of aluminium, a very small heat evolution occurs during cooling at 563°-566° C. and this increases with rising aluminium to a maximum at 12-13 per cent. This coincides with the appearance and growth to a maximum of a dark needle-like structural constituent in the alloy.

**Heat Treatment.**—Aluminium bronze is softened by chilling, but with little if any change in structure. "To get the bronze to its maximum elasticity and hardness it must be cooled very slowly. Articles of bronze can be heated red-hot in charcoal powder, and allowed to cool embedded in it."\* With the alloys containing over 7.5 per cent. of aluminium the influence of heat treatment on the microstructure is very marked. With sand castings the structure is, as might be expected, coarser than that of the chill castings, and the structure is not much modified by rolling. By short annealing the constituents are broken up, so as to produce a banded structure, and by prolonged annealing they are separated so as to produce a coarse-grained structure. On quenching from 900° C. the structure becomes finely acicular.

Richards states that aluminium bronze can be worked well at full redness, but that above this (bright red), or below it (low red), it works with much less ease, and that if it be rolled at this temperature it does not become brittle by working; whilst if worked cold it rapidly becomes hard and brittle, and needs frequent annealing. For rolling, owing to the hardness of the metal, strong rolls are required, and for drawing very hard dies. "In regard to forging aluminium bronze, the statement that it can be forged perfectly at all temperatures from a bright-red to cold does not coincide with the experience of many workers. At a cherry-red, the suitable temperature for

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\* Richards.

rolling, it hardly forges at all. A much lower temperature must be used—a low redness—and at that it forges perfectly. Metal hammered from this heat till it is cold has its strength much increased.”\*

Aluminium bronze can be rolled into thin sheets drawn into wire, spun, stamped, or pressed like ordinary brass. It is said also to be very suitable for an anti-friction metal. It is tough and malleable, and has “a peculiar unctuousness or smoothness which seems to resist abrasion and to render it one of the best anti-friction metals known ”\*

**Corrosion.**—Aluminium bronze has always had a high reputation for its power of resisting corrosion, and it does seem to tarnish much less in air than ordinary bronzes, and it seems to resist the action of fresh water, but sea water attacks it slightly. The experiments of the Alloys Research Committee show that it is much less acted on than Muntz metal or naval brass, providing the percentage of aluminium be not too low.

The following table (A.R.C.) shows the change in weight in pounds per square foot experienced by exposure to sea water for one month :—

Aluminium per cent.	
1·06	0·0028lbs. loss.
2·99	0·0001 „ „
5·07	0·0000
7·35	0·0000
9·90	0 0001lbs. gain.
Muntz Metal	0·0014lbs. loss.
Naval Brass	0·0018 „ „

Aluminium bronze does not oxidise readily when heated to redness in air—it is stated that it has been kept at a bright red heat for several months without showing any oxidation.

**Comparison with Steel.**—The Alloys Research Committee in the report give a most interesting comparison of the alloy containing 9·90 per cent. of aluminium with a Swedish Bessemer steel of about 0·35 per cent. of carbon.

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\* Richards.

(a) *Similarity of Mechanical Properties (Rolled Materials Tension Test):—*

	Yield Point.	Ultimate Stress.	Elastic Ratio.	Elongation on 2 inches.
Steel ... ..	15.2	38.0	0.40	26.0
Aluminium bronze	14.8	38.1	0.39	28.8

*Alternating Stress.*

Maximum limit of resistance for 1,000,000 reversals at 800 per minute with a ratio of tension to compression of 1.4:—

Steel ... ..	29.5
Aluminium bronze	28.3

*Impact.*

Foot-pounds absorbed on fracture (without deformation):—

Steel ... ..	4.3
Aluminium bronze	4.5

(b) *Similarity of physical properties, hardness, and hardening capacity.*

*Hardness Numbers.*

	Annealed.	Quenched in Water at 20° C.	Hardening Capacity.
Steel .....	156	402	2.58
Aluminium bronze...	210	349	1.66

The similarity is probably closer than the above table represents. The hardness number (210) is that of the unannealed alloy; a lower value would probably be obtained for the annealed alloy. The hardening capacity figures would thus be raised and brought nearer that of the steel.

*Structures.*

(a) Rolled Bars.

Structural Constituents.

Steel ..... Ferrite, white (soft), pearlite, dark (harder)  
Aluminium bronze Yellow crystals (soft), dark crystals (harder)

(b) Bars annealed for a short time.

The structure remains duplex in both cases, a banded structure is developed in the harder of the two constituents.

(c) Bars annealed for a long time.

The pearlitic structure eventually disappears. In both cases the resulting structure is almost featureless.

*Structural Constituents.*

Steel ..... Ferrite (white)... Massive cementite white.  
Aluminium bronze... Yellow crystals... Light brown crystals.

(d) Bars quenched from a high temperature in water.

The structure becomes markedly acicular in both cases.

**Uses of Aluminium Bronze.**—Aluminium bronze has been and is used for a large number of purposes, some of which have been mentioned above. It is largely used for articles of jewellery on account of its colour and its resistance to tarnish, and for many parts of machinery on account of its great strength. M. Cowles has urged the value of the metal for casting heavy guns, and it has been used for propeller blades for ships, its great strength and resistance to corrosion rendering it specially suitable for this purpose, and there are innumerable other purposes for which it could be used.

**Aluminium Bronze with Other Elements.**—The Cowles Company have prepared silicon aluminium bronze with 2 to 6 per cent. of silicon and aluminium in equal quantities. They claim to have made an alloy which is strong, tough, and does not oxidise, and with 10 per cent. of aluminium and with 2 or 3 per cent. of silicon an alloy which is the strongest known. Phosphor-aluminium and boro-aluminium bronzes have also been prepared.

COPPER-LEAD ALLOYS.

When copper and lead are melted together in equal proportions and allowed to cool slowly they separate—the lead going to the bottom and the copper rising to the top. The separation is never complete, nor is there a sharp line of demarcation, but the lead seems to pass gradually into the copper. The copper at the top is not free from lead, nor is the lead at the bottom free from copper, however slowly the cooling may have been brought about; but there seems to be no true alloy formed, for on examination under the microscope the copper is found to contain the lead distributed through it in the form of globules, and similarly the lead

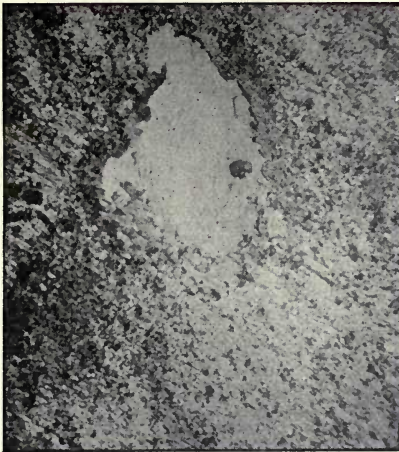


FIG. 92.  
Lead-copper alloy.  
Copper 1 per cent.  
The white mass is a separated crystal of copper  $V \times 75$ .



FIG. 93.  
Copper-lead alloy.  
Lead 25 per cent.  $V \times 230$ .

contains separated copper. This is well shown in the microsections, Figs. 92 and 93. Probably the separated lead contains a small quantity of copper in solution, and

the copper a small quantity of lead. Alloys containing a large proportion of copper do not separate into layers on cooling—probably, as in the case of bronzes containing lead, because the copper, having a very high melting point, solidifies so rapidly that it forms a network which entangles and retains the lead.

#### COPPER, MANGANESE.

These metals alloy readily, forming alloys which may be brittle or malleable according to the proportions of the metals present. Manganese copper is made commercially, and is used in the manufacture of manganese bronze and other alloys.

#### COPPER AND IRON.

Copper and iron alloy in all proportions. Alloys containing less than 2.73 per cent. of iron are homogeneous, and under the microscope show only one constituent, and the presence of the iron does not destroy the colour of the copper. Alloys with from 2.73 to 97.20 per cent. of copper show two distinct constituents, the new substance rich in iron appearing at first as six-rayed crystal-lites, then as the quantity of iron is increased they gradually occupy the greater portion of the mass and by interference yield rounded crystal grains which are separated by the solid solution of iron in copper. As the fracture follows the lines of the copper-iron solution it is still copper coloured, but a polished section may show little or no copper colour.

When the iron is above 97.2 there again seems to be only one constituent—a solution of copper in iron.

None of these alloys are of any commercial importance.

#### COPPER AND ANTIMONY.

Copper and antimony alloy in all proportions, but the alloys are very brittle and are of no practical importance.

The most striking feature about the series is the occurrence of an alloy of a fine purple colour (Regulus of Venus) which contains 51.5 per cent. of copper and has approximately the formula  $Sb Cu_2$ . The structure of the

alloys is very complex, as different constituents crystallise out during solidification of alloys of varying composition. Five classes of alloys have been determined, viz.,

(1)	Antimony, 100·	to 75·8.	Copper, 24·2	to 0·
(2)	„	75·8 to 48·5.	„	51·5 to 24·2.
(3)	„	48·5 to 38·57.	„	61·43 to 51·5.
(4)	„	38·57 to 31·00.	„	69·00 to 61·43.
(5)	„	31·0 to 0·00.	„	100·0 to 69·00.

A full account of these alloys will be found in a paper by Mr. J. E. Stead, F.R.S., in the "Journal of the Society of Chemical Industry," December 31st, 1898.

**Magnetic Alloys.**—A series of very remarkable alloys have recently been prepared by Dr. Huesler which, though they contain no iron, are distinctly magnetic.

Two samples of these alloys contained\* :—

		<i>A</i>		<i>B</i>
Copper ... ..	...	60·49	.....	68
Manganese ... ..	...	22·42	.....	18
Aluminium ... ..	...	11·65	.....	10
Lead ... ..	...	—	.....	4

*A* also contained intermixed slag mostly consisting of oxide of manganese and silica and carbon 1·52, silicon 0·37 per cent., and iron 0·21. The alloys are brittle and cannot be forged. The magnetic power is weak compared with that of iron.

The limits of composition between which the magnetic properties can be detected are not yet known, but the magnetic power seems to reach a maximum when aluminium and manganese are present in atomic proportions.

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\* Fleming and Hadfield. "Page's Weekly," July 7, 1905, p. 29.

## CHAPTER X.

### WHITE ALLOYS.

#### ALLOYS IN WHICH TIN IS THE PRINCIPAL CONSTITUENT.

TIN alloys readily with most metals, and some of the alloys are of considerable practical value, and only such will be considered here.

**Tin and Lead.**—Tin and lead alloy in all proportions, forming a series of alloys to which the name *Pewter* may be given, small quantities of other metals being sometimes added and special names being given to the alloys.

As tin is added to lead, the alloy becomes harder than lead, and therefore the power to mark paper is gradually diminished; but all lead alloys containing less than 75 per cent. of tin mark paper, though less than pure lead, and the darkness of the mark increases with the percentage of lead. No determinations of the hardness of this series of alloys seem to have been made. Tin and lead alloys expand on alloying, so that the density of the alloy is less than that calculated from the densities of the constituents assuming them to be mere mixtures. The following table gives the results of Kupffer's experiments.\*—

Lead.	Per Cent.		Specific Gravity.		Diff.
	Pb.	Sn.	Calculated.	Found.	
Pb	1	0	—	11·3803	—
Sn Pb	63·7	36·3	9·4366	9·4263	0·0103
Sn Pb <sub>2</sub>	77·82	22·18	10·0936	10·0782	0·054
Sn Pb <sub>3</sub>	84·04	15·96	10·4122	10·3868	0·0254
Sn Pb <sub>4</sub>	87·42	12·58	10·6002	10·5551	0·0431
Sn <sub>2</sub> Pb	47·73	53·27	8·7518	8·7454	0·0064
Sn <sub>3</sub> Pb	36·90	63·10	8·3938	8·2914	0·0069
Sn <sub>4</sub> Pb	30·49	69·51	8·1516	8·1730	0·0096
Sn <sub>5</sub> Pb	25·85	74·15	8·0372	8·0279	0·0093
Sn <sub>6</sub> Pb	17·04	82·96	7·9526	7·9210	0·0116
Sn	0	100	—	7·2911	—

\* Watt's Dictionary, 1st Edition, Vol. III., p. 534.



**Melting Points.**—As tin is added to lead the solidifying point falls from the freezing point of lead ( $326^{\circ}\text{C}$ .,  $619^{\circ}\text{Fah}$ .) till at  $180^{\circ}\text{C}$ . a eutectic separates, which contains a little less than 70 per cent. of tin; as the quantity of tin is increased the freezing point steadily rises to the melting point of tin,  $231^{\circ}\text{C}$ . The lead solidifies as a whole, that is as a solid solution of tin in lead, till there is about 4 per cent.

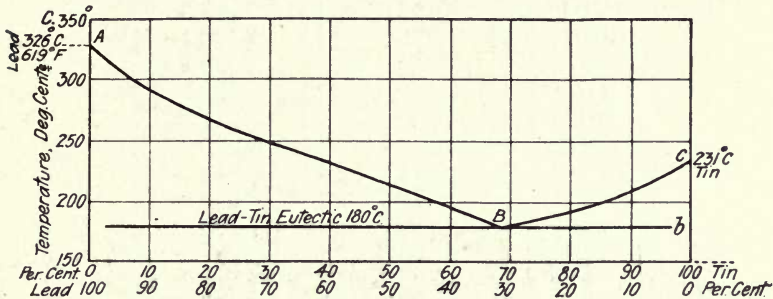


FIG. 94.—FREEZING-POINT CURVE OF LEAD-TIN ALLOYS.

of tin present, after which it ceases to solidify as a whole, but commences to solidify at a temperature which continually falls as the percentage of tin is increased, there being a second solidification point at  $180^{\circ}$ , the freezing point of the eutectic. Starting from the other end the phenomena are exactly similar, the tin solidifies as a whole till it contains about 2 per cent. of lead, after which the eutectic begins to separate. These phenomena are indicated in the diagram Fig. 95.

Various tables of the freezing points of these alloys have been published, the freezing point given being always that at which freezing begins and corresponding therefore to the upper branches of the freezing curve in Fig. 95.

The following abstract of a table of melting points determined by Messrs. Parkes & Martin, which is given by Mr. Hiorns in his "Mixed Metals," may be useful, though some, at least, of the temperatures do not agree exactly with those given by more recent work.

Tin.	Lead.	M.P. C°.
85·7	14·3	194·6
83·3	16·7	192
81·8	18·2	189
80	20	186
77·8	22·2	183
75	25	179
71·4	28·6	175·5
66·7	33·3	170
60	40	169
50	50	189
40	60	211
33·3	66·7	228
28·6	71·4	243
25	75	250
20	80	259
16·7	83·3	267
14·3	85·7	270·5
12·5	87·5	275
10·5	89·5	279·5
10	90	281
9	91	283
8	92	286·5
6	94	291·7
5·5	94·5	291·7

} The  
eutectic

The microstructure of the alloy containing between 4 per cent. and 98 per cent. of tin shows the two constituents distinctly.

Mr. E. S. Sperry, of New York, has made an exhaustive research on the physical properties of the tin-lead alloys. The results of his experiments are shown in the diagram Fig. 96, and he sums up his results thus :—\*

- (1) Tin and lead combine in all proportions.
- (2) The colour of the alloys ranges from that of pure tin to that of lead.
- (3) All the alloys can be rolled in the same manner as that employed for rolling tin.
- (4) The plastic alloys† are not so fluid as the non-plastic compositions unless superheated.
- (5) The yellow colour (due to surface oxidation of the

\* J.S. C. I., 1899, p. 113.

† By plastic alloys is meant those which pass through a long plastic stage during solidification.

tin) can be produced on alloys up to and including tin 44 per cent. After this point the lead characteristics begin to predominate. In order to obtain the best results, the metal must be poured at the proper temperature. It was noticed that metal which had been poured "hot," and consequently devoid of the yellow film, became coloured by it on standing exposed to the air for some time.

(6) The "tin cry" can be produced from the alloys (starting from pure tin) up to and including about 50 per

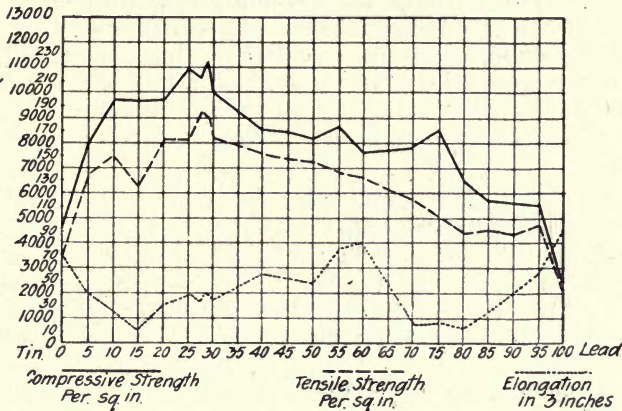


FIG. 95.—COMPRESSIVE STRENGTH, TENSILE STRENGTH, AND ELONGATION OF ALLOYS OF TIN AND LEAD.

cent.; it is nearly absent, however, in the last few combinations.

(7) The strongest alloy in tension is, tin 72.5 per cent., and lead 27.5 per cent.

(8) The strongest alloy in compression is, tin 71 per cent., lead 29 per cent.

(9) The most ductile alloy is, tin 40 per cent., and lead 60 per cent.

(10) The alloy with most reduction of area is, tin 5 per cent., lead 95 per cent.

(11) The best alloy for ordinary use is, tin 50 per cent., and lead 50 per cent., as the surface of the bar is perfectly smooth and free from the matt surface found in some other alloys.

(12) The alloys from tin 15 per cent. and lead 85 per cent. to tin 30 per cent. and lead 70 per cent., inclusive, are not so homogeneous. The outside of the test bar

fracture showed a fibrous nature, while the core consisted of granular material.

(13) The alloys begin to assume a plastic nature at tin 34 per cent. and lead 66 per cent., and end at tin 15 per cent. and lead 85 per cent. The other alloys do not pass through a true plastic state, but pass almost immediately from the solid to the liquid condition. If an attempt is made to use such alloys in place of the plastic compositions, it will be found that the whole mass will be filled with hard lumps, which prevent the successful attainment of the end. The alloys between the limits just mentioned are the so-called wiping solders, and in commerce are known as 3 and 1 and 2 and 1.

(14) The alloys showing the most crystalline nature are those containing from 10 to 20 per cent of lead, inclusive.

(15) The shrinkage more nearly approaches that of tin, and is considerably less than that of lead. The average shrinkage of solder may be said to be 0.06in. to the foot.

Pewter was at one time largely used for the preparation of drinking vessels and other articles of domestic use, but they have almost completely disappeared, having been replaced by more durable and cheaper materials, pewter, owing to its softness, being very liable to be dented and put out of shape. Ordinary pewter consists of tin 80 per cent. and lead 20 per cent., a little antimony or copper being often added to harden it, but the quantity of tin may sometimes be as low as 50 per cent. Pewter was decidedly objectionable as a material for drinking vessels owing to the possible solution of the poisonous lead; but it has been stated that, provided the percentage of lead was not above 20 per cent., none was dissolved. In the days when pewter was largely used, the Pewterers' Company made attempts to keep up the quality of pewter, but, owing to the great difference in the price of lead and tin, this was always difficult to do.

**The Solders.**—The most important use of the tin-lead alloys is probably the preparation of soft solders for the use of plumbers and whitesmiths. In soldering metal surfaces, it is necessary to use for a solder an alloy which will unite with the two surfaces to be joined, and at the same time it must melt at a lower temperature so as to avoid risk of melting the metals. As one of the metals

which it is most frequently required to solder is lead, it is evident that solder must have a lower melting point than lead, and an alloy of lead and tin, if near the eutectic composition, fulfils that requirement.

Best plumbers' solders are made by melting together two parts of tin to one part of lead, and therefore would contain 66·7 per cent. of tin, which is almost exactly the eutectic proportion, but as variations up or down are of little importance, the alloy is usually made by mixing the metals in approximately the required proportion by guess. The solder is usually cast in sticks for convenience, and these sticks can at once be distinguished from sticks of tin by the absence of the cry which is so characteristic of the metal.

As tin is now a very costly metal, solders are often made very much poorer in tin, equal portions of each metal being often used. An alloy of 33·3 per cent. tin and 66·7 per cent. of lead is also often used under the name of plumbers' sealed solder, and is marked by the Plumbers' Company. It is used for wiping joints, and its value for this purpose depends on the fact that it passes through a pasty stage, the lead, containing of course a small quantity of tin in solution, solidifies as cooling goes on, but the mass does not solidify completely till the eutectic temperature is reached, so that as the alloy is being worked between the temperature at which freezing begins and the eutectic temperature it consists of a mass of the still-liquid eutectic entangled in a network of the solid and solidifying lead.

#### TIN AND ANTIMONY ALLOYS.

Tin and antimony alloy readily in all proportions with the production of alloys that are of little commercial importance. The antimony does not affect the colour of the alloy, but renders it much harder so that it can be used for purposes for which tin, owing to its softness, would be unsuitable.

As antimony is added to the tin, a definite eutectic, which contains about 7·5 per cent. of antimony, seems to be formed; but according to Mr. Stead this eutectic does not consist, as is the case of most eutectics, of more or less parallel plates, and on treating it with dilute hydrochloric acid a very fine black amorphous powder is obtained which seems to be a definite compound of

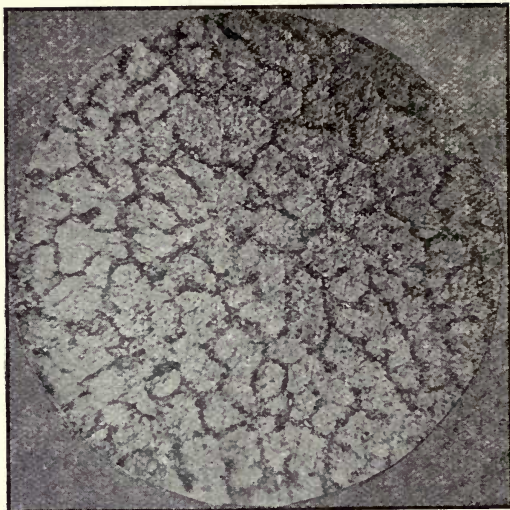


FIG. 96.—TIN-ANTIMONY ALLOY (Antimony 7%)  $\times 75$  diams.

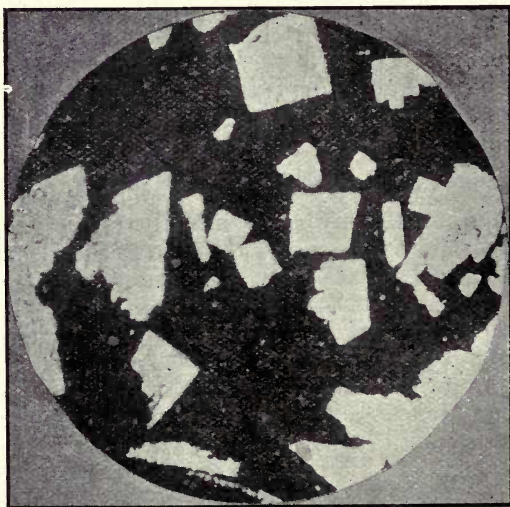


FIG. 97.—TIN-ANTIMONY ALLOY (Antimony 25%)  $\times 75$  diams.

antimony and tin, having the formula  $\text{Sb Sn}$  (Sb 50.21, tin 49.79). As the tin is increased beyond 7.5 per cent., definite crystals separate and these seem to be cubes. As the quantity of antimony is still further increased, the crystals increase in quantity, gradually interfere with one another so as to break up the true crystal form, and when the composition 50/50 is reached they practically occupy all the space; but as the percentage of antimony reaches 40 per cent. the crystals change in form and probably in composition, the crystals being no

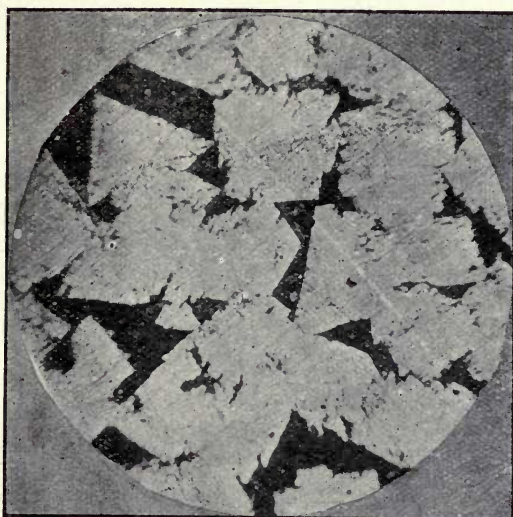


FIG. 98.—TIN-ANTIMONY ALLOY (Antimony 40%)  $\times 75$  diams.

longer cubes but thick plates. As the percentage of antimony is further increased, the crystals change their forms and appearance to those of antimony crystals.

All alloys of tin and antimony with less than 7.5 per cent. of antimony seem to have only one freezing point.

The specific gravity of the alloys is less than that of a mean of the constituents, so that the metals expand on union.

Antimony hardens tin, but up to 20 per cent. of antimony the alloy is quite malleable, and can be hammered or rolled cold, and can also be cast; and all the useful

alloys of tin and antimony contain not more than this proportion of antimony, except where greater hardness and less ductility is required, when it may exceed this limit.

**Britannia Metal.**—The best known alloy of antimony and tin is Britannia metal, and this, though essentially an alloy of the two metals, usually contains some other hardening metal in small quantity. It has a white, almost silver-white, colour, and is capable of taking a

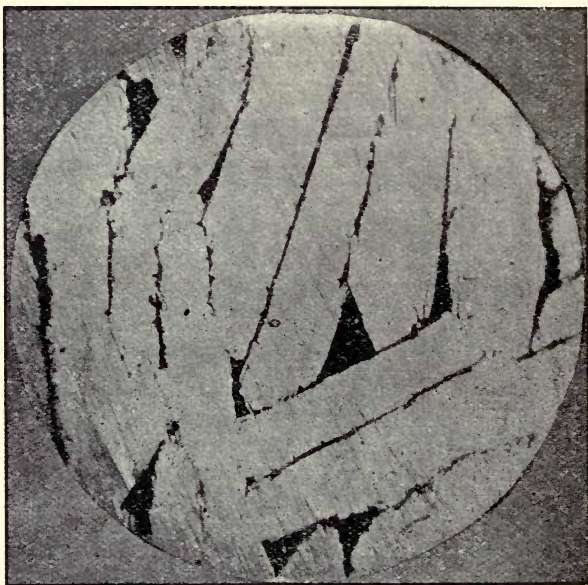


FIG. 99.—TIN-ANTIMONY ALLOY (Antimony 50%)  $\times 75$  diams.

high polish. The object of the antimony is to harden the metal and at the same time diminish its ductility as little as possible. Other metals are sometimes added, iron or zinc increase the hardness, but at the same time increase the brittleness; copper increases the hardness, and does not interfere much with the ductility, but except in very small quantities interferes with the colour, giving a yellowish tinge. Lead does not harden the metal, but makes it give cleaner castings, and also darkens the colour. The best Britannia metal would probably contain



tin 90 per cent., antimony 10 per cent., and would be free from other metals. Such an alloy could be cast, stamped, or spun into the required form.

When articles were largely made of polished Britannia metal the colour was of the utmost importance; now that such articles are usually electro-plated with silver the colour is of much less importance, and therefore the colour of the alloy need not be considered.

The following figures given by Brandt will indicate the general composition of Britannia metal:—

	Tin.	Antimony.	Copper.	Zinc.	Bismuth.
English.....	81·90	16·25	1·84	...	...
„ .....	90·62	7·81	1·46	...	...
„ .....	90·1	6·3	3·1	·05	...
„ .....	85·4	9·66	0·81	3·06	...
Queen's Metal .....	88·5	7·1	3·5	0·9	...
German .....	84	9	2	5	...
Birmingham (sheet)	90·60	7·80	1·50	...	...
„ (cast)	90·71	9·20	0·09	...	...
Karmaischs .....	85·00	5·0	3·60	1·40	1·60

The cast surface of Britannia metal is dull and crystalline, and before use it is always polished.

**Other Tin Alloys.**—Tin and zinc do not alloy readily, and the alloys are of no commercial importance. Tin and aluminium alloy, yielding white alloys. Owing to the very high price of tin, tin is now used as little as possible in the manufacture of alloys.

#### LEAD ALLOYS.

Lead alloys on the whole are of very little importance. The alloys with tin have already been considered, and with copper and zinc lead does not form useful alloys. Lead will dissolve small quantities of other metals, which impart to it a certain amount of hardness and at the same time diminish its ductility, whilst in some cases they increase the sharpness of castings which can be obtained from the alloy.

The most important addition is probably that of antimony, which very rapidly hardens the lead and makes it brittle. Lead containing antimony when accidentally produced is known as hard lead. The eutectic seems to

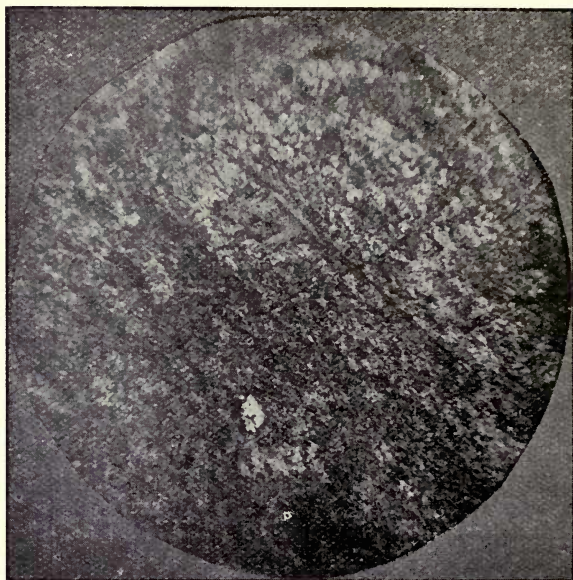


FIG. 100.—LEAD-ANTIMONY ALLOY (Lead 90, Antimony 10)  $V \times 75$  diams.



FIG. 101.—LEAD-ANTIMONY ALLOY (Lead 60, Antimony 40)  $V \times 75$  diams.

contain about 13 per cent. of antimony. When there is more lead than this the mass seems to consist of crystals of lead embedded in a matrix of a very brittle eutectic, whilst when the quantity of antimony is over 13 per cent. it is the antimony that crystallises out. All the alloys are very brittle.

**Type Metal.**—This is the only lead-antimony alloy that need be considered. The alloy must cast readily, and be capable of taking a very sharp impression; it must be hard enough to resist crushing by the pressure of the press, and must be so soft that the edges do not cut the paper. Lead and antimony are always the basis metals of this alloy, but other metals may be present in small quantity.

The following table is that given by Brandt, but the mixtures are calculated into percentages:—

	1	2	3	4	5	6	7	8	9
Lead .....	75	83	91	77	70	60	55	55	59.5
Antimony ...	25	17	9	15.4	18	20	25	30	18.0
Copper... ..	—	—	—	—	2	—	—	—	4.8
Bismuth ...	—	—	—	7.6	—	—	—	—	1.7
Zinc .....	—	—	—	—	—	—	—	—	—
Tin.....	—	—	—	—	10	20	20	15	11.2
Nickel .....	—	—	—	—	—	—	—	—	4.8

**Lead and Arsenic.**—The only interest in these alloys lies in the fact that for shot making lead is always alloyed with a small proportion of arsenic. The addition of

arsenic hardens the metal and increases the fusibility, and it is on account of the latter property that it is used in shot making, as the increased time taken in solidifying gives the metal a better opportunity of forming a spherical drop in its fall from the top of the shot tower. The quantity of arsenic added is small, always under 1 per cent., probably usually nearer .5 per cent.

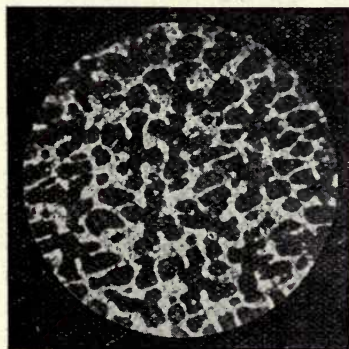


FIG. 102.—LEAD WITH 2.2% ARSENIC  
V 40 X

## CHAPTER XI.

### WHITE ANTI-FRICTION ALLOYS.

FRICTION causes such a large loss of energy in all machines that it is important to reduce it to the lowest possible amount, and as the friction between two metals, the one sliding over the other, depends on the nature of the metals it is important to select the metals so as to give as little friction as possible. The one surface, the moving part, the rotating axle or shaft, will necessarily be of steel, but the other, the bearing surface on which it runs, can be made of almost any metal. The bearing may be of some hard, strong metal, such as phosphor bronze, or it may consist of a shell of iron, bronze, or other strong metal, with a bed of some softer metal cast in to form the actual working surface. Lead seems to have been the first metal suggested for the purpose, but this was soon replaced by alloys of some kind, and now the number of such alloys on the market is very large. Gradually white metals came largely into use, it being found that suitable alloys were very durable, and diminished the friction very considerably, the friction being with such alloys less than that of hard bronze, and the wear being also less. As a rule, bearings are well lubricated, so that the metal is only in contact with the film of oil or other lubricant, and therefore it should be independent of the metals in contact, and to a certain extent, if the surfaces were perfectly smooth, this would be so.

According to the ordinary law (Coulomb's law) of friction, the amount of friction should be directly proportional to the load, and should be independent of other conditions, except the nature of the surfaces in contact. This is found to be the case within limits, but as the pressure becomes considerable the law ceases to hold good, and the resistance increases much more rapidly than the load, and the bearing therefore may

heat, or, to put it in another way, for moderate loads the coefficient of friction remains constant, but it increases considerably as the load is much increased. The point at which this increase takes place is much higher with hard metals than with softer ones ; and hence hard alloys such as phosphor bronze have been largely used for bearing metals.

With a hard metal, however, it is almost if not quite impossible to secure a uniform bearing surface. The bearings will be more or less rough, so that instead of the weight being uniformly distributed over the whole surface, it is borne on a larger or smaller number of points on which therefore the pressure becomes very great, and heating may take place. To avoid this, the bearing metal should be sufficiently plastic to accommodate itself to the form of the shaft, and thus to give the maximum of bearing surface. The wear, of course, during running is also more or less irregular, and with a hard unyielding metal the irregularities might increase, but if the metal be soft and plastic it will to a certain extent flow under the pressure, and it will automatically correct such inequalities. On the other hand, the metal must not be too plastic, or it will flow too readily, and at the same time will tend to "cut." Two properties are therefore required which seem incompatible, hardness and plasticity. The best result is obtained, as already pointed out in the consideration of the plastic bronzes, by combining a soft metal with a hard one, that is, by the use of an alloy which consists of a soft ground mass in which harder, but not too hard, particles are embedded. Indeed, M. Charpy states that this is characteristic of all bearing alloys. He says, "The load is carried by the hard grains which have a low coefficient of friction, and the cutting of which can only take place with great difficulty. The plasticity of the cement makes it possible for the bearing to adjust itself closely around the shaft, thus avoiding local pressures which are the principal cause of accidents."

In testing a bearing alloy, therefore, M. Charpy says : "The plasticity may be ascertained by a compression test ; it must be sufficient to enable the bearing to adjust itself round the shaft, and must not exceed a certain limit in order to prevent its undergoing any per-

manent distortion under the action of the load. The compression test provides also a means of ascertaining whether the alloy is brittle, which would be a serious defect."

The microscope will, of course, be necessary to make out the structure, and M. Charpy says that the difference in hardness will usually be so great that the different portions can be detected after polishing without etching; but, of course, they will be made more distinct by etching. As the boxes will usually be filled by casting, it is necessary that the alloy should cast well. If the above considerations are true, the value of a bearing alloy depends mainly on its physical structure, and little directly on its chemical composition.

The frictional resistance, however, does seem to depend to some extent on chemical composition, certain elements increasing and others diminishing it. Prof. Goodman has pointed out that it sometimes happens that alloys supposed to have the same composition gave frictional results which differed by 100 per cent., whilst on analysis they were found to have their principal constituents in almost exactly the same proportions, but that there were differences in the quantities of impurities present. Further investigation showed that very minute quantities of some elements had a very marked effect on the friction, some increasing and others diminishing it, and further that those elements of low atomic volume\* increased the frictional resistance, whilst those of high atomic volume decreased it, provided that they were present in small proportions. The addition of 0.1 per cent. of aluminium, which has an atomic volume of 10.6, increased the frictional resistance by about 30 per cent., whilst the addition of bismuth, which has an atomic volume of 21.1, immediately reduced the friction. An amount of bismuth equal to only 0.025 per cent. was sufficient to perceptibly reduce the frictional resistance, and it was further reduced by additions of bismuth till the amount reached 0.25 per cent., after which further additions produced increased resistance. A small quantity of bismuth is now added to many anti-friction metals. It is difficult to say if this is any real

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\* See note p. 11.

advantage, because, as already remarked, in practice lubricants are used to keep the metallic surfaces apart.

Many anti-friction metals are on the market, some of them known by very high-sounding names, and for some of them most absurd claims are made. A consideration of the principles laid down above, and a study of the alloys themselves, will enable any one to understand the qualities which are required in a good anti-friction metal.

**Babbitt's Metal.**—This is one of the best-known of the bearing metals. The original formula was "to melt separately 4 parts copper, 12 parts tin, and 8 parts antimony, then after fusion to add 12 parts of tin, this mixture constituting the hardening. For use this hardening was melted with more tin in the proportion of 1 part hardening to 2 of tin, so that the composition of the alloy would work out to copper 3.5 per cent., antimony 7.4 per cent., and tin 88.9 per cent. Babbitt metal, as now made, however, cannot be considered as

Number of Alloy.	Composition.			Load corresponding to a Compression of 7.5 mm.
	Tin.	Copper.	Antimony.	
2	66	34	—	Broken
3	75	25	—	"
4	83	17	—	2000
5	88	12	—	1550
6	75	8	17	Broken
7	88	4	8	2258
8	50	25	25	Broken
9	66	17	17	"
10	75	72.5	12.5	"
11	83	8.5	8.5	2550
12	88	6	8	2550
13	75	17	8	2550
14	83	11.5	5.5	2750
15	88	8	4	2475
16	50	—	50	Broken
17	66	—	34	"
18	75	—	25	2600
19	83	—	17	2650
20	88	—	12	2150

having any definite composition, as each maker modifies it to suit himself, and the name has become a general one to indicate bearing metals consisting of tin, with a small quantity of copper and antimony. The quantity of tin is always over 50 per cent., usually over 80.

M. Charpy has examined the series of alloys of these three metals, with special reference to their use as bearing

Tin.	Copper.	Antimony.	
90	2	8	Quoted by Thurston. Russian railroad car bearings.
88-9	3-7	7-4	Normal Babbitt metal.
88-8	3-7	7-4	Quoted by Thurston and Bolley as Karmarsch metal.
88	6	8	Best alloy. Charpy.
87	6	7	Quoted by Hiorns for bearings heavily loaded.
85	5	10	Quoted by Ledebur and Hiorns as Jacoby metal for light pressures.
83-33	5-55	11-11	Car bearings.
83	6	11	Quoted by Ledebur. Used by Berlin railroads.
82	6	12	Quoted by Ledebur. Used by the Orleans and Western Austrian railroads.
82	8	10	Bearings for valve rods and eccentric collars. Compagnie du Nord.
81	5	14	Quoted by Hiorns for very hard bearings.
80	10	10	Quoted by Thurston. Used by Swiss railways.
78-5	10	11-5	Quoted by Thurston. Used by Russian railroads.
76-7	7-8	15-5	Quoted by Ledebur and Thurston as English alloy.
71	5	24	Thurston standard white metal.
67	22	11	Quoted by Thurston. Used by the Great Western Railway.
67	11	22	French State railroads.



metals, by compressive tests and by microscopic examination. The table on page 187 gives the results of some of his experiments.

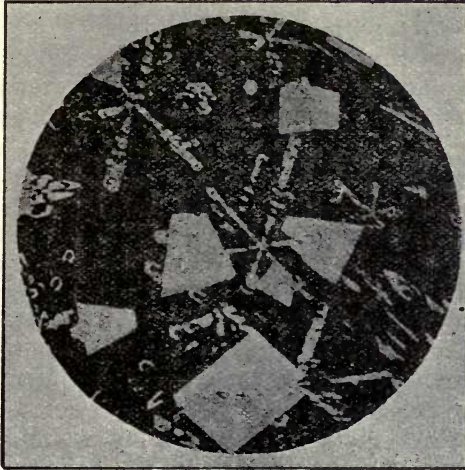


FIG. 103.—ALLOY.

83.3 per cent. Tin. 11.11 per cent. Antimony. 5.5 per cent. Copper (Charpy).  
V 30 ×

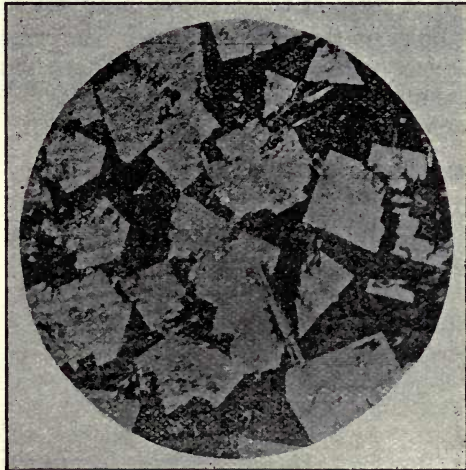


FIG. 104.—ALLOY.

70 per cent. Tin. 25 per cent. Antimony. 5 per cent. Copper (Charpy).  
V 30 ×

Nos. 4, 10, 13, and 18 showed internal cracks before reaching a compression of 7.5 mm. Those which broke and these numbers are therefore too hard for use as bearing metals, and the one which seemed most suitable for the purpose judged by this test was No. 14.\*

Alloys of tin and antimony containing excess of tin examined under the microscope show a ground mass of tin with definite cubic crystals of an antimonide of tin  $\text{Sn Sb}$  (in Fig. 98, p. 179), whilst alloys of tin and copper containing excess of tin show needle-like crystals of  $\text{Sn Cu}_3$  (Fig. 73, p. 128). When both metals are present a definite compound does not seem to be formed, but the mass consists of tin with both sets of crystals scattered through it. So that these bearing metals consist of a ground mass of soft tin with hard crystals of  $\text{Sb Cu}_3$  and  $\text{Sb Sn}$  scattered through it. The addition of both metals is an advantage, because to obtain the same number of hard crystals with one metal only would require so much of that metal that the alloy would be brittle. As brittleness appears sooner in the copper series than in the antimony series, the quantity of antimony should be larger than the quantity of copper. The table on page 188, abridged from M. Charpy's paper, gives the composition of some of these alloys in actual use.

It will be seen therefore that the composition of the alloys in use varies very much. According to Mr. Clamer, the addition of a small quantity of lead to these alloys is advantageous.

**Lead and Antimony.**—Lead and antimony seem to alloy very readily and under some circumstances the alloy may be used as a bearing metal. When the antimony rises above 13 per cent. it crystallises out, so that the alloy consists of a ground mass of lead with hard crystals of antimony. M. Charpy says that alloys containing 15 to 25 per cent. of antimony are most suitable for bearing metals, but Mr. Clamer states that alloys with less than 13 per cent. are often very useful, and that he has seen "many instances in service where alloys containing between 15 and 20 per cent. were greatly

\* The test pieces used were 15 mm. long, so that this corresponds to a compression to half the original length.

inferior to alloys containing between 8 and 12 per cent. owing to their frequent renewal due to wear."

A lead-antimony alloy is probably the cheapest white metal, as there is no costly tin in it. Mystic metal contains :

Lead	..	..	..	88·7
Antimony	..	..	..	10·8
Iron	..	..	..	Trace
Bismuth	..	..	..	Nil

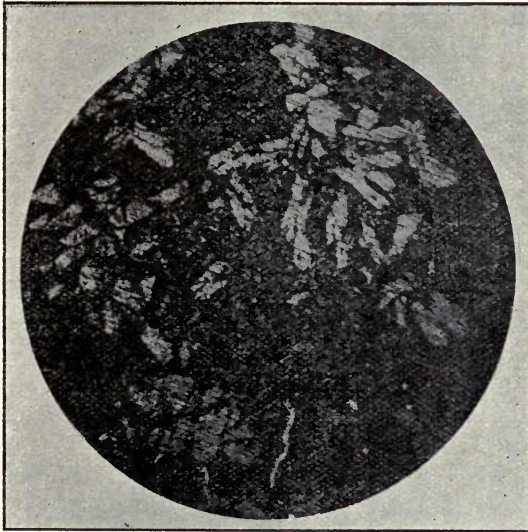


FIG. 105.—MAGNOLIA METAL.  
V × 100.

The best known of the alloys of this group is probably Magnolia metal, which has been very extensively advertised. It contains :—

	(1)	(2)	(3)
Lead .. ..	78	79·41	78·27
Antimony .. ..	21	20·15	17·81
Iron .. ..	1	Trace	—
Bismuth .. ..	—	Trace	—
Tin .. ..	—	—	3·88
Copper .. ..	—	—	·04

No. 1 is from Hiorn's mixed metals. No. 2 an analysis made in the author's laboratory. No. 3 from "Metallurgie," Vol. 3, p. 607.

Alloys Consisting of Lead and Tin and Antimony.—  
Lead and tin alloys, usually with the addition of antimony, have often been used for bearing metals. Lead and tin alloy readily, there being usually

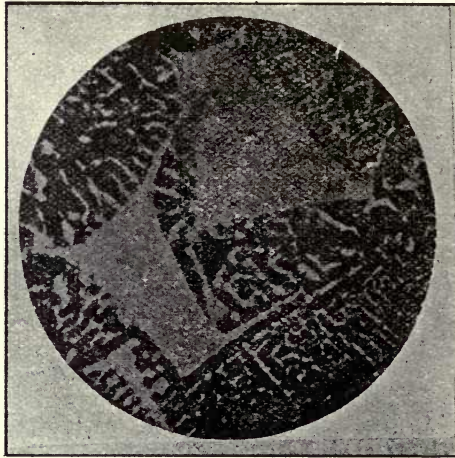


FIG. 106.—ALLOY.  
76 per cent. Lead. 14 per cent. Tin. 10 per cent. Antimony (Charpy).  
V  $\times$  200.

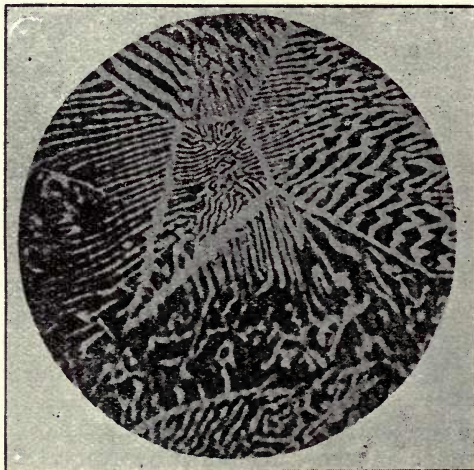


FIG. 107.—SMALL PORTION OF ALLOY, FIG. 106 (Charpy).  
V  $\times$  500.

crystals of one or other of the metals embedded in the eutectic alloy. As lead and tin are both very soft, a mixture of the two would not form a good bearing metal. The addition of antimony, however, gives the necessary hardness, and at the same time greatly increases the compressive strength, the increase, according to M. Charpy, being about the same for all the alloys except those very rich in lead, in which case the influence of the antimony is much less marked.

The following table is given by M. Charpy as the result of his experiments :—

No.	Lead.	Tin.	Antimony.	Load corresponding to a compression of 7.5 mm.
1	—	100	—	1060
2	20	80	—	1750
3	40	60	—	1475
4	60	40	—	1400
5	80	20	—	1150
6	10	80	10	2700
7	20	60	20	2200
8	40	40	20	1825
9	60	20	20	1700
10	80	10	10	1775

The alloys 7, 8, 9 were badly cracked by the compression test.

To avoid brittleness, the percentage of lead should not exceed 15 to 18 per cent., and to obtain the best results the alloy should contain over 10 per cent. of tin, but it is not necessary to exceed 20 per cent.

Under the microscope, the alloys, if containing over 10 per cent. of antimony, are seen to consist of hard crystals embedded in the tin-lead eutectic. "In alloys of lead and antimony these grains are composed of pure antimony; in alloys of tin and antimony they are composed of the compound Sn Sb, and it is probable that in remaining alloys they are made up of a solid solution of Sn Sb and Sb. It is, indeed, known that pure antimony and the compound Sb Sn are capable of crystallising together in alloys of tin and antimony containing more

than 50 per cent. of antimony.”\* The alloys have a constitution much like the binary alloys of lead and antimony. “The tin, however, intervenes—1st, as a constituent of the hard grains, diminishing their hardness, but also their brittleness; 2nd, as a constituent of the eutectic alloy, increasing its compressive strength.”

Another well-known alloy, Jacana metal, contains:—

Lead	..	..	..	70.33
Antimony	..	..	..	18.99
Tin	..	..	..	10.11
Bismuth	..	..	..	.01

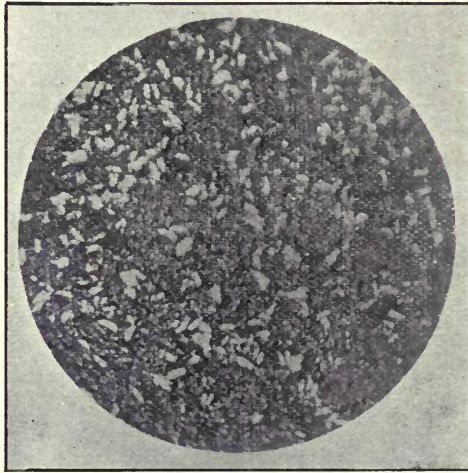


FIG. 108.—JACANA METAL.  
V × 100.

Hoyle's alloy contains about tin 46 per cent., antimony 12 per cent., lead 42 per cent.

**Alloys of Zinc, Tin, and Antimony.**—The structure of these alloys is uncertain. Tin and zinc do not alloy well, but the alloys consist of a eutectic containing about 10 per cent. of tin with crystals of the excess metal.

\* Charpy, "The Metallographist," Vol. II., page 43.

“Alloys of zinc and antimony contain one definite compound at least which is very hard and forms with zinc a eutectic alloy containing about 3 per cent. of zinc.” Alloys of the three metals do not seem to form true ternary alloys, but to consist of mixtures of the several constituents due to the metals being united in pairs; some of them show a high compressive strength. Alloys which contain free zinc have not been found to be very

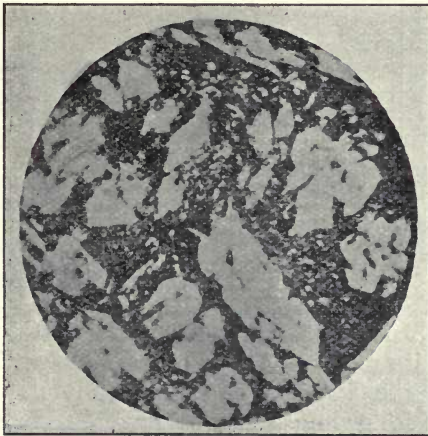


FIG. 109.—ALLOY.

80 per cent. Zinc. 10 per cent. Antimony. 10 per cent. Tin.  $\times 30$ .

satisfactory, the zinc having a great tendency to adhere to iron when slightly heated, and the alloys are brittle when heated.

Many other alloys have been suggested for bearing purposes, but they are usually inferior to those already described.

The following table, abridged from that compiled by M. Charpy, gives some of the more important alloys, excluding the brasses and the bronzes which have been already considered.

Copper.	Tin.	Lead.	Zinc.	Iron.	Anti- mony.	
10	—	65	—	—	25	{ Bearings for Locomotives.
5	—	—	85	—	10	{ Quoted by Ledebur.
8.3	7.6	3	83.3	—	3.8	{ Beauquot White Bronze used in France for Naval Construction.
5.6	17.5	0.7	76.2	—	—	{ White Bronze used for Ship Engines.
—	25	25	50	—	—	{ Quoted by Ledebur. Kneiss Metal.
4.01	9.91	1.15	85.57	—	—	{ Salge Anti-fric- tion Metal.
5.5	17.5	—	77	—	—	{ Quoted by Ledebur for high- speed shafts.

**White Metal Patterns.**—In the foundry patterns are often made of white metal. Alloys of lead and antimony with or without the admixture of other metals are usually used. The following mixtures have been described as being well suited for the purpose :—

- (1) Lead .. .. 8 $\frac{3}{4}$ lbs. = 87.5 per cent.  
Antimony .. 1 $\frac{1}{4}$ lbs. = 12.5 „
- (2) Lead .. .. 8lbs. = 80.0 „  
Antimony .. 1lb. = 10.0 „  
Tin .. .. 1lb. = 10.0 „
- (3) Lead .. .. 8lbs. = 80.0 „  
Antimony .. 1 $\frac{1}{2}$ lbs. = 12.5 „  
Bismuth .. ..  $\frac{1}{2}$ lb. = 2.5 „

**Zinc, Cadmium, and Antimony.**—Messrs. Siemens and Halske have patented an alloy which they state is superior to most anti-friction metals. It casts well, is hard, has a low coefficient of friction, and machines well.

It consists of equal parts of zinc and cadmium with from 5 to 10 per cent. of antimony. The antimony must not exceed 10 per cent., and 5 per cent. is best, nor must the relative proportions of zinc and cadmium be much varied.



## CHAPTER XII.

### LIGHT ALLOYS AND FUSIBLE ALLOYS.

ALUMINIUM (sp. gr. 2.58) is the lightest of the metals in common use, and it has been suggested for many purposes where lightness is essential. The properties of the metal, however, unfit it for purposes where it is likely to be subjected to stress or to wear, as it is weak and soft. It may, however, be strengthened and hardened to some extent by the addition of foreign constituents without its white colour being impaired or its weight seriously increased. A large number of light alloys, of which aluminium is the principal constituent, are now upon the market. The purer the aluminium the softer it is, and the metal now produced by the electric processes is very pure, and therefore very soft. Silicon, for instance, which may be present accidentally or may be added, distinctly hardens the metal, and one at least of the light alloys on the market is simply an aluminium containing a little silicon. When the amount of silicon is over 2 per cent. the colour of the metal is impaired, and it becomes less malleable; but it is stated that 5 per cent. may be present without interfering with its use for castings. Silicon is readily taken up when aluminium is melted in contact with silica or any siliceous material, so that the presence of silicon may sometimes be accidental.

The specific gravity of the alloy, of course, increases with the percentage of copper, but the actual increase is so small that under 10 per cent. of copper does not seriously alter the weight of the metal, with 8 per cent. its specific gravity being less than 2.9. The weight of a cubic foot of the alloys is given by the Alloys Research Committee in the table on the following page.

Copper.	Sand Casting.	Chill Casting.	Ro.led Bars, $\frac{1}{2}$ in. diam.	Drawn Bars, $\frac{1}{2}$ in. diam.
0.00	168	169	169	169
0.86	170	170	170	170
1.90	171	172	172	172
2.77	172	173	173	173
3.76	173	174	174	174
4.97	173	175	175	—
6.15	175	177	177	—
6.97	176	178	178	—
8.01	178	180	180	—

so that even with 8 per cent. of copper the alloy may still be regarded as being a very light metal.

**Aluminium-Copper Alloys.**—The principal metal used for hardening aluminium is copper, and alloys of the two metals are largely used. Copper alloyed with a small

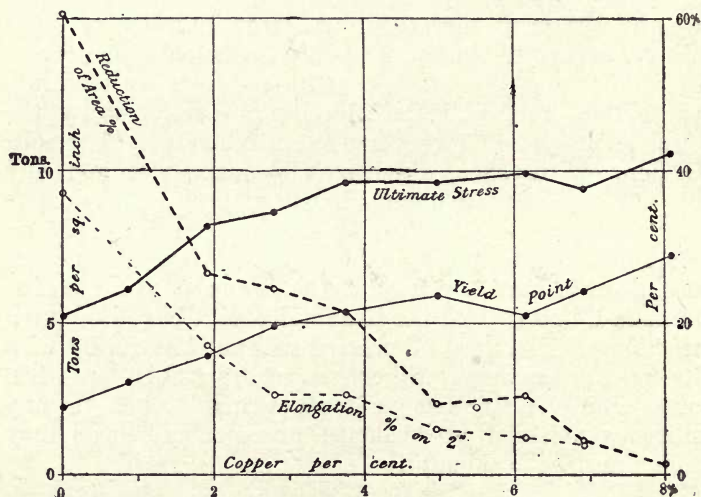


FIG. 110.—PROPERTIES OF ALUMINIUM ALLOYS (Chill Castings).  
(Alloys Research Committee.)

proportion of aluminium (aluminium bronze) has already been considered. The alloys with nearly equal quantities of the two metals are of little use, so that only those will be considered here which consist of aluminium with 10 per cent. or less of copper. These have been

fully investigated by the Alloys Research Committee, and details of the work will be found in the report.

Although copper has a dark colour, it does not seem to modify the colour of the aluminium in the slightest when only present in small quantity ; indeed, up to 10 per cent. the alloys retain their white colour.

The tensile strength increases with the percentage of copper, the increase in the case of chill castings being

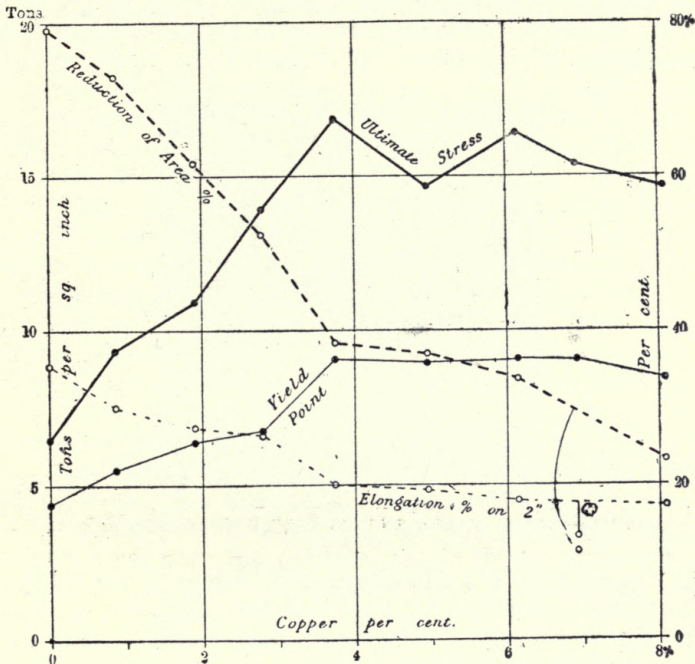


FIG. 111.—PROPERTIES OF ALUMINIUM ALLOYS (Worked Bars). (A. R. C.)

shown in Fig. 110, and for worked bars in Fig. 111, whilst the elongation rapidly decreases, the metal becoming harder, less ductile, and more brittle.

With the worked bars the variation was much the same, but the actual strengths obtained were greater, a maximum strength of 17 tons being obtained with 3.76 per cent. of copper. The worked bars were also much more ductile than the castings, an elongation of 17.2

per cent. on 2in. being given with 8 per cent. of copper. The strength and ductility of the alloys are such that they are not likely to be used for purposes where great strength is required.

Aluminium is largely used for cooking utensils and other purposes, and as the pure metal is soft it is frequently alloyed with a small quantity of copper. Aluminium is not attacked by pure water, but it is attacked to some extent by salt, by weak acids, and more strongly by alkalis, the surface becoming rough and traces of the metal being dissolved. Experiments

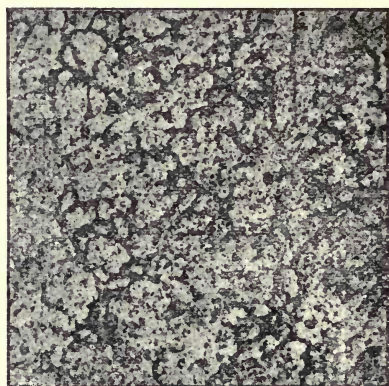


FIG. 112.—ALUMINIUM ALLOY (Chill Casting) 8.08 per cent. Copper  $\times 120$ .  
(A. R. C.)

on the corrosion of the alloys were made by the Alloys Research Committee by boiling strips with dilute acids for six hours. The strips were then weighed, and the loss of weight calculated to the loss in pounds per square foot per hour. The results are given in the following table.

Copper per cent.	Water.	1 per cent. Aqueous Oxalic Acid.	1 per cent. Aqueous Acetic Acid.	2 per cent. Aqueous Citric Acid.
0.0	Nil	0.0010	0.0002	0.0001
1.57	„	0.0019	0.0002	0.0002
2.36	„	0.0020	0.0001	0.0002
3.74	„	0.0021	0.0002	0.0002
4.74	„	0.0022	0.0002	0.0002
5.34	„	0.0023	0.0003	0.0003

The amount dissolved in the case of the pure metal is by oxalic acid 7 grains, by the aqueous acetic acid 1.4 grains, and by the 2 per cent. citric acid 0.7 grain per square foot per hour. In no case was any trace of copper dissolved, but it is evident that addition of copper so far from preventing corrosion rather increases it.

Under the microscope the alloys show two constituents, a ground mass of aluminium and threads of a separated eutectic.

**Aluminium and Magnesium.**—Alloys of these metals under various names have recently been put upon the market. When either metal contains any considerable quantity of the other the resulting alloys are brittle, but with only small quantities of magnesium in aluminium alloys which have useful properties are produced. The best known of these alloys is that to which the name magnalium has been commercially given. The alloy is lighter than aluminium, its specific gravity varying from 2.4 to 2.57. Its tensile strength is from 14 to 21 tons per square inch. It casts well, is very ductile, and malleable, and therefore can be spun, drawn, forged, or rolled, the forging or rolling being best carried out at a temperature of about 300° to 350° C. It is not more corrodible than aluminium. The alloys all contain under 2 per cent. of magnesium, and according to the analysis of Mr. Barrett\* contain copper and tin. Three commercial alloys, marked X, Y, Z, are made, and Mr. Barrett gives samples of these as containing :—

	X	Z
Magnesium ..	1.60	1.58
Copper .. ..	1.76	..
Nickel .. ..	1.16	..
Tin .. .. .	..	3.15
Lead .. .. .	..	.72
Antimony } Present not		
Iron .. .. } estimated		Present.

Also traces of titanium. The alloy Y he states to be intermediate between X and Z.

\* J. S. C. I., 1905, page 832.

In an article in the "Brass World," special attention was called to these alloys, and it was stated that for sand casting a good alloy was made by melting aluminium 9 parts with magnesium 1 part. Or for rolling, aluminium 9.8 parts and magnesium .2 part.

Rapid cooling in water makes the alloys tough and ductile, slow cooling hardens them.

The following details of tests of aluminium-magnesium alloys are given by Mr. J. W. Richards, in a paper read before the American Society for Testing Materials :—

	2% Mg.		4% Mg.		6% Mg.		8% Mg.		10% Mg.	
	T.S.	E.	T.S.	E.	T.S.	E.	T.S.	E.	T.S.	E.
Cast in sand ...	17900	3 00	—	—					21400	2.40
„ „, chills...	28600	2.00	28600	2.60					33600	3.40
Castings water chilled .....	40000	1.00	—	—	57600	1.00	54900	1.60	61100	4.20
Annealed sheet.....	25600	18.00	28200	8.00	28100	17.00	—	—	—	—
Hard sheet.....	41300	2.70	44900	2.10	44100	1.00	—	—	—	—

Tensile strength in pounds per square inch.

Elongation per cent.

**Aluminium Copper-zinc Alloys.**—These alloys are made commercially. An analysis of the Aluminium Company's No. 6 alloy gave :—

Aluminium	..	..	87.7
Copper	..	..	2.8
Zinc	..	..	8.9

and it had a specific gravity of 2.96.

**Aluminium and Nickel.**—Nickel alloys with aluminium and small quantities harden the metal very much, at the same time making it brittle. Lejeal states that an alloy he prepared containing 4.5 per cent. of nickel had a coarsely-crystalline fracture, was easily worked, rolled well, but gave poor mechanical tests, as follows :—

	Lbs. per sq. in.	Elongation per cent.
Forged cold and annealed ...	21,000	6
Forged at low red heat ...	22,800	5.5
Forged at weak cherry red ...	23,000	11.5

An alloy with from 7 to 10 per cent. of nickel is said to last well, and to be tough and hard.

Richards states : "The Pittsburg Reduction Company has recently commenced selling aluminium hardened by a small percentage of nickel, made by adding nickel oxide directly to the bath in which alumina is being electrolysed. They claim for these alloys a tensile strength in castings of 25,000lbs. to 30,000lbs. per square inch, and in rolled bars or plates of 45,000lbs. to 50,000lbs. A bar of this metal shown to the writer was certainly very strong, and possessed of great elasticity, suggesting its probable use for light wagon or carriage springs."\*

These nickel alloys do not resist corrosion well. Copper-nickel aluminium alloys are also sometimes made. An alloy made by adding 2 to 3 per cent. of German silver to aluminium is described by Richards as being of a pure-white colour, strong, and quite elastic. "When rolled hard its tensile strength exceeded 40,000lbs. with an elongation from 3 to 5 per cent., while in casting its strength is 22,000lbs. or 50 per cent. stronger than aluminium. The white colour and elasticity of this alloy commend it for many purposes where pure aluminium is too soft and non-elastic."† It is said that an alloy of aluminium with 4 per cent. of nickel falls to powder at ordinary temperatures soon after being cast.

**Aluminium and Iron.**—Iron is a very constant impurity in aluminium, since any oxides that remain with the alumina will be reduced. A small quantity of iron darkens the colour of aluminium, hardens it considerably, makes it less malleable, and causes it to crystallise more readily. When the iron is present in considerable quantity, say 10 per cent., some of the aluminium can be liquated out. The presence of iron raises the melting point of aluminium very considerably. With 5 per cent. of iron Prof. Carnelly found the melting point of the alloy to be close on 700° C., whilst a specimen with 5 per cent. of iron commenced to fuse at 730° C. The fused alloy is also much more pasty than the pure

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\* "Aluminium," p. 511.

† "Aluminium," p. 538.

metal. With larger proportions of iron still the metal becomes very crystalline. "Deville states that the alloy containing 10 per cent. of iron has colour and brittleness of native antimony sulphide." The only alloy of aluminium and iron made commercially is ferro-aluminium, which contains varying proportions of aluminium, and which is used in steel making. The alloy is yellowish-white, and is very hard and brittle.

**Aluminium and Tin.**—Tin and aluminium alloy readily, and when the quantity of aluminium is large and that of tin small (about 3 per cent.) the resulting alloy is very brittle, but with a larger quantity of tin the alloy seems to become stronger.

"M. Bourbouze has recommended the use of an aluminium-tin alloy for the interior parts, especially, of optical instruments in place of brass. The alloy formed of 100 parts aluminium to 10 of tin, or 9 per cent. tin, is recommended as being the best for this purpose. It is white, and has a specific gravity of 2.85, only slightly above that of aluminium itself. It may therefore be used in place of aluminium where great lightness is desired, and it is further superior to aluminium itself in resisting alterations better and being more easy to work, and, finally, it can be soldered without any special apparatus as easily as brass." An analysis of some of this metal exhibited at the Paris Exhibition in 1889 gave

Aluminium	..	..	85.74
Tin	..	..	12.94
Silicon	..	..	1.32
			<hr/>
			100.00

A test of a similar alloy containing aluminium 88 per cent. tin 10 per cent., silicon 1.30 per cent., and iron 0.65 per cent. gave a tensile strength of 14,000lbs. per square inch with an elongation of only 4.11 per cent. It is therefore no stronger than aluminium.



The following table of the melting points of the tin-aluminium alloys is from Richards' "Aluminium," as quoted from Minet.

Aluminium.	Tin.	Melting Point.
100	0	619° C
92	8	595°
80	20	575°
70	30	535°
60	40	575°
50	50	570°
20	80	530°
10	90	490°
0	100	233°

**Aluminium and Zinc.**—Zinc and aluminium alloy readily, the alloys being in general harder and more fusible than aluminium. A very small quantity of zinc is sufficient to make aluminium brittle. The alloys are of no practical value. A small amount of aluminium added to zinc is said to make the metal more fluid, and thus in galvanising to increase the surface a given weight of zinc will cover, and also to diminish oxidation. Alloys with 25 to 33 per cent. of zinc are in use. That with 33 per cent. of zinc is said to be very hard and to have a specific gravity of 3.8. With 25 per cent. zinc the alloy gives good castings, is easily worked, and has a specific gravity of 3.4. With about 18 per cent. of zinc the alloys can be rolled or drawn. The use of aluminium for this purpose has been patented in the United States, and it is believed to be largely used.

An alloy commercially known as Ziskon contains about 25 per cent. of zinc. It is white in colour, has a specific gravity of 3.35, and is said to have a tensile strength of 11 tons.

**Tungsten and Aluminium.**—The addition of a small quantity of tungsten to aluminium has been recommended by Mannesmann, as improving its resistance to corrosion and greatly increasing its strength.

Richards gives the following figures for an alloy with 7.5 per cent. of tungsten :—

	T. S. lbs. per sq. in.	Elongation per cent.
Cast ... ..	22,000	1.5
Rolled hard ... ..	35,000	4.0
Annealed ... ..	25,000	10.0
„ ... ..	22,000	14.0

The alloy known as Wolframium belongs to this class. An analysis by Mr. J. C. S. Jones gave aluminium 99.4 per cent., tungsten 0.1 per cent.

#### FUSIBLE ALLOYS.

As is well known, alloys usually melt at a temperature which is a good deal below the mean melting point of their constituents, and in some cases below the melting point of their most fusible constituent. When easily-fusible metals are used, very fusible alloys known as fusible metals are produced.

The fusible metals are essentially alloys of bismuth and tin, though generally other metals such as lead and cadmium are also present.

Bismuth and tin alloy very readily, and seem to form definite compounds. A small quantity of bismuth added to tin makes it harder and more sonorous, and increases its lustre and fusibility.

When the metals are in the proportions required for the formula  $\text{Sn}_3 \text{Bi}_2$  the alloy has only one solidifying point at  $143^\circ \text{C}$ ., and this may be taken as being the melting point of that compound. With other alloys there are always more solidifying points, the lowest being  $143^\circ \text{C}$ . Several definite compounds of tin and bismuth are said to exist, and Hiorns gives the following table :—

Formula.	Tin.	Bismuth.	Freezing Points.
$\text{Sn}_3 \text{Bi}_2$ ... ..	45.73	54.27	$143^\circ \text{C}$ .
$\text{Sn}_4 \text{Bi}_2$ ... ..	69.21	30.79	$190^\circ$
$\text{Sn}_2 \text{Bi}$ ... ..	52.91	47.09	$160^\circ$
$\text{Sn}_3 \text{Bi}_3$ ... ..	27.25	72.72	$170^\circ$
$\text{Sn Bi}_2$ ... ..	21.93	78.07	$190^\circ$

When lead is added the alloys become more fusible, and the triple alloy of the three metals is the base of most of the fusible alloys.

The most fusible alloy is usually stated to contain 25 per cent. lead, 25 per cent. tin, and 50 per cent. bismuth, and to melt at about  $94^{\circ}$  C., so that it will melt in boiling water. The behaviour of the alloy when heated is said to be very anomalous. "It expands regularly from  $32^{\circ}$  C. to  $95^{\circ}$  C., and then contracts gradually to  $131^{\circ}$  C. at which point it occupies less bulk than it did at  $32^{\circ}$  C.; it then expands till it reaches  $176^{\circ}$  C., and from that point the expansion is uniform." This alloy is used for taking impressions from dies, &c. It passes through a long pasty stage, during which it is quite soft, and thus can be used like sealing-wax for taking sharp impressions. This is partially due to the separation of a solid portion of the alloy which is retained in a still liquid eutectic.

Another curious phenomena in connection with this alloy is an evolution of heat after solidification. If it is cooled in cold water, and then left, it becomes hot again. This is due to some change in the alloy which is attended with evolution of heat. If the alloy be broken before the evolution of heat the fracture is almost vitreous, but afterwards becomes "grey, dull, and fine grained." In the vitreous state the tensile strength is about 1 ton per square inch, but after the molecular change it is about  $2\frac{1}{2}$  tons per square inch. By a pressure of about 4 tons on the square inch the thermal change is prevented.

M. Charpy gives the most fusible alloy as containing 32 per cent. lead, 16 per cent. tin, and 52 per cent. of bismuth, which fuses at  $96^{\circ}$ . This is probably the alloy of eutectic composition. An alloy of 40 per cent. bismuth, 20 per cent. lead, and 40 per cent. tin softens at  $100^{\circ}$  C., and can be kneaded between the fingers.

The following table, by Messrs. Parkes and Martin, of alloys with definite melting points that can be used for tempering steel, may be of interest. The results are calculated into percentages from the published table:—

Bismuth.	Lead.	Tin.	M.P. Deg. C.	Bismuth.	Lead.	Tin.	M.P. Deg. C.
50	31.2	18.8	94	16.6	33.2	50.2	158
47	35.5	17.7	98	16	36	48	155
42.1	42.1	15.8	108	15.3	38.8	45.9	154
40	40	20	113	14.8	40.2	45	153
36.5	36.5	27	117	14	43	43	154
33.3	33.3	33.3	123	13.7	44.8	41.5	160
30.8	38.4	30.8	130	13.3	46.6	40.1	165
28.5	43	28.5	132	12.8	49	38.2	172
25	50	25	149	12.5	50	37.5	178
23.5	47	29.5	151	11.7	46.8	41.5	167
22.2	44.4	33.4	143	11.4	45.6	43	165
21	42	57	143	11.2	44.4	44.4	160
20	40	40	145	10.8	43.2	46	159
19	38	43	148	10.5	42	47.5	160
18.1	36.2	45.7	151	10.2	41	49.8	161
17.3	34.6	48.1	155	10	40	50	162

The addition of cadmium gives alloys of still lower melting point.

The following table includes the best known of these:—

	Cadmium.	Lead.	Tin.	Bismuth.	Melting Point.
Lipowitzs' alloy...	10	26.6	13.3	50.1	70° C.
Fusible alloy ...	6.2	34.5	9.3	50	77° C.
"  "  ...	34.5	27.5	10	27.5	75° C.
"  "  ...	16.6	—	33.3	50.1	95° C.
"  "  ...	11.1	—	33.3	55.6	95° C.
"  "  ...	25	—	25	50	95° C.
"  "  ...	12.5	25	12.5	50	65° C.
Woods' alloy ...	15.4	30.8	15.4	38.4	71° C.
Fusible alloy ...	25	25	50	—	86° C.

## CHAPTER XIII.

### NICKEL ALLOYS.

NICKEL is one of the comparatively rare metals, which has only recently come into use, but its use has largely increased of late, as it has been cheapened by the discovery of new sources of supply and improvements in the methods of production.

It is white—almost silver white—in colour, malleable and ductile. In its properties it generally closely resembles iron, but there is one difference of very great practical importance—that is, it does not rust on exposure to moist air; indeed, apart from the noble metals, it is the most stable metal in use. Nickel melts at about  $1,450^{\circ}$  C. ( $2,642^{\circ}$  Fah.), and is therefore but little less fusible than carbon free iron. Its high melting point is a difficulty in its use for many purposes.

Nickel is largely used for the manufacture of small articles, where resistance to oxidation is important. It has been used for coinage, but the most of the so-called nickel coins are alloys. It is frequently electrolytically deposited to give a bright metallic surface, either for ornamental purposes or to protect the underlying metal from rust.

Cube nickel is obtained by moulding nickel oxide with some reducing agent into cubes, and then heating these to a temperature at which reduction takes place, but below the melting point of the nickel. The cubes are more or less porous, and are often impure, containing carbon and other disseminated impurities. For melting purposes, however, the cubes are quite suitable, as the intermixed impurities are separated.

Nickel does not cast well, as it absorbs gas (CO), which is given out on cooling, causing holes in the castings. This difficulty is now overcome by the addition of a small quantity of magnesium. The amount

originally added by Fleitman, who discovered its action, was  $\frac{1}{8}$  per cent., but much less is frequently used. The magnesium seems to have much the same effect that aluminium has in the case of steel. A small quantity of magnesium always remains in the metal. Some other metals have a similar effect, and the use of aluminium and phosphorus have been suggested in place of magnesium.

The following analyses of commercial nickel will indicate the impurities that are likely to be present, and the degree of purity to be expected.

	1	2	3	4
Copper ... ..	0·41	—	—	0·10
Iron ... ..	0·62	0·464	0·108	0·36
Sulphur ... ..	0·24	0·049	0·266	—
Silicon ... ..	—	0·303	0·130	0·06
Silica ... ..	1·41	—	—	—
Carbon ... ..	0·65	0·530	1·104	—
Magnesium ... ..	—	—	—	0·11
Nickel and Cobalt ... ..	—	—	—	99·93

(1) Nickel cube. (2) Cast nickel (Thurston). (3) Cast nickel (Thurston). (4) Nickel cast with magnesium.

#### COPPER-NICKEL ALLOYS.

Copper and nickel alloy readily in all proportions. The alloys show under the microscope a crystalline structure which varies very little with variations in the composition of the alloy, at least until the percentage of nickel approaches 80, after which the structure changes. In all probability the metals are soluble, the one in the other, in all proportions in the solid condition, so that the alloys are non-eutectiferous. At present the structure of these alloys has not been fully investigated. As nickel is added to copper, the colour is much more slowly destroyed than in the case of some other metals. The alloy with 20 per cent. of nickel is distinctly red, and with 30 per cent. the coppery colour is still distinguishable, but the colour disappears as the nickel approaches 40 per cent., and the alloy becomes silver white, and continues unchanged in

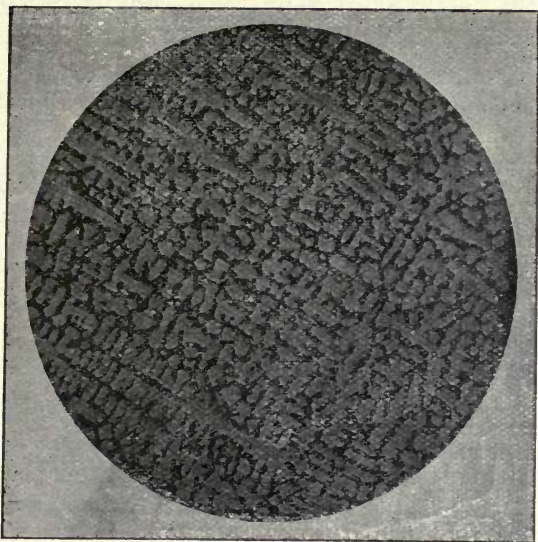


FIG. 113.—COPPER NICKEL ALLOY. Cu. 49 per cent.  $V \times 50$  diameters.

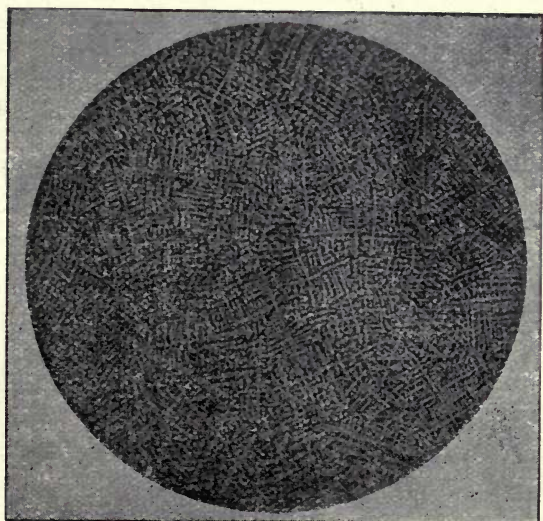


FIG. 114.—COPPER NICKEL ALLOY. Cu. 80 per cent.  $V \times 50$  diameters.

colour till the nickel reaches about 80 per cent., after which the colour darkens considerably.

Copper-nickel alloys are rarely used except in some cases for coinage, but it is doubtful if such alloys have any advantage over pure nickel. The United States coinage contains 75 per cent. copper and 25 per cent. nickel.

**German Silver.**—Under the name, German silver, are included a large number of alloys, containing copper, nickel, and zinc, sometimes with the addition of other metals which are extensively used for various purposes. As might be inferred from the name, the alloys are always white, and are sometimes used as imitations of silver. Before the introduction of electro-plating, forks, spoons, and other similar articles were made to resemble silver as closely as possible by using a white nickel alloy, and even now, when the articles are electro-plated, it is important that the basis metal should be as white as possible, so that the colour may not show conspicuously when the plating wears off. German silver is largely used for the manufacture of the so-called nickel coins used in many parts of the world. A large number of white alloys, used for the manufacture of forks, spoons, &c., are on the market, but almost all of these are simply German silver, the name given being merely a trade designation, not implying any special composition. In some cases the alloys contain other metals in small quantity which are supposed to improve the colour.

The properties required in a German silver are, of course, very different from those required in an alloy used for structural purposes. Generally, the alloys will be of two classes; the one to be used only for castings will require to cast well; the other, to be used for the manufacture of articles by working, stamping, spinning, or otherwise, must be malleable and ductile and must flow sufficiently readily to allow of ready shaping. Coinage alloys must be of this class, as the coins are struck by a die. When the alloy is to be subject to wear, as in the case of coins, it should be as hard as is compatible



with the necessary flow, and all the alloys must be white.

Where a very white colour is required, the alloy should contain at least 25 per cent. of nickel, but as such an alloy is costly, the proportion is often much less, and therefore when the articles are to be electroplated the basis metal is often distinctly yellow, in fact, is often "little better than brass."

The addition of zinc to the alloy cheapens it, zinc being much cheaper than either of the other metals, lowers the melting point of the alloy, makes it whiter and enables it to take sharper castings. At the same time, it tends to harden the metal, and to make it more brittle; but when the constituents are in suitable proportions the alloy will roll and work well. Mr. Hiorns states that about 30 per cent. of zinc, with less than double that amount of copper, gives the best results as to malleability and whiteness; 32 per cent. of zinc makes the alloy more brittle and requires more frequent annealing during the rolling process.

Mr. Sperry has found that the addition of a small quantity of aluminium to a German silver makes it much more fluid, so that it casts better; the castings are sound, and do not adhere to sand, so that it can be readily cast in sand moulds, and also that the alloy is whiter. The quantity of aluminium used may be from .25 per cent. upwards, the properties of the alloy varying with the quantity of aluminium. It becomes tougher as the aluminium is increased, *i.e.*, it reaches  $3\frac{1}{2}$  per cent. after which the alloy tends to become brittle.

When the aluminium reaches about 3 per cent. an alloy is obtained which Mr. Sperry says "is quite stiff and strong, and will only bend slightly without breaking; casts free from pinholes, blowholes, and other imperfections; gives castings true to pattern; the cost of casting is not more than that of brass; is non-corrodible and comparatively non-tarnishing; the colour is silver white, and it is hard enough to take a high polish."

The best composition for the alloy is

Copper	..	..	57.00
Nickel	..	..	20.00
Zinc	..	..	20.00
Aluminium	..	..	3.00

If required to be very stiff, the aluminium may be increased by  $\frac{1}{2}$  per cent. The nickel and copper, which should be pure, are melted together under charcoal, taking care to see that the surface is well covered; the aluminium is then added. When it is melted, stir vigorously. The temperature of the mixture rises considerably. The mass is again stirred, best with a plumbago stirrer, allowed to cool somewhat; the zinc is added as usual. The metal is then poured.

This alloy is sometimes called aluminium silver.

Of other metals that may be added :—

Iron in small quantity “makes the metal whiter, increases the tenacity, but makes it harder.” Mr. Hiorns found “1 to 2 per cent. of iron to have no deteriorating effect, except with regard to hardness, and the colour of an alloy containing 12 per cent. of nickel was equal to one containing 16 per cent. when no iron was present, the same quantity of zinc being used in each case.” Iron, therefore, may be regarded as not being deleterious when the alloy is to be cast, but as being objectionable, except in very small quantities, when a very malleable alloy is required.

Tin is very injurious, giving the metal a decidedly yellow colour, and tending to make it brittle.

Silver has been sometimes added, the idea being that it would improve the colour of the alloy. This, however, does not seem to be the case, but a little silver does not impair its properties. Alloys of copper, nickel, and silver, containing 20 to 30 per cent. of silver, are said to be used in the manufacture of jewellery and to resemble silver very closely.

**Cobalt.**—This metal is very like nickel, but it seems to darken the colour of the alloy.

**Tungsten** is sometimes added to German silver to form an alloy called platino'd, which has a very high resistance, and is used for electrical work. The amount of tungsten added is 1 to 2 per cent.

**Varieties of German Silver.**—Mr. Hiorns gives the following as being the composition of varieties of German silver used by the best makers as used in Birmingham:—

Name.	Percentage Composition.		
	Nickel.	Copper.	Zinc.
Extra White Metal.. ..	30	50	20
White Metal .. ..	24	54	22
Arguzoid .. ..	20.5	48.5	31
Best Best .. ..	21	50	29
Firsts of Best .. ..	16	56	28
Special Firsts .. ..	17	56	27
Seconds .. ..	14	62	24
Thirds .. ..	12	56	32
Special Thirds .. ..	11	56.5	32.5
Fourths .. ..	10	55	35
Fifths for Plated Goods ..	7	57	36

He also gives the following as being three qualities made by the same maker.

No.	Nickel.	Copper.	Zinc.	Iron.
1	8.2	66.0	25.3	5
2	16.0	59.2	23.8	1.0
3	20.7	55	23.3	1.0

As examples of the alloys used for coinage the following analyses may be quoted:—

	France.	Belgium.	Switzerland.
Nickel ... ..	96.5	26	26.3
Copper ... ..	—	74	73.9
Zinc ... ..	3.5	—	—

But little has been published on the microstructure of these alloys, but the microscope seems to give little information. Alloys containing zinc differ very little from those containing no zinc, at anyrate when the percentage of nickel is fairly high, the structure showing a dark network on a light ground. It seems as if the alloy is simply a solid solution of the three metals, and therefore that the zinc simply replaces a portion of the nickel. When the alloys are worked the structure

becomes highly crystalline, and the network structure completely disappears.

**Other Nickel Alloys.**—The most important alloy of nickel is that with iron, which constitutes nickel steel, but the iron alloys are not being considered in this book.

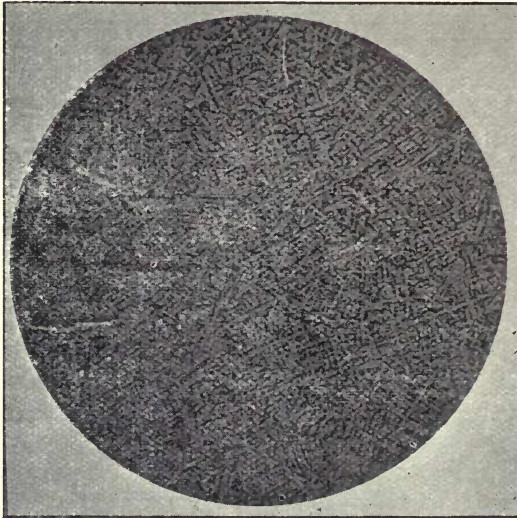


FIG. 115.—COPPER NICKEL ZINC ALLOY. Cu. 53, Zn. 19, Ni. 28.  $V \times 50$  diameters.

A few complex alloys are made, but these usually consist of German silver, with the addition of small quantities of foreign metals, antimony, tin, lead, and iron being among the metals added. Alloys of nickel and aluminium are described on page 202.

**Soldering Nickel Alloys.**—German silver articles are soldered by means of similar but more fusible alloys than those to be united—that is, usually containing more zinc.

## CHAPTER XIV.

### ALLOYS OF THE PRECIOUS METALS.

#### GOLD ALLOYS.

GOLD is the most valuable of the metals in common use, its value depending partly on its properties and partly on its scarcity. It cannot be called a rare metal, since the annual output is considerable, but this does not more than meet the demand.

The properties which render gold valuable are : Its colour, which is unique among the metals ; its malleability, which allows of its being hammered out into the thinnest leaves ; and its durability, that is, its power of resisting the ordinary destructive agents to which the other metals yield. It does not oxidise in air, wet or dry, at ordinary temperatures, nor is it oxidised at a red heat, and it resists most corroding agents. It is not dissolved by any single acid, but is attacked by a mixture of nitric and hydrochloric acid (hence called aqua-regia) on account of the chlorine which is evolved. Its specific gravity is about 19.4. It melts at about 1060° C., and is non-volatile.

Gold is mainly used for two purposes—(1) for jewellery and other ornamental purposes, including, of course, the coating of articles of other material by gold in the form of gold leaf, or by electro-deposition ; and (2) for coinage, gold now being the standard in most countries.

For either purpose pure gold is too soft, as it would wear away too rapidly, and to overcome this difficulty it is alloyed with some other metal in such proportions that the colour and malleability will not be seriously impaired, but the hardness will be considerably increased. The alloying metal—technically called the alloy—is almost always either copper or silver, generally the former. It will be noticed that in speaking of gold alloys the term alloy is somewhat ambiguous, as it may mean either the resulting alloy of the two metals or

the foreign metal added to the gold. This, however, will not lead to confusion if the double meaning be always borne in mind.

The amount of gold in a gold alloy is not usually expressed in percentages, but in parts in a thousand, this being called the fineness of the gold. A gold alloy containing 98·5 per cent. of gold would therefore be said to be 985 fine.

In alloys to be used for jewellery or coinage still another method of expression is used. Gold 1,000 fine is said to be fine or pure gold, or 24 carat, and the value of alloys is expressed by the number of parts in 24 which are gold. Thus 24 carat is  $\frac{24}{24}$  or 100 per cent. gold. In 22-carat gold  $\frac{22}{24}$  or  $\frac{11}{12}$  or 91·6 per cent. of the alloy is gold.

The gold alloys used for jewellery are :—

Carat.	Gold.		Per cent.	Fineness.	
22	$\frac{22}{24}$	=	$\frac{11}{12}$	= 91·6	916·6
18	$\frac{18}{24}$	=	$\frac{3}{4}$	= 75	750·0
16	$\frac{16}{24}$	=	$\frac{2}{3}$	= 66·6	666·6
14	$\frac{14}{24}$	=	$\frac{7}{12}$	= 58·3	583·3
9	$\frac{9}{24}$	=	$\frac{3}{8}$	= 37·5	375·0

It will be noticed that the richness of the alloy is stated as depending only on the quantity of gold, and as being independent of the nature of the alloying metal.

It is, of course, impossible for a purchaser to have an article of jewellery assayed, and so to avoid fraud, the possibilities of which are, it will be seen, considerable. assay offices are established in the various large towns where jewellery is made, and the article can be assayed and stamped before it is quite completed, so that it may not be damaged by the removal of the necessary portion for the assay. The mark, which is called the "Hall-mark," is only put on articles of 9, 16, 18, or 22 carat in this country, but in other countries alloys of other values are stamped.

Twenty-two carat gold is called standard gold, and it is the gold of which our gold coins are made. That is, a sovereign contains 91·6 per cent. of gold, or it is 916 fine.

Since the sovereign is simply a weight of gold the price of gold as measured in sovereigns can never fluctuate.

When it is said that the value of gold has gone up it simply means that its purchasing power for other commodities has increased—that is, that prices have fallen. This is in general the result of gold being scarce. When, on the other hand, gold is very plentiful its price falls—that is, its purchasing power diminishes or prices rise.

The following table, slightly altered from Streeter's "Gold," p. 138, gives the value of 1oz. of gold of any degree of fineness, and the amount of foreign metal to be added to pure gold to make 24 parts of the alloy:—

Quality.	Fineness.	Value. £ Sterling per Ounce.			Value. Dollars per Ounce.	Alloy to be Added. Parts.
		£	s.	d.		
24	1000	4	5	0	20·68	0
23	958·3	4	1	5½	19·82	1
22	916·6	3	17	11	18·95	2
21	875·0	3	14	4½	18·09	3
20	833·3	3	10	10	17·23	4
19	791·5	3	7	3½	16·37	5
18	750·0	3	3	9	15·51	6
17	708·3	3	0	2½	14·65	7
16	666·6	2	16	8	13·78	8
15	625·0	2	13	1½	12·92	9
14	583·3	2	9	7	12·06	10
13	541·6	2	6	0½	11·2	11
12	500·0	2	2	6	10·34	12
11	458·3	1	18	11½	9·47	13
10	416·6	1	15	5	8·61	14
9	375·0	1	11	10½	7·84	15
8	333·3	1	8	4	6·89	16
7	291·6	1	4	9½	5·83	17
6	250·0	1	1	3	5·17	18
5	208·3	0	17	8½	4·3	19
4	166·6	0	14	2	3·44	20
3	125·0	0	10	7½	2·58	21
2	83·3	0	7	1	1·72	22
1	41·6	0	3	6½	·86	23
						24

The English sovereign weighs 123·27447 grains, and remains legal tender till it is reduced to 122·5 grains.

These figures give the actual mint value of the gold in the alloy. The price at which the gold can be purchased will be always a little higher, up to 1s. an ounce, according to the amount purchased, and the alloying metal, especially if it is silver, will be of some value, and this must be allowed for.

In the reports of mines the value of the bullion obtained is often stated in £ or \$. It will be seen that this at once gives the fineness, since the value is fixed.

Of course, in most articles of jewellery the value of the gold used is small compared with the total value, which is due to the labour put upon it in finishing it into the required form.

The gold coinage of other countries is not of the same standard as the British, so that the coins cannot always be compared weight for weight.

	Fineness.	Carats.
Hungarian Ducats .. .. .	989	23·76
Austrian „ .. .. .	986	23·6
Dutch „ .. .. .	982	23·75
English, Portuguese, Turkish, Brazilian	916·6	22
German, French, Belgian, Italian, Swiss, Spanish, Greek, United States, and Chinese gold coins..	900	21·6
Old German coins (pistoles) ..	895	21·5
Egyptian, Mexican, Spanish ..	875	21

The alloying metal may either be copper or silver, or a mixture of the two, which of the three is used being a matter of small importance, as the value of the alloying metal in any case is very small compared with the value of the gold. When silver is used, as in some of the Australian coins, the alloy is paler in colour than the British coins, in which copper is used. In jewellery generally a mixture of silver and copper in approximately equal quantities is used.

#### GOLD AND SILVER ALLOYS.

Gold and silver alloy readily in all proportions, and the alloys differ in some respects from those which have already been considered.

Whatever be the composition of the alloy, it has only one freezing point, or rather perhaps it should be said



freezing range. There is no second freezing point; that is, there is no definite eutectic separated. As silver is added to gold the freezing point is lowered, very little at first, then more rapidly, but with a continuous more or less steady fall from the freezing point of gold to that of silver. It does not, of course, follow that the alloy will be perfectly homogeneous, for there still may be selective freezing, the mother liquor being richer in the one metal than the solidified portion; but in these alloys there seems to be little if any segregation, and therefore, as Sir W. Roberts Austen pointed out, they are specially well suited for making trial plates for mint use.

Under the microscope these alloys are seen to be highly crystalline; but, as might be expected, show no sign of the formation of a eutectic. They are, in fact, non-eutectiferous through the whole range.

The electric conductivity curve has the characteristic U form, falling to a minimum when the metals are present in about equal quantities, then rising again; but there is no distinct break, such as would indicate a critical point.

The colour of gold is rapidly destroyed by the addition of silver—the colour becoming paler, the Australian gold coins, in which the alloying metal is silver, being distinctly paler in colour than pure gold. Gold containing silver is often spoken of as pale gold. The change of colour begins apparently when there is about 5 per cent. of silver present; the colour becomes paler and assumes a greenish tint when the silver approaches 30 per cent., and when it reaches 50 per cent. the alloy is white, and is sometimes called electrum, though the alloy usually known by this name is simply a German silver.

Alloys of gold and silver containing small quantities of silver are not attacked by dilute nitric acid. As the percentage of silver increases this metal is partially dissolved out, and when the percentage of gold falls to about 30 the silver is completely dissolved by warm nitric acid, the gold being left insoluble. Advantage is taken of this in the parting of gold and silver on the large scale and in assaying. The ordinary jewellers' test for gold,

as is well known, is to treat its surface with a drop of strong nitric acid, by which gold of high carat is not attacked at all, poorer golds are slightly attacked, and most of the gold-like alloys, brasses, &c., are rapidly dissolved.

Silver hardens gold and makes it more sonorous, but it does not interfere with its malleability, so that it can still be used for the manufacture of coins and other articles which have to be struck by a die.

#### GOLD AND COPPER.

Gold and copper also alloy very readily. The influence on the colour of the gold is, as might be expected, much less than that of silver, the golds alloyed with copper being redder than those alloyed with silver only, so that the colour of an alloy of gold can be modified by varying the alloying metal. In some respects the

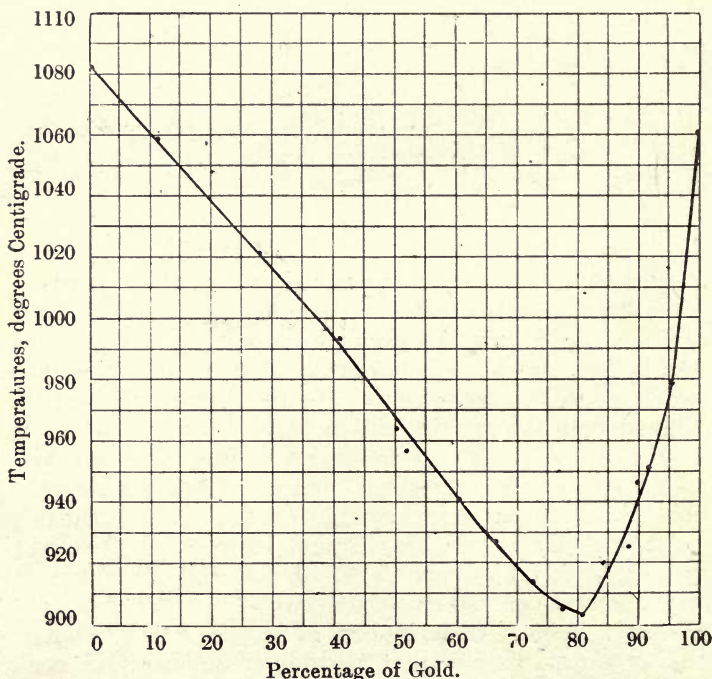


FIG. 116.—FREEZING POINT CURVE OF COPPER-GOLD ALLOYS.

gold-copper alloys resemble those of gold and silver, and it was at one time thought that the metals did not segregate. Sir W. Roberts Austen has shown that this is not the case, that whilst segregation is not as marked as in many other alloys it certainly does take place to a sufficient extent to render trial plates cast of such an alloy unhomogeneous.

When copper is added to gold (melting point  $1,063^{\circ}$ ) the melting point of the alloy rapidly falls till it reaches a minimum, when the number of atoms of gold is 59.69 per 100 of alloy, that is, when the alloy contains 82.05 per cent. of gold, when it is  $905^{\circ}$  C. Beyond that the temperature rises as the percentage of copper is increased till the melting point of copper,  $1,083^{\circ}$ , is reached. Copper apparently dissolves in gold, but it is not soluble in the solid condition in all proportions as is silver. When an alloy containing only a small proportion of copper is examined, *e.g.*, standard gold, it is found to consist of definite crystals differing from those of pure gold only in colour, and no second constituent can be made out. This may therefore be regarded as being a solid solution of gold in copper. As the quantity of copper increases a second constituent makes its appearance when there is about 27 per cent. of gold present, and when about 82 per cent. of gold is reached the alloy has a true eutectic structure. As the quantity of copper is increased the structure shows crystals of copper containing gold in solution embedded in the eutectic.

In the case of the copper-gold series Sir W. Roberts Austen points out that the eutectic is weak and brittle, so that where strength is required the alloy must be some distance on either side of it. Sir W. Roberts Austen has also shown that the alloy with 82 per cent. gold, *i.e.*, the eutectic, is the only one that has a definite freezing point, and in which therefore the temperature remains constant till the solidification is complete. It is impossible to say exactly how far the eutectic line extends in his diagram. Prof. Roberts Austen only shows it in the copper direction, and he says that the eutectic makes its appearance before the gold reaches 27 per cent.

## JEWELLERY GOLD.

Gold for jewellery consists of gold alloyed with silver or copper, or more usually both, and the properties of these alloys are therefore similar to those already described. It will be quite obvious that a gold may have

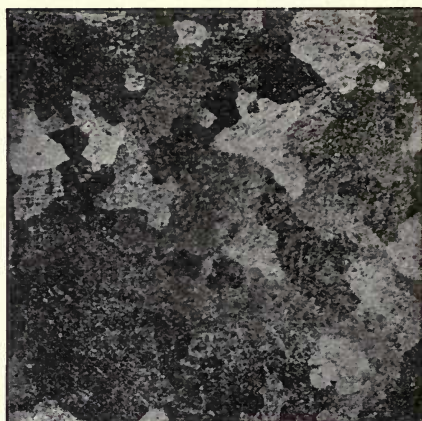


FIG. 117.—STANDARD GOLD  $\times 4.5$  DIAMS. (ROBERTS AUSTEN).

a definite fineness, *i.e.*, may contain a certain amount of gold, and yet its properties, colour, &c., may vary as the proportion of the alloying metals are varied. Mr. Hiorns quotes the following table from Gee's "Goldsmiths' Handbook" as the proportion of metals used in various jewellers' alloys :—

Carat.	Copper.	Silver.	Gold.
23	5	.5	23
22	1	1	22
20	2	2	20
18	3	3	18
15	6	3	15
13	8	3	13
12	8.5	3.5	12
10	10	4	10
9	10.5	4.5	9
8	10.5	5.5	8
7	9	8	7

It is obvious that as the quantity of alloying metal increases the value of the silver will increase so that it will be of importance to reduce it, also if silver be used alone the alloy will become paler and paler. A 10-carat gold, for instance, in which the alloying metal was all silver would be quite white.

The colour of a gold of given fineness may be varied very much by varying the proportions. Thus, taking 15 carat as a type:—

	Gold.	Silver.	Copper.
Red gold contains	.. 15	6	8.4
Green gold contains	.. 15	9	—

Gold may be coloured in other ways, as, for instance, by dissolving away some of the base metal by means of solvents, preferably assisted by an electric current, thus

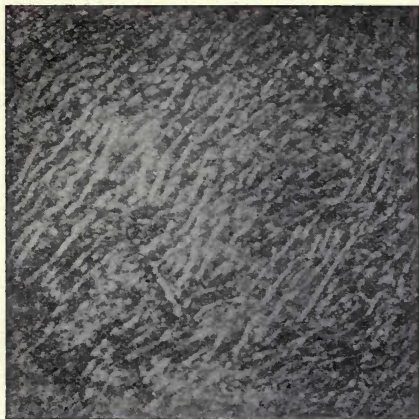


FIG. 118.—EUTECTIC (80 PER CENT. GOLD, 20 PER CENT. COPPER)  $\times$  1,580 DIAMS. (ROBERTS AUSTEN).

leaving a surface of a different composition and richer in gold than the bulk of the alloy, or by heating the gold with some substance which will have the same effect. If the gold is too poor, say below 13 carat, the surface left is too rough owing to the large amount of alloy dissolved away.

A little zinc is sometimes added to poor golds, the zinc usually being added in the form of brass. The colour of the alloy is darker than when silver is used. Zinc-golds are brittle and difficult to manipulate, but occasionally as much as 15 per cent. of zinc is present.

## OTHER ALLOYS.

Gold alloys well with other metals, but the alloys formed are of no importance. Lead dissolves gold in all proportions, and is used as a solvent for gold in certain metallurgical operations.

Some metals, especially antimony, bismuth, and arsenic, when present even in minute quantities, make the alloys so brittle that they are useless for coinage purposes.

Iron combines readily with gold, and is occasionally added to gold for ornamental purposes, as it modifies the colour of the alloy.

The alloys of gold and aluminium are of no importance, but they are of some interest. An alloy of gold and aluminium having the formula  $Au Al_2$ , and containing therefore 78.48 per cent. of gold, was discovered by Sir W. Roberts Austen, and has an intense red colour. A small quantity of aluminium is said to greatly improve the soundness of gold castings.


## GOLD SOLDERS.

A solder must have as nearly as possible the colour of the metal to be soldered. The solders are of two kinds—soft solders which melt at a very low temperature, and hard solders which melt at a temperature but little below that of the metals being united.

The hard solders used for gold are gold alloys containing either a little more of the more fusible constituent or a more fusible metal, and the more fusible it is the softer is the solder said to be.

Gee gives the following table of solders :—

	Fine Gold.	Fine Silver.	Copper.
Best solder .. ..	12.5	4 5	3
Medium solder .. ..	10	6	4
Common solders .. ..	8.5	6 5	5

The solders for use are usually rolled out into thin sheets, and cut into pieces of suitable size for use. 

The table on the following page is from Mr. Hiorns' "Mixed Metals," the figures having been calculated into percentages.

	Gold.	Silver.	Copper.	Zinc.
Hard solder for gold	62·5	31·2	—	6·3
Hard solder for 16-carat gold ..	75	16·6	8·3	—
Easier " " "	54·5	31·9	13·6	—
Solder for 14-ct. gold	50	33·3	16·6	—
" " " "	66·8	16·6	16·6	—
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Very easy solder ..	11·54	54·74	28·17	5·55

## SILVER ALLOYS.

Silver is another of the metals usually regarded as a precious metal, and which is used mainly for ornamental purposes, and for coinage. Silver has a pure silver-white colour, and it does not oxidise either at ordinary temperatures or at a red heat, but it tarnishes very rapidly in presence of traces of sulphur compounds such as are always present in the atmosphere of towns. Hence it is not very suitable for ornamental purposes under such conditions. It is much more abundant and much cheaper than gold. It is largely used for the subsidiary coinage in gold-using countries, and for the standard coinage in many countries, such as India and most of the South American Republics, where it has not been replaced by gold. As the ratio of value between gold and silver is constantly fluctuating, the standards of value between gold-using and silver-using countries must vary from time to time.

Pure silver is very soft, and is therefore always alloyed with some other metal before use.

**Silver-Copper Alloys.**—These are the most important of all the silver alloys, and they are generally used for the silver coinage of all countries.

Silver and copper alloy readily in all proportions, the alloy expanding in formation, so that the specific gravity of the alloy is less than that calculated from the proportions of its constituents.

When copper is added to silver, the freezing point falls rapidly, and reaches a minimum when the alloy has the composition  $\text{Ag}_3 \text{Cu}_2$ , and contains therefore

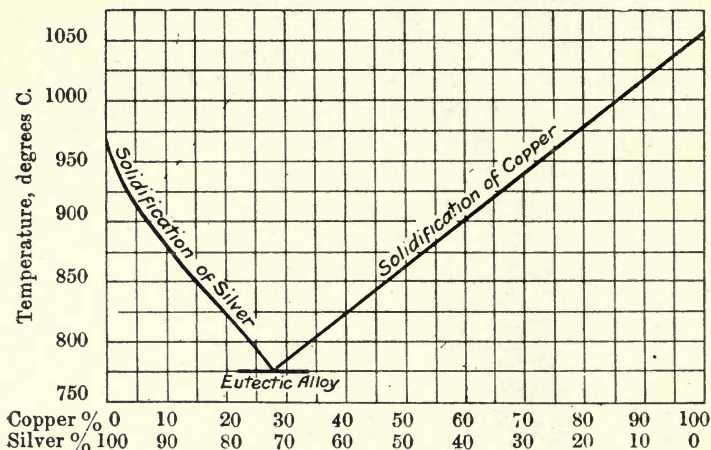


FIG. 119.—CURVES OF FUSIBILITY OF SILVER AND COPPER ALLOYS.

71.893 per cent. of silver and 28.107 per cent. of copper, and then the freezing point rises again rapidly. The alloy of lowest freezing point is a true eutectic, and it is

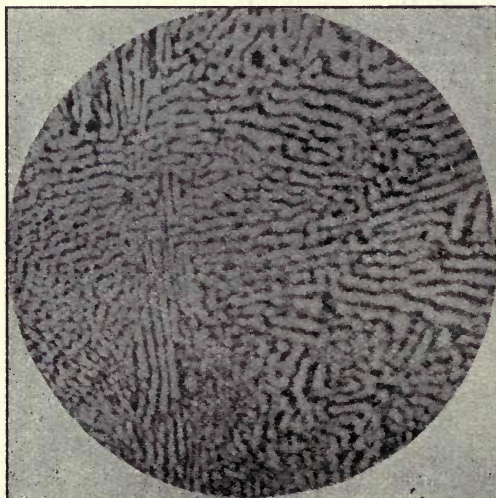


FIG. 120.—COPPER, 28 PER CENT.; SILVER, 72 PER CENT. (CAST). REHEATED TO A PURPLE COLOUR. MAGNIFIED 1,000 DIAMS.



the only member of the series which has a definite melting point. It was discovered by Levol to solidify without liquation, and is therefore known as Levol's homogeneous alloy.

At each end of the series the alloy consists of a solid solution of copper in silver or of silver in copper, but as the richness approaches the eutectic point there are two distinct freezing points, so that the alloy is for a certain

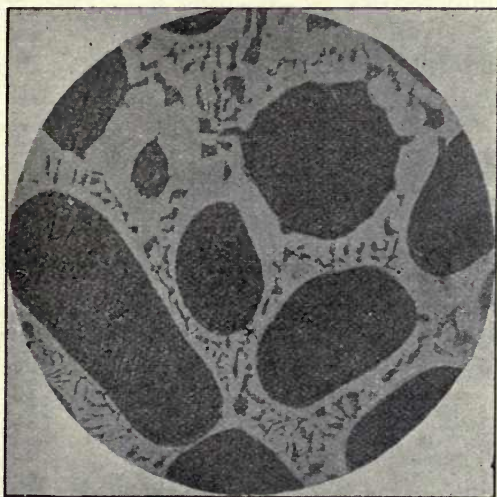


FIG. 121.—COPPER, 15 PER CENT.; SILVER, 85 PER CENT. (CAST).  
REHEATED TO A PURPLE COLOUR. MAGNIFIED 600 DIAMS.

range at least truly eutectiferous, and all alloys except the eutectic will be subject to more or less liquation.

The addition of copper hardly changes the colour of the alloy until the quantity is considerable; indeed, the alloy retains its white colour till the copper reaches 50 per cent. The colour then becomes yellowish till it is about 70 per cent., and then reddish. The addition of copper to silver hardens the metal, and makes it more sonorous. The hardest alloy is that which contains about one-third its weight of silver.

The only alloys of any commercial importance are those near the silver end of the series, which are used for coinage and ornamental purposes.

**Standard Silver.**—Silver coins and articles which are to be hall-marked are in every country made of some definite standard. In Great Britain the standard is 925, *i.e.*, it contains 92·5 per cent. of silver, the alloying metal being always copper. This is commonly called sterling silver, and no other quality is hall-marked. The colour is silver white, but it is harder than pure silver.

An alloy of the standard fineness contains 11 oz. 2 dwts. of silver to the pound troy (12 oz.). In actual manufacture the makers take care to add a little more, because if the alloy falls below the standard the article is not only not marked, but is destroyed. When articles are not to be hall-marked, a poorer alloy may, of course, be used.

The following alloys are used for manufacturing purposes :—

				Silver.		Copper.
1	..	..	..	90	..	10
2	..	..	..	80	..	20
3	..	..	..	75	..	25
4	..	..	..	70	..	30
5	..	..	..	66·5	..	33·5
6	..	..	..	65	..	35
7	..	..	..	62·5	..	36·5
8	..	..	..	60	..	40

If the copper be increased beyond 40 per cent. the alloy has a yellowish colour.

The value of silver alloys is often stated in pennyweights per ounce. As there are 20 pennyweights in an ounce troy the percentage divided by 5 will always give the value in pennyweights per ounce. Thus 90 per cent. silver is  $90 \div 5 = 18$  dwts. per ounce.

In Germany Mr. Hiorns states that four silver standards are used.

Silverware	...11 ozs.	8 dwts.	per lb.	or 950 parts	silver in 1,000	
Coinage	...10 ozs.	16 dwts.	..	900	..	..
Silverware	... 9 ozs.	12 dwts.	..	800	..	..
..	... 9 ozs.	0 dwts.	..	750	..	..

**Coinage Alloys.**—As in the case of gold alloys, the standard used in different countries varies.

Countries.	Fineness.
Netherlands .. .. .	945
Great Britain, Australia, South Africa, Canada, Newfoundland .. .. .	925
East Indies, Burmah, Ceylon, Mauritius, Brazil, Portugal .. .. .	911·67
Mexico .. .. .	902·7
France, Belgium, Switzerland, Italy, Greece, Servia, Roumania, Austria, Hungary, Spain, Argentine Republic, Bolivia, Chili, Peru, Germany, Egypt, Persia, United States, Japan .. .. .	900
Russia .. .. .	868·06
Bulgaria .. .. .	835
Turkey .. .. .	830
Denmark, Sweden, Norway .. .. .	800

Silver coins are not kept as closely to the standard as are gold coins, nor is it necessary, since the coins are really only tokens, the actual value of the metal being far less than the nominal or face value.

In a few cases other metals have been added in addition to the copper, but the advantage of this is very doubtful. Swiss coins are said to contain silver, zinc, copper, and nickel, and Mr. Hiorns gives the following table :—

	20 Centimes.	10 Centimes.	5 Centimes.
Silver .. .. .	15	10	5
Copper .. .. .	20	55	60
Nickel .. .. .	25	25	25
Zinc .. .. .	10	10	10

and such alloys have been used for ornamental purposes.

Silver alloys readily with other metals, but the alloys are of no commercial importance. Attempts have been made to use aluminium-silver alloys, but they have not so far been successful. The alloys are harder than silver, white in colour, do not tarnish in air, and are malleable provided the amount of aluminium does not exceed 10 per cent.

**Colouring Silver and its Alloys.**—The silver alloys used commercially have a white colour, and take a high polish, and on these properties their value to a large extent depends, but for various purposes either a matte or a coloured surface is required, and these may be imparted in various ways.

To obtain a very bright surface, the alloy is, of course, polished, the very finest polishing materials being used so as to avoid the formation of scratches. A dead-white surface is given by processes which practically consist in roughening the surface, usually by dissolving away some of the copper, and leaving a slightly rough surface of silver. Various methods may be used. Mr. Hiorns describes these :—

“An old method is to dip the work in a thick solution of borax, then place in a copper annealing pan, sprinkle it over with charcoal dust, and place the pan and its contents upon a clear fire. Heat until red hot, then withdraw and allow to cool. The work is next boiled with dilute sulphuric acid, and if the right colour is not obtained, the process is repeated one or more times. The lower standards require five or six operations to effect the proper degree of whiteness.”

“Another plan is to dip the work in a mixture of 4 parts powdered charcoal and 1 part nitre well mixed with water. The work is heated till the coating is thoroughly dry, when it is removed from the fire, allowed to cool, and boiled out in a solution of bisulphate of potash. After two or three operations a beautiful dead-white colour is the result. It is then washed in soda and water containing a little soap, or scratched and burnished if required bright. The process is completed by drying in warm boxwood sawdust.”

“Gee’s method of whitening consists of making the work red hot and boiling in dilute sulphuric acid (1 of acid to 40 of water). The process is repeated if necessary until the requisite colour is obtained.”

It will be seen that all these methods depend on the oxidation of the copper by heat, and then the solution of the copper oxide by suitable solvents. The direct action of solvents is not applicable, as the silver would be dissolved as readily as the copper.

In the case of very poor alloys these oxidation and solution processes cannot be used, as the amount of copper dissolved would leave the surface too rough. In such cases a layer of silver is usually deposited on its surface by electro-deposition, or by simple immersion in a solution of a silver salt.

A dark surface colour is sometimes imparted to silver goods under the name of oxidised silver. The name is not correct, because silver does not oxidise. The dark surface may generally be produced in two ways: (1) By treatment with a sulphide such as potassium, barium, or ammonium sulphide, by which a very thin layer of black silver sulphide is formed on the surface; or (2) by depositing on the surface of the metal a layer of some dark metal, preferably platinum, which is deposited from its solution as chloride by the action of the silver alloy.

**Silver Solders.**—For soldering silver alloys, an alloy more fusible than that being united must be used. Obviously, if an alloy of silver and copper only is to be used as a solder, it should be the most fusible member of the series, *i.e.*, the eutectic, as any increase of either constituent will diminish the fusibility. Where this is not fusible enough, some other metal which gives more fusible alloys will be added, the metal usually used being zinc.

Various formulæ have been given. An alloy of 4 parts silver and 1 part copper is sometimes used, but this is not the most fusible alloy, and is said to be too infusible for ordinary work. A good solder often used consists of 2 parts silver and 1 part brass. Assuming the brass to be a 50-50, this would give:—

Silver .. .. .	66·68
Copper.. .. .	16·66
Zinc .. .. .	16·66
	100·00

If copper and zinc are to be used together, a brass must be selected which has been made from very pure metal, as the presence of lead is very objectionable. For articles which have to be hall-marked, the solder should be as near as possible to the standard, because in taking the sample for assay the solder may be

included, and therefore if the solder used is too poor the bulk of the alloy must be made richer than would otherwise be necessary.

Solders of standard fineness can be made by replacing part of the copper by zinc, but they are not easy to work. The richest solders that answer well have a fineness of about 800, the zinc and copper either being present in equal quantities or the zinc being in larger proportions. Mr. Hiorns found that a solder containing

Silver .. .. .	80
Copper .. .. .	2.5
Zinc .. .. .	17.5
	100.0

ran quite readily, and gave good results. Ordinarily, the percentage of silver is considerably lower.

The following composition is quoted by Hiorns as a French solder used for soldering wares of a 980 standard:—

Silver .. .. .	66.6
Copper .. .. .	23.3
Zinc .. .. .	10
	100.0

In preparing solders it is always well to alloy the zinc and copper, making, of course, due allowance for loss of zinc, and then to use the resulting brass for alloying with the silver. The use of brass gives uncertain results, as the percentage of copper may vary.

**Silver-Tin Alloys.**—These are of little importance, but they have been studied by several workers. The alloys are white, and when the quantity of silver is large seem to be homogeneous in structure, probably being solid solutions. With less than 60 per cent. of silver the structure is seen to be duplex, the white silver crystallising out in a dark ground mass of eutectic. The eutectic contains about 5 per cent. of silver. Several definite compounds are said to have been detected. The hardest alloys contain from 60 to 85 per cent. of silver.

**Silver-Antimony Alloys.**—Silver and antimony alloy readily, the most fusible, *i.e.*, the eutectic alloy, containing 50 per cent. of each metal, but the cooling curves also show breaks at 20 per cent., and 80 per cent. of silver. The alloys rich in antimony are very hard.

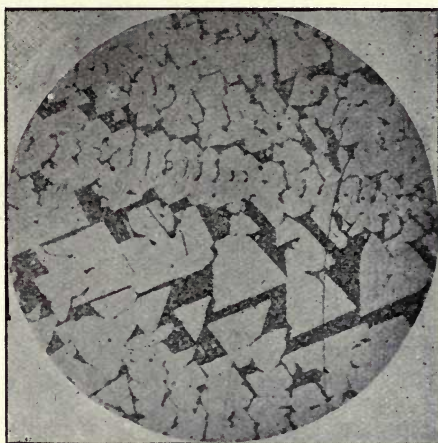


FIG. 122.—ALLOY OF SILVER AND ANTIMONY.  
SILVER, 16 PER CENT.; ANTIMONY, 84 PER CENT. V 30 X.

**Silver-Nickel.**—Alloys of these metals have been prepared, but do not seem to have been investigated. Berthier prepared one containing 13·5 per cent. of nickel, which was white, took a high polish, rolled well, and was very tough.

**Silver-Lead Alloys.**—Silver and lead alloy in all proportions, but the alloys are of no importance. The metals dissolve in all proportions in the liquid condition, but liquation takes place on solidification.

**Scorification and Cupellation.**—Silver (and gold) may be recovered from substances containing them by melting with lead and scorifying and cupelling the resulting lead-silver alloy. The silver (and gold) dissolves in the lead, thus separating it from earthy and other impurities. When the lead-silver alloy is heated to redness in an oxidising atmosphere, *i.e.*, with free access of air, the lead is oxidised to litharge, and the silver remains.

Scorification, which is used to reduce the quantity of lead, is usually carried out in a fireclay dish (a scorifier) and is continued till the surface of the lead is covered with a layer of litharge, when the molten mass is poured into a mould. When solid, the litharge is broken away, and the lead if necessary is returned to the scorifier.

Cupellation is carried out in a dish (the cupel) made of bone ash, which absorbs the litharge as fast as it is formed, so that when the lead is all removed, a bead or prill of pure silver is left.

The behaviour of other metals when alloyed with silver is of some interest.

Gold and platinum, being unoxidisable, are entirely left with the silver.

Cadmium and bismuth are oxidised and entirely removed with the litharge.

Copper is oxidised and removed, provided the quantity of lead is sufficiently large, the cupel at the same time being stained a dark olive green. The larger the quantity of copper the more lead is required, and the greater will be the loss of silver.

Antimony is carried away with the lead, and usually causes the cupel to crack, if present in large quantity, and also causes loss of silver by volatilisation.

Tin is carried away with the lead if the quantity of lead be large; if not, it is left as an infusible oxide.

As a rule, when foreign metals are present in large quantity, they are best removed by scorification before cupellation. When a silver or gold alloy is heated in air, the base metal present often oxidises—thus standard silver becomes black from the formation of copper oxide, which can be dissolved away, as already remarked, leaving a white surface of silver. With standard gold oxidation does not take place, but with poorer golds it frequently does.

#### PLATINUM ALLOYS.

PLATINUM is one of the most valuable of the metals, indeed of late it has been more valuable than gold, but its alloys are of little importance. It is white, almost silver white, in colour, and is both malleable and ductile. It is not acted on by any single acid, but is converted into a chloride ( $\text{Pt Cl}_4$ ) by the action of the mixture of nitric and hydrochloric acids known as aqua regia. It does not oxidise in air at any temperature. It is very difficultly fusible, its melting point being about  $1,775^\circ \text{C}$ ., which is a higher temperature than is attainable in any



ordinary furnace fired with either gaseous or solid fuel ; but it can be melted in the heat of the electric arc or the oxy-hydrogen flame. It must be melted in vessels free from silica, as this might be decomposed at the very high temperature, and the silicon pass into the platinum, making it brittle. Platinum is also said to take up carbon at high temperatures. Platinum is the heaviest of the metals in common use, its specific gravity being about 21·5, which is only slightly less than that of the heaviest known metals which are closely related to it, and which are members of what is called the platinum group of metals. Platinum alloys readily with most metals, but its alloys are of little technical importance, though they are used for some purposes.

**Platinum and Copper.**—These metals alloy readily in all proportions. An alloy containing equal proportions of the two metals is said to be yellow in colour, to have the same specific gravity as gold, and to be easily worked. With a larger proportion of platinum the alloys are white.

The following alloys are said by Mr. Hiorns to have a golden-yellow colour, and No. 4, which is known as Cooper's gold, is malleable and ductile, and closely resembles 18-carat gold.

	1	2	3	4	5	6	7	8
Platinum.....	18·2	5	29·3	18·75	57·7	66·7	29·1	19
Copper .....	45·5	...	66·7	81·25	38·5	29·1	66·7	81
Zinc .....	...	...	4	...	3·8	4·2	4·2	...
Silver .....	9·5	5	...	...	...	...	...	...
Brass .....	18·3	60	...	...	...	...	...	...
Nickel.....	9·0	30	...	...	...	...	...	...

The brass is, of course, an alloy of copper and zinc, but the quality of the brass to be used is not stated. Mr. Hiorns also mentions the following alloys :—

**Cooper's Mirror Metal.**

Platinum ..	..	..	..	..	..	9 49
Copper ..	..	..	..	..	..	57·85
Zinc ..	..	..	..	..	..	3·51
Tin ..	..	..	..	..	..	27 49
Arsenic ..	..	..	..	..	..	1·66

The inventor claims that this alloy is indifferent to the weather, takes a beautiful polish, and is suitable for pens.

**Cooper's Pen Metal.**

Platinum	..	..	..	..	..	50
Copper	..	..	..	..	..	13
Silver	..	..	..	..	..	36

Both alloys are hard, non-corrosive, and could be used for many purposes.

**Platinum and Iridium.**—An alloy of platinum with 10 per cent. of the rare metal iridium is hard, elastic, as infusible as platinum, quite unalterable in the air, and is not attacked by acids, even by aqua regia. It has been used for the manufacture of standard weights and measures for the Commission on the International Metric System, as being the most unchangeable alloy that could be found. Iridium is heavier than platinum (sp. gr. 22·421), and the specific gravity of the alloy is 21·615.

Platinum vessels for laboratory use are said to usually contain iridium, which makes the alloy harder, and does not in any way detract from its valuable properties.

**Platinum and Rhodium.**—An alloy of platinum with 10 per cent. of the rare metal rhodium has recently acquired some importance as forming with platinum the thermo couple used in the Le Chatelier pyrometer. It is as infusible as platinum, resists corrosion as powerfully, and is sufficiently ductile to be drawn into wire.

**Platinum and Silver.**—Platinum and silver unite, forming alloys which are white in colour, and when the metals are in some proportions are malleable and ductile, the fusibility decreasing and the malleability increasing with the quantity of platinum. The alloys high in platinum do not tarnish, and are largely used in dentistry.

The behaviour of platinum-silver alloys with solvents is somewhat peculiar and varies with the amount of platinum present. When the alloy is rich in platinum it is unacted upon by nitric acid; when the platinum is about 25 per cent. the silver is dissolved by nitric acid, leaving the platinum almost completely; but when the percentage of platinum is reduced to about 5 per cent., the whole of it dissolves with the silver. For this reason platinum cannot be parted from silver by nitric acid as gold can.

Messrs. Johnson, Matthey, & Co. prepare commercially an alloy of silver 2 parts, platinum 1 part, which is very ductile, and is therefore easily drawn into wire, and which is used as a standard for electric resistance.

**Other Alloys.**—The other alloys are of little or no importance commercially. Their properties are not such as to make them useful, and the presence of platinum makes them costly. The alloys with fusible metals, such as lead, in excess are very fusible, so that the platinum metals are rapidly corroded by contact with such metals. For that reason metallic oxides should never be heated in platinum vessels. Even oxides of iron and copper are to a small extent reduced, probably by means of reducing gases which penetrate the platinum, and the reduced metals alloy with the platinum. This is one of the limitations to the use of platinum vessels.

#### AMALGAMS.

Mercury is the only metal liquid at ordinary temperatures. It is silver-white in colour, and from the way in which globules of it run over a dry surface without wetting it, it was called quick, *i.e.*, living, silver, a name which is still frequently used. Its specific gravity is 13·59. It freezes at 38·5° C. and boils at 360° C., but at much lower temperatures, even, indeed, at the ordinary temperature of the air, it gives off vapour.

Alloys of mercury differ in many respects from those of the other metals which have been considered, not that there is any essential difference, but that the alloys have to be used and studied at a temperature above the melting point of one of the constituent metals. The alloys, which are called amalgams, may be either liquid, solid, or pasty, according to the quantity of mercury which is present, and the nature of the other metal. Mercury alloys with or dissolves almost all metals.

**Gold Amalgam.**—Gold and mercury alloy very readily, forming a white amalgam, the smallest trace either of the liquid metal or its vapour being sufficient to whiten a gold surface. Mercury will dissolve a quantity of gold, the alloy being liquid at first, then

becoming pasty and ultimately waxy. A definite amalgam seems to be formed which remains suspended in its excess of mercury, from which it can be separated by filtering through chamois leather or some very fine fabric. As it can be separated by filtration, it is evidently not in solution. The pasty amalgam separated in this way contains about two-thirds its weight of mercury and one-third gold.

On heating to above the boiling point of mercury, the mercury is expelled and gold is left which does not retain more than a trace of that metal.

A definite solid amalgam, Au Hg, containing 49.9 per cent. of gold, which crystallises in four-sided prisms and retains its lustre in air, has been obtained by heating the pasty amalgam with dilute nitric acid. It is not soluble in nitric acid, and its melting point is above the temperature at which the mercury is expelled. As pasty masses very often consist of an intimate mixture of a solid and a liquid, the pasty amalgam may consist of this solid amalgam disseminated through excess of mercury.

Advantage is taken of the solubility of gold in mercury in the metallurgy of gold. Crushed rock containing gold is mixed with mercury which dissolves out the gold, and the gold is recovered from the amalgam thus formed by straining and distillation. The process is called amalgamation, and it is the most common method of treating gold ores.

The old method of fire-gilding metallic articles, which is still used to a small extent, is carried out by means of an amalgam containing about 66.6 per cent. of gold. The article is thoroughly cleaned and is then dipped in a solution of a mercury salt by which a layer of mercury is deposited on the surface; this is then rubbed over with some of the amalgam, which adheres, and on heating to redness the mercury is expelled, and a layer of gold in a fine state of division is left, and this is finally burnished to make it bright. Some amalgams of gold have been found native.

**Silver Amalgam.**—Silver dissolves in mercury, forming amalgams which closely resemble those of gold. It dissolves less readily than gold in the cold, but very

readily when heated. A definite solid amalgam having the formula  $\text{Ag Hg}_2$  is found in nature, and crystallises in the cubic system. It is known mineralogically as amalgam.

Silver amalgam can be separated from excess of mercury by filtration, exactly as in the case of gold. Mercury is to some extent used for the extraction of silver from its ores, but not very largely, because the silver is usually present in combination in compounds which are not decomposed by mercury. Silver amalgam was at one time used for dry silvering just as gold amalgam was used for dry gilding.

**Copper Amalgam.**—Copper and mercury unite when finely divided copper is mixed with mercury, but the amalgams are more generally prepared by decomposing solutions of mercury salts by means of metallic copper. If the copper be dissolved in mercury the excess of mercury can be removed by filtration exactly as in the case of the amalgams of gold and silver.

An amalgam containing from 25 to 30 per cent. of copper may be obtained as a plastic mass of about the consistency of clay by continued pounding or kneading in a warm mortar; on being left to itself for a few hours it becomes crystalline and hard, so hard, indeed, that it can be broken up in a mortar. On warming and well tritulating in a warm mortar it returns to its plastic condition, and this change can be repeated any number of times. The soft and hard forms have the same density, so that the change is not attended either with contraction or expansion. This alloy is used to some extent for stopping teeth, but it is not suitable for the purpose on account of the nature of the metals of which it is composed. It may be used, however, for other purposes where the change from the plastic to the solid condition would be of use. Watt's dictionary gives the following method of making this amalgam:—

Finely-divided copper is prepared by precipitating copper from copper-sulphate solution by means of iron. Ten grammes of mercury is heated with 10 grammes of sulphuric acid and the copper obtained from 23·5 grammes of copper sulphate is added. The materials are tritu-

rated together under hot water for from 20 to 30 minutes, the water is then poured off and the process is repeated with fresh quantities of water until the water shows no blue colour. The amalgam is then dried again, triturated, well kneaded, and formed into small cakes, which become quite hard in from 36 to 48 hours. The amalgam produced contains about 3 parts of copper to 7 parts of mercury. Another method of preparing it is to moisten the copper with a solution of mercurous nitrate, then pour hot water upon it, add the required quantity of mercury, and triturate under hot water.

**Tin Amalgam.**—Mercury and tin unite readily at ordinary temperatures, but more readily on heating. Mercury applied to the surface of a rod of tin penetrates it very rapidly, and makes it so brittle that it breaks short off, and tin immersed in mercury splits up from the expansion of the amalgam which is formed. The amalgam is white. Solid and crystallised amalgams have been obtained; they may be definite compounds, but this is uncertain; while various formulæ such as  $\text{Sn Hg}$ ,  $\text{Sn Hg}_2$ ,  $\text{Sn}_3 \text{Hg}_2$ , have been assigned to them. The silvering on the back of mirrors is an amalgam of tin and mercury, which being soft can be pressed into optical contact with the glass.

A tin amalgam is said to be used by dentists for filling teeth. One part of finely-divided tin is rubbed in a mortar with 4 parts of mercury. The excess of mercury is then removed by squeezing through a bag of chamois leather. A plastic mass is left which hardens in a few days. Another alloy is formed of 2 parts tin, 1 part cadmium, and excess of mercury; the tin and cadmium are melted together and mercury added. The whole is poured into an iron mortar and well stirred with a wooden pestle till it acquires a soft buttery consistency. The excess of mercury is then squeezed off. The amalgam is soft and plastic when kneaded in the hand.

An amalgam of tin, silver, and gold is said to be used as a cement for teeth. It is prepared by melting together 1 part gold, 3 parts silver, and adding 2 parts tin to the

melted mass, pulverising the resulting alloy and kneading it together with an equal weight of mercury.\*

**Sodium-Amalgam.**—Sodium combines very readily with mercury at ordinary temperatures and more rapidly on warming. Heat is evolved and vivid combustion takes place, some of the sodium burning away. The two metals may be triturated in a dry mortar provided with a cover, and the amalgam should be covered with petroleum as soon as the combustion is over. The amalgam is liquid or solid, according to the proportions of the metals. With about 3·5 per cent. of sodium it is solid, crystalline, and can be filed; with 2·5 per cent. of sodium it is still solid, but softer; with 1·5 per cent. it forms a thick paste; with 1 per cent. it is viscid, and consists of a solid and a liquid portion.

Sodium amalgam decomposes water, liberating hydrogen and separating mercury. On this account it is largely used in chemistry as a reducing and hydrogenating agent, the liberated hydrogen being in the nascent condition. Amalgams are often more readily made by the action of sodium amalgam than of mercury itself, and many can be readily prepared by treating solutions of salts of the metal with sodium amalgam. On exposure to the air the sodium oxidises readily, so that the amalgam must be kept under oil of some kind. Sodium amalgam is sometimes added to the mercury in gold amalgamation.

Most metals combine with mercury more or less readily. In addition to those mentioned, bismuth, cadmium, zinc, lead, antimony, magnesium, and the alkaline metals form amalgams readily by direct union of the metals in the cold, or by gentle heating. Nickel, cobalt, iron, manganese, and platinum amalgams are not readily prepared, but can be obtained by the action of sodium amalgam on salts of the metals.

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\* Watt's "Dictionary of Chemistry," first edition, vol. iii., p. 891.

## CHAPTER XV.

### PREPARATION OF ALLOYS.

ALLOYS are almost invariably prepared by melting together the constituent metals. As the fusibility and volatility of the metals varies widely, the details of the methods must be different in different cases.

The object aimed at is to secure a perfectly homogeneous mixture with as little loss of metal as possible. When metals are melted they will as a rule mix perfectly, like all miscible liquids, and in due time uniformity would be brought about by diffusion without stirring, even if the metals were very different in specific gravity, but diffusion is so slow that other means of ensuring mixture must be adopted.

If the metals have melting points not very different, a mixture will to some extent take place even if the metals are merely melted together, and the more finely divided the metals are and the more intimately mixed they are in the solid condition, the more perfect is the mixture likely to be; but if one of the metals is much more fusible than the other, then the more fusible metal will melt first, and either fall to the bottom or rise to the top of the crucible, according to its density, and though it will certainly dissolve some of the less fusible metals there will be a tendency to form two layers which can only be brought together by mechanical stirring.

When one of the metals has a much higher melting point than the other, it is usual to melt it, and then to add the metal of lower melting point, very often holding the portion in the tongs and stirring it in so that it may dissolve gradually. This must be done with care, the cold metal only being added in small portions at a time, so as not to chill the less fusible metal below its solidifying point. As the melting point of the alloy falls as the more fusible metal is added, the danger of solidification is greatest when the first portions are added. When the



amount of the less-fusible metal is very large, and the melting points of the metals are very different, it is often advisable to make two alloys, and then to melt the less fusible of these and to stir in the more fusible. Examples of this practice will be mentioned later. Where one of the constituents is a volatile metal such as zinc, the temperature must be very carefully regulated.

To ensure homogeneity several methods may be used, the usual one being vigorous stirring by means of an iron rod. The stirring must be vigorous and long continued to ensure uniformity, except in the case of metals which diffuse readily, so that complete mixture by stirring is not always easy. When an iron rod is used, this may be attacked, and iron may pass into the alloy; indeed the iron almost invariably present in alloys is largely derived from the stirring rods. Rods of fireclay or graphite are therefore much better, but they are too fragile for ordinary use.

The pouring of the metal from the crucible does something towards ensuring mixture, and this may be made much more efficacious, where the alloy is of sufficiently low melting point, by a double pouring—that is, by pouring the metal into another crucible and thence into the moulds. The same principle is applied in the case of alloys of high melting point, by casting into small ingots, then breaking these ingots and remelting them. In some cases alloys are said to be very much improved by remelting, and this improvement is mainly if not entirely due to the greater homogeneity which is produced.

In the case of alloys of low specific gravity, such as those containing a large proportion of tin, the stirring has an additional advantage. Such alloys are very apt to retain scattered through them particles of oxide, which do not rise readily to the surface, but which are brought up by stirring. Stirring with a stick of wood is often of great advantage in such cases, as the evolved gases tend to carry up with them the oxides, &c., and these form a scum which can be skimmed off, or left in the crucible when the alloy is poured. In some cases, also, stirring tends to facilitate the escape of occluded gas.

When metals are melted, there is always a tendency to oxidise on exposure to the air; to avoid this, the molten

metal should always be covered with a layer of powdered charcoal, or some similar material. Oxide formed may simply form a scum on the surface, or it may in certain cases be dissolved and impair the qualities of the alloy.

Dissolved oxides can often be removed by the addition of some metal or non-metal which will decompose the oxide, and form an oxide which, not being soluble, will float up, and can be removed. To this action is due the great improvement in the properties of certain alloys produced by the addition of minute quantities of aluminium, manganese, phosphorus, or other easily oxidisable element, some examples of which have already been discussed. As a rule a molten metal will dissolve its own oxide to a small extent, but will not dissolve oxides of other metals.

In the case of alloys, one metal will usually oxidise more readily than the other, so that oxidation will tend to alter the composition of the alloy.

As a rule, an alloy should be cast immediately after stirring, as there is sometimes a tendency to segregation, even whilst in the liquid condition.

**Preparation of Alloys of Low Melting Point.**—Alloys of this class, consisting mainly of lead and tin, are very easily prepared by melting the metals together in the required proportions under charcoal. A crucible may be used, or even an iron ladle heated over a fire. As both the metals oxidise readily, the covering layer of charcoal is important. When the metals are melted they should be vigorously stirred with a stick, and then should be poured into a mould, the scum being kept back by means of an iron rod or a stick. The addition of various elements has been suggested for the removal of impurities likely to be present, such as a little sulphur, but this is never advisable; the stirring with a stick will do all that can be done in this direction, and if the metals are too impure they should not be used.

Where other less-fusible metals have to be added, the methods are modified. The metal of higher melting point may be melted first, and the less-fusible metal then added, the whole being well stirred after fusion.

In the manufacture of pewter, which is an alloy of tin with a small quantity of copper, some copper is first melted and then its own weight of tin is added, and this alloy is cast into ingots. When it is required to make the pewter, a portion of this alloy is added to the required amount of tin, and the whole is melted. A little zinc is often added, it being claimed that the zinc carries the oxides to the surface as a scum, and also that by its oxidation it saves the tin.

In the manufacture of metal for casting shot, a little arsenic is added. This is almost always added in the form of white arsenic (arsenious oxide). Lead is melted in an iron pot covered with charcoal, and the temperature is raised considerably above the melting point of lead; the white arsenic, usually wrapped in a sheet of lead, is then put into the lead and pressed down, and the whole is vigorously stirred with a wooden pole. The mass is kept melted for some hours to ensure complete reduction, and the alloy is ladled into moulds for use. As there is considerable loss of arsenic, the lead pot must be covered with a suitable hood. In some works enough arsenic is added to make an alloy containing about 2.0 per cent. of arsenic, which is added to the shot lead in the required proportions; in others the white arsenic is added directly to the shot lead. The amount of arsenic present in the shot lead is very minute. The quantity of white arsenic added, when it is added directly to the shot lead, varies from about 3 to 6 parts per 1,000 parts of lead. Brannt states that the lead should never contain more than 1 per cent. of arsenic; it actually always contains very much less.

**Preparation of Bronze.**—In the case of bronze, the two metals have very different melting points and specific gravities. As a rule, the copper is melted first under charcoal either in a crucible or reverberatory furnace, according to the amount being melted, and when it is completely melted the tin is added, or very frequently the tin, being very fusible, is placed in the ladle in the form of ingot, and the molten copper is poured upon it. The tin being much lighter than the copper will tend to float, so that vigorous stirring is necessary in order to ensure complete mixture.

The tin is also much more easily oxidisable than the copper, so that it tends to oxidise, and as oxide of tin seems to be soluble in bronze, some of this may be retained. The addition of a little phosphor copper, or other easily oxidisable metal which will decompose the tin oxide, is therefore often advisable.

Sometimes the tin and copper are melted together, but owing to the oxidisable character of the tin this is never advisable. The casting temperature is a matter of very great importance; too low a temperature is particularly to be avoided.

**Preparation of Brass.**—In the case of brass not only have the two metals very different melting points, but the zinc is very volatile, and this complicates the process of manufacture very considerably. Also the quantity of zinc to be used is as a rule very much larger than the quantity of tin in bronzes. Brass may be made from copper and zinc, but almost always in practice a considerable quantity of scrap will be used.

The copper is always melted first under charcoal, either in a crucible or a reverberatory furnace, as the case may be. When the copper is melted and has reached a temperature somewhat above its melting point, but not too hot, the cover of the crucible is removed and the zinc is added. The zinc is in the form of fragments of cakes of spelter. These are taken one by one in the tongs and are carefully stirred into the molten copper, so that they may dissolve gradually. This addition requires great care. Usually the spelter is warmed by leaving it on the furnace top for some time before it is added. The temperature of the copper must not be too high, since the higher the temperature the greater will be the loss of zinc. The cold zinc at once tends to chill the copper, and it must be kept moving, so that no copper is solidified. If the lump of spelter be let fall into the crucible it may cause some of the copper to solidify, and this cannot be remelted without undue loss of zinc. As soon as the zinc is all added, the whole is well stirred, and the metal is poured without delay into the moulds.

As soon as the zinc touches the copper some of it is volatilised, and the vapour coming into the air at once

burns, forming oxide of zinc, which is deposited in white, woolly flakes—called philosopher's wool. The oxide of zinc is extremely irritating, but its formation cannot be avoided. All the time the zinc is being added, and whilst the brass is kept melted, zinc is being given off, so that there will always be a considerable loss of zinc, and a loss which will vary very much according to the conditions of working. To minimise the loss the temperature of the copper must not be too high, and all the operations must be performed rapidly. As the brass will usually be too cool for casting after the copper has been added, the temperature must be rapidly brought up to the required point.

In most cases scrap will be added as well as the zinc, and where accurate composition is required it is obvious that the composition of the scrap must be known. The way in which the scrap will be added will depend on circumstances. The usual method is to place the copper on the bottom of the crucible or furnace, then put the scrap on the top and melt the two together; or, if in large pieces, it may be stirred in in the same way as the zinc, if in smaller pieces it may be added in small portions at a time, the whole being well stirred after each addition; but in this case the copper must be very hot before the addition is made. It may be added cold, as is usual when a small quantity is being added, or it may be heated to redness if a large quantity is being used.

When brass is required to a specified composition, great care must be taken in the manufacture. The composition of the scrap used must be known, and allowances must be made for the loss of zinc, but the allowance must not be too great. It is only with the richer brasses, say those with about 70 per cent. of copper, that is, with brasses which have to be worked, that accuracy of composition is usually required; with ordinary cast brass a few per cent. either way is of little or no moment. It is quite impossible to make a brass with a perfectly definite composition, but the variation should be within 1 per cent. of copper above or below the specified percentage. As the copper is the more costly constituent a minimum copper is usually specified, no notice being taken of

variations in the other direction. For a 70/30 brass the amount of allowance for loss in manufacture will usually be 2 per cent. on the whole weight (that is, nearly 7 per cent. of the zinc used), or for 100lbs. of brass the total weight of mixture will be 102lbs., thus :—

Copper	..	..	..	..	..	70
Zinc	..	..	..	..	..	32
						102

When scrap is to be used, allowance must, of course, be made for the zinc contained in it. Suppose it be required to cast 100lbs. of 70/30 brass, using 20lbs. of scrap containing 68.5 per cent. of copper. The scrap will contain 13.7lbs. of copper and 6.3lbs. of zinc. The mixture will be :—

Copper	..	..	..	70	-	13.7	=	56.3
Zinc	..	..	..	32	-	6.3	=	25.7
Scrap	..	..	..	..	..	..	..	20
								102.0

It will be noticed that the less the loss of zinc the poorer will be the resulting alloy, so that very careful work may lead to saving in zinc, and thus to a reduction in the value of the alloy. When the percentage of copper is very closely specified, it is better only to allow for 1 per cent. loss, as it sometimes happens that the actual loss is below 2 per cent.

One of the great causes of the uncertainty of the composition of brass is the use of scrap of uncertain composition, and often intermixed with bronze and other scrap. Scrap should always be melted and cast into ingots, the composition of which can be determined before it is used in the foundry for any except the commonest castings.

The remelting of brass always entails a considerable loss of zinc, so that remelted brass is always richer in copper than that before remelting. The loss may vary from 1 to 5 per cent., according to the conditions of melting.

The addition of phosphorus, or other deoxidising agent, is not so necessary in the case of brass making

as for bronze, but the addition of manganese is often advantageous, as manganese oxide is fusible. The zinc is so readily oxidised that it decomposes oxides of copper that may be present, and oxide of zinc does not seem to be soluble in brass, but it is infusible and may remain disseminated through the brass, rising slowly to the top and forming a scum. If there is much copper oxide in the molten copper, as when it has not been properly protected during melting, a large quantity of zinc oxide will be formed, and this may take a long time to rise; or if a very large quantity be present a mixture of zinc oxide and metal, called a "salamander," which will not melt, may be formed.

Even when the quantity of zinc oxide is not large enough to bring this about, it may be quite large enough to reduce the fluidity of the metal and make it pour badly. Such a brass will not give clear, sharp castings, and the castings produced will be poor and weak, and will probably crack if the metal has to be rolled.

Sometimes a brass is improved by remelting, because a better chance is given to the entangled oxide to rise. When there is no entangled oxide remelting does not seem to improve the quality of the brass.

Mr. Sperry states that melting the brass under common salt improves the quality of the brass by removing, or rather preventing, the formation of copper oxide. The explanation which he gives is that salt dissociates, and that the sodium removes the oxygen from the oxide. Admitting the fact, the explanation is probably not correct. It is more likely that in presence of the molten salt oxychlorides of copper are formed, and that these yield fusible oxychlorides of zinc which rise readily.

Molten alloys, as indeed all molten metals, tend to absorb gases, and the evolution of these on solidification causes blowholes. The gases are probably mainly carbon-monoxide and nitrogen, and perhaps sulphur dioxide. Though but little is known as to the absorption of gas by brass, that it is sometimes absorbed or given out is proved by the formation of blowholes in brass castings. The higher the temperature, and the longer the metal is exposed to the gas, the more likely is gas to be absorbed.

Mr. Sperry gives the following directions for brass melting :—

“ Place a small amount of scrap in the bottom of the crucible. This serves as a cushion for the copper ingots, and the small amount of zinc which is present also has a reducing action on the oxide of copper that is formed. Over this scrap place the copper ingots, but do not pack them so tightly that the crucible will be cracked when they expand with the heat. Also see that too many ingots are not placed in the crucible. Ingots which cannot be covered with charcoal are oxidised in melting. Excellent results are obtained by cutting the copper so that the pieces pack well in the crucible and leave none projecting above the top. In this manner the whole may be covered well with charcoal.

“ When the ingots have been placed in the crucible on top of the scrap, some charcoal is put in around them and the melting begun. A fire that is too fierce is objectionable, as it is apt to ‘ burn ’ the top of the copper ingots before the bottom is melted. A fire that allows the metal to melt uniformly is the best. Forced draught must be carefully regulated so that the metal is not rapidly ‘ burnt.’ Watch the metal carefully, and when the first signs of melting are seen add one or two pounds of common salt (to a No. 60 crucible). Now add some more charcoal so that no part of the copper is exposed. The charcoal should be granulated and not in large pieces, as the latter do not cover the metal well. When the copper begins to melt add some more scrap. The addition of scrap will cause the copper to melt more quickly. When the scrap has melted add the remainder of the copper, and then another dose of salt. Stir the salt into the metal, and then add more charcoal if the surface is not well covered. The best results will be obtained when no part of the copper is exposed.

“ Do not attempt to add the spelter when the copper is just melted. The cold spelter will cause the copper to chill in the bottom of the crucible. The zinc will then float on the top of the copper, until finally the rise in temperature will cause the zinc to volatilise almost instantaneously with a flash and its complete loss. On the other hand, it is not conducive to the best results to



overheat the copper so that the spelter will 'sing' when it is introduced. There seems to be a widespread notion among brass casters that good brass cannot be made unless the spelter 'sings' when it is added to the copper. This idea is false, as the best brass is produced when the temperature of the copper is as low as it can be and yet melt the spelter. The heating of the spelter so that it is not brittle is also helpful, as it does not then chill the copper to such an extent.

"When the copper has arrived at the right heat—experience only can tell this point—the spelter is added. If the 'heat' of the copper is right, the spelter will 'sizzle' somewhat, but will not 'sing.' The whole is then carefully stirred and more scrap added if necessary. The spelter has now cooled the brass to such an extent that to pour it would mean an imperfect casting. The caster is now brought face to face with two evils: First, the pouring of the brass at too low a temperature or 'heat,' and thus saving the excessive spelter loss. Second, pouring the brass at a good heat so that it smokes freely, and thus losing considerable spelter. Of the two evils choose the less, and the 'less' in this instance is the loss of spelter. Brass which is poured too cold does not produce good castings, particularly in chill moulds for the casting of rolling-mill plates. Unless the heat of the brass is sufficiently high the oil which is used on the moulds and which burns at the mouth of the mould will not reduce the film of oxide that envelops the stream of metal as it is poured. For this reason a dirty casting results.

"In order that the oil shall reduce the film of oxide which forms on the stream of oxide as it enters the mould, it is necessary to pour at a suitable temperature. This 'suitable temperature' is determined by the eye. Pyrometers have not yet proved advantageous for it. The temperature for pouring must be high enough, so that the brass smokes freely. At this 'heat' the stream of metal, provided the oil burns at the mouth of the mould, is clear and free from oxidation.

"While the foregoing directions are somewhat general in their scope, there are a few very important rules to be strictly adhered to. These are of such importance that

they may really be called axioms. They are three in number, and the whole subject of brass melting may be said to hinge upon them :—

“(1) Do not overheat the copper. More brass is ruined by not following this rule than anything else. Brass may be overheated with less danger than the copper. Heat the copper to the required point and then *immediately* add the spelter.

“(2) Do not ‘soak’ the copper or the brass in the fire. The longer metals are allowed to remain in the fire the greater the oxidation and the more gas is absorbed. As soon as metal is ready for pouring, it should be at once removed from the fire and poured. Leaving metal in the fire after the right temperature for pouring has been reached is injurious.

“(3) Do not pour the metal at too low a temperature. Even if the brass smokes it does not indicate that the loss is enormous. It is better to lose the spelter than the casting.”

The brass may take up sulphur from the fuel if a sulphurous fuel be used, and though the actual quantity is small, it is enough to impair the quality of the alloy.

**Calamine Brass.**—Brass was made before zinc was known in the separate condition. It was then made by melting copper with zinc oxide—roasted calamine—and carbon, and was therefore known as calamine brass. The copper was always finely divided, usually in the form of granulated copper, the zinc oxide was reduced, and the zinc liberated, the reduction taking place at a temperature below the melting point of copper. The reduced zinc was volatilised, and the vapour attacked and combined with the copper. The loss of zinc was always very high, and the brass of very uncertain composition. As the oxide of zinc was never pure, a considerable quantity of slag was produced which was often very infusible. This process is not now used.

**Aluminium Alloys.**—Aluminium alloys may be prepared in two ways : (1) The ordinary foundry method, by melting together the component metals ; and (2) the Cowles process, by reducing the aluminium by carbon in

the electric arc, in presence of the metal to be alloyed with it.

The second method was largely used before the electrolytic methods enabled metallic aluminium to be produced almost pure and at a cheap rate. It is now but little used, probably because the bronze produced is apt to be impure, owing to the conditions of production. When it is used, a copper-aluminium alloy rich in copper is first made, and this is diluted by the addition of copper. It is almost always more satisfactory for users to buy the materials and prepare their own alloys.

As aluminium bronze is hardened by the presence of iron, silicon, and other impurities, the metals used should be as pure as possible.

The following instructions are given by the Magnesium and Aluminium Fabric of Hemelingen for the preparation of the aluminium bronzes: "Melt the copper in a plumbago crucible, and heat it somewhat hotter than its melting point. When quite fluid and surface clean, sticks of aluminium of suitable size are taken in tongs and pushed down under the surface, thus protecting the aluminium from oxidising. The first effect is necessarily to chill the copper more or less in contact with the aluminium, but if the copper was at a good heat to start with the chilled part is speedily dissolved and the aluminium attacked. The chemical action of the aluminium is then shown by a rise of temperature, which may even reach a white heat; considerable commotion may take place at first, but this gradually subsides. When the required amount of aluminium has been introduced the bronze is let alone for a few minutes, and then well stirred, taking care not to rub or scrape the sides of the crucible. By the stirring, the slag which commenced to rise even during the alloying is brought almost entirely to the surface. The crucible is then taken out of the furnace, the slag removed from the surface with a skimmer, the melt again stirred to bring up what little slag may still remain in it, and it is then ready for casting. It is very injurious to leave it longer in the fire than is absolutely necessary; also, any flux is unnecessary, the bronze needing only to be covered with charcoal powder. The

particular point to be attended to in melting these bronzes is to handle as gently as possible when once melted."

When the bronze is to be made by diluting a high-aluminium alloy, either the one constituent or the other may be melted first, usually the one largest in quantity, and the other is then stirred in, or the two may be melted together. Aluminium itself should never be melted in clay crucibles, or in contact with siliceous materials, as it may decompose them and take up silica and other impurities; plumbago (graphite) crucibles are generally used; these, however, also contain enough clay to impart silicon to the metal.

The difficulties in the way of making alloys rich in aluminium are generally two-fold.

If the mixture is too hot or is kept too long melted, the aluminium will attack the crucibles in which the melting takes place, reducing silicon and iron, which pass into the metal and make it brittle. As aluminium alloys are very light, the oxide scum rises comparatively slowly, and therefore sufficient time must always be allowed before pouring.

The other difficulty is that known as burning. Molten aluminium seems to absorb gases, probably nitrogen and carbon-monoxide, and these being given out on solidification make the metal porous and brittle.

Mr. J. E. S. Jones says, speaking of aluminium :—

"The ingot structure of 'burnt' metal, *i.e.*, its appearance to the naked eye, is often quite distinctive. We have :—

"(1) A great profusion of crystals on the top surface of the ingot, like those on galvanised ironware which have been dipped in spelter containing tin. The crystals are beautifully filicoid or fern-shaped, and occur on the good metal as well; but in that case there are only a few, and their size is nothing like that attained in a really 'well-burnt' sample. The opinion is consequently suggested that these crystals are always indicative of 'burning,' incipient or pronounced, and that per-

factly good aluminium should show no crystals at all on the ingot surface.

“(2) The centre of the top surface is usually not only sunk in like every cast ingot, but large cracks have appeared traversing the crystals. In my opinion, and also in that of other men who are qualified to say, these cracks are *absolutely indicative* of poor metal. I have never seen them in undoubtedly good ingots, and as a rough-and-ready test to differentiate (before subsequent examination) good from bad aluminium, the presence or absence of cracks is a good guide.

“(3) The top ingot surface is nearly always also covered with numerous parallel streaks, mainly at the edges. These streaks in appearance are exactly like that of a piece of skin, not caught evenly at the edges, which is pulled tight and ‘ruckles’ up. I imagine that it is the skin of oxide on the metallic surface which does the same, and that the streaks are produced as a concurrent effect from the same cause which gives the central cracks. We also get fine streaks sometimes on the good metal, but in nothing like the size and quantity that the ‘burnt’ material shows.

“The above tests, therefore, will give the aluminium foundryman a good idea as to whether his metal is good or bad when it arrives, but, of course, none are absolute proofs. For this recourse must be had to the more scientific examination by physical, microscopical, and chemical means.”

Aluminium oxidises very readily, and thus removes every trace of oxygen from the copper; the oxide slag formed is no doubt partly produced in this way and partly by the direct oxidation of the aluminium.

The metals copper and aluminium diffuse readily. Many workers think that to obtain a homogeneous alloy remelting is necessary, this sometimes being repeated two or three times. This, however, is quite unnecessary if ordinary care be used, though it may be advisable when casting very small heats. At each remelting there is some loss of aluminium, but if the surface be kept covered with charcoal this will be very small.

When zinc is to be added, it is added just before casting, as in the manufacture of brass.

**Nickel Alloys.**—The preparation of nickel alloys presents some difficulties, owing to the very high melting point of nickel. Where only copper is to be alloyed, the difficulties are not serious, since neither of the metals is volatile. The two metals, preferably in a fine state of division, are mixed and melted under charcoal; the copper melts and dissolves the nickel, or the nickel may be melted first, and the copper in ingot form is heated red-hot and then added to the nickel.

When, however, zinc is to be added, the volatility of the zinc introduces a difficulty, and the method is usually modified.

The three metals to be used are made into alloys, each containing two metals. Thus part of the copper is alloyed with the nickel by fusing the metals together so as to form an alloy which may contain from 1 part copper to 1 part nickel to 2 parts copper to 1 part nickel. The zinc is alloyed with copper, so as to form a brass, either equal quantities of copper and zinc, or 1 part copper to 2 parts zinc, as the case may be. The two alloys are cast into ingots of suitable form, and the zinc alloy may be broken up into pieces. The required amount of the less-fusible, *i.e.*, the copper-nickel, alloy is melted in a graphite crucible, and the more fusible alloy is then stirred in, exactly in the same way as the zinc is added in making brass. By this method of working the loss of zinc is much reduced, because the temperature is much below the melting point of nickel. The alloy is then cast, and very frequently is remelted for use so as to make it more homogeneous.

**Platinum Alloys.**—Platinum is so infusible that it can only be melted in the electric furnace, in the oxy-hydrogen flame. The latter is usually used. The platinum is melted in lime crucible before the oxy-hydrogen flame, and the metal to be added is stirred in. If a small quantity of platinum only is to be added to an alloy, the alloying metal may be melted and the platinum stirred in till it is dissolved.

**Amalgams.**—These alloys are usually easily prepared by grinding the finely-divided metal with mercury, or in

some cases by liberating the metal by chemical means from its compounds in presence of mercury.

#### FURNACES.

Since alloys are always prepared by fusion, the construction of furnaces for the fusion is a matter of great importance.

The furnaces are in general of two kinds :—

- (1) Crucible furnaces ;
- (2) Reverberatory or air furnaces.

In the former the metal to be melted is contained in a crucible which is heated by contact with the fuel or by the products of combustion ; in the latter the metal is heated on the hearth of the furnace by the products of combustion and by radiation from the hot masonry of the furnace.

Cupola furnaces—such as are used in iron founding, in which the metal is heated by contact with the solid fuel—are rarely used in the manufacture of alloys.

**Crucible Furnaces.**—These are almost always used for dealing with small quantities of metal, up to about 160lbs., but larger quantities are difficult to deal with owing to the large size of the crucibles needed, and the difficulty of handling them. They have the great advantage that the metal is protected from the fuel and the products of combustion, and therefore is much less likely to take up deleterious impurities such as sulphur, and as it is quite easily kept covered with a layer of charcoal, oxidation can be reduced to a minimum. Such furnaces are, however, very wasteful of heat, and the crucibles are always costly.

Crucible furnaces may be fired either with solid fuel, gas, or oil.

**Solid Fuel Crucible Furnaces.**—A furnace of this type consists of a fireplace with firebars at the bottom, and a suitable cover at the top, and with an opening by which the products of combustion can be drawn away. Beneath the firebars is an ashpit to receive the ashes from the fuel.

The size of the furnace will vary with the size of the crucibles to be used, and this will in its turn depend on the amount of metal to be melted at one time. For pots

up to 150lbs. capacity, the furnace must be about 18in. square. As the pot must not come in contact with the bars or the bottom would be chilled, a fireclay support, often half a brick, is placed on the bars to support it. The furnace must be sufficiently deep for the top of the pot to be 6in. or 8in. below the flue, otherwise the air entering it at the furnace top and passing to the flue may chill the surface of the metal. The furnace must be large enough to contain a layer of ignited fuel all round the pot, but this layer need not be very thick; 3in. or 4in. is quite sufficient. It must be remembered that the crucible will only be heated by the coke which is in contact with it, as the hot coke is quite opaque to radiation from the external layers of the fuel. It will be obvious, therefore, that for a single pot a circular furnace will be better than a square one, because the fuel in the corners of the latter will be of little use. Similarly for two pots an elliptical furnace will be better than one which is rectangular, but furnaces holding two crucibles are never to be recommended for making or melting alloys.

The chimney must be of sufficiently large area and sufficiently high to produce a good draught.

The body of the furnace may be built of ordinary brick, but the lining must always be of a refractory material, firebrick, ganister, or similar material. When a circular furnace is used, the bricks should be made to fit the curve, so that as they are "cut" away there will be no gaping joints. For square or rectangular furnaces ordinary firebricks may be used. In any case they must be set in good fireclay mortar, and the joints should be

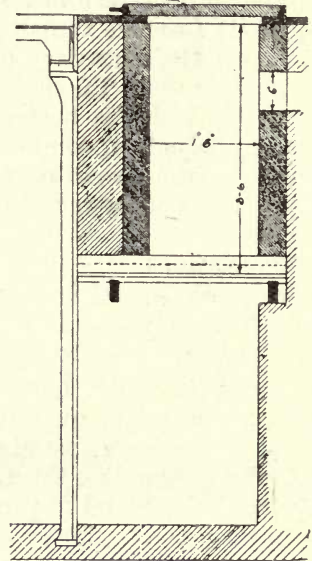


FIG. 123.—SOLID FUEL CRUCIBLE FURNACE. (CROSS-SECTION).



as thin as possible; as the wear is always very much greater with thick joints than with thin ones. Very durable linings may be made with ganister or some similar material. A wooden core is made the size and form which the interior of the furnace is to have. This is placed in position, and ganister, mixed with enough water to make it plastic, is rammed round. This is then dried gently. For circular furnaces this is often better than a brick lining, and is more easily made. It is the method usually used when lining the Sheffield steel-melting furnaces, which have to stand a very high temperature.

The masonry of the furnace must be held together by iron stays and ties, the ties passing through the masonry between the furnace openings.

The position of the furnace will vary. For very small work the whole structure may be above the floor level, the furnace top being about 2ft. 6in. above the floor, but for larger work the furnaces must be below the floor, so that the working floor is on a level with the top of the furnace. This allows the workman to work from above, and gives him a good position over the crucibles. For heavy charges the crucible is always lifted by means of a crane.

The arrangement of the bars is a matter of importance. The masonry of the furnace will be carried on iron bars, and the firebars will be supported on cross-bars below. The firebars may be of the ordinary firebar shape, but they are better simply rectangular bars of malleable iron, so that they can be moved and turned when necessary, and they may be fixed with a diagonal vertical by resting them in V grooves in the supporting bars. It is very important that the bars should fit close up to the furnace masonry, so that all the air that finds its way in passes between the bars, and none is admitted round the edges of the furnace. The gases find a much easier passage up the wall than through the mass of the fuel, and if the air can pass up in this way the combustion at the outer edge of the fire is very rapid. This means loss of heat, because as already pointed out the heat evolved there cannot be utilised, and at the same time the temperature close to the wall being very high the brick-

work is apt to be rapidly destroyed. An alteration in the arrangement of the firebars of a furnace has often greatly improved its working. The air spaces between the bars should be as large as possible, so that a maximum of air can be admitted when required.

The furnace should always be provided with dampers for regulating the draught, and preferably there should be

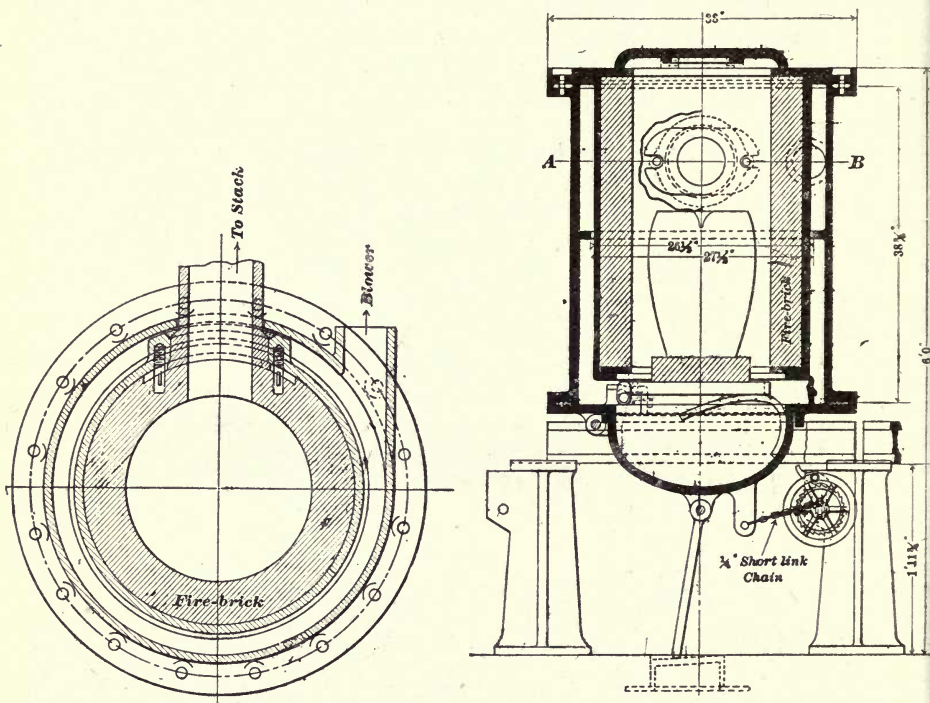


FIG. 124.—DETAIL SECTIONAL VIEWS OF CRUCIBLE BRASS FURNACE.

two, the one in the chimney to control the outflow of the products of combustion, and the other at the ashpit to control the inflow of air. The careful worker will keep the rate of combustion under strict control by means of the dampers.

An excellent form of furnace for alloy melting used in the United States is shown in Fig. 124. The furnace consists of two cast-iron cylinders one within the other. The inner cylinder is lined with firebrick

in the usual way. The outer cylinder is closed at the bottom by a circular casting provided with legs resting on the supporting beams and has a circular opening for the insertion of the grate. The lower portion of the furnace is closed by a bell-shaped casting swinging on hinges and operated by a chain wound round a shaft which is held in position by a ratchet and pawl. The surfaces of the castings are machined so as to form a reasonably tight joint, and when the bottom is up it is secured in place by an iron rod. The bell-shaped receiver has a curved piece secured to its inner side by which the grate is raised into place when it is closed. The air is supplied by a fan, and passes into the annular space between the cylinder and thence to the furnace.

Crucible furnaces may, of course, be modified in many ways. One of the best known modifications is that of Mr. Carr, of Birmingham, and his furnaces are largely used. The furnaces are self-contained, the sides of the furnace are supported independently, the grate being a little below the bottom, so as to leave a free air space all round. The ashpit is provided with a damper. It is stated by the makers that with these furnaces 100lbs. of brass can be melted in three-quarters of an hour with 36lbs. of coke.

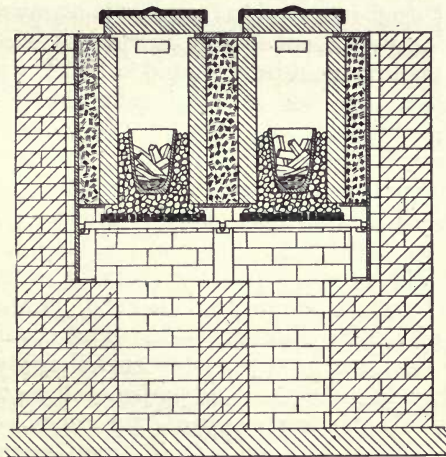


FIG. 125.—CARR'S FURNACE.

A very simple modification of the ordinary crucible furnace has recently been introduced by Messrs. Weir, of Cathcart, Glasgow, whereby a great improvement in efficiency has been obtained. The ordinary firebars are replaced by a perforated truncated cone of specially worked out dimensions. In this arrangement the crucible sits directly on the cone, and does not sink down as the fuel is consumed. The combustion of the fuel is very perfect, and there is practically no carbon-monoxide in the escaping gases.

The resulting advantages are :—

- (1) Greatly increased speed of melting ;
- (2) Consumption of coke greatly reduced ;
- (3) Labour cost considerably lowered.

A careful trial has shown that the quantity of coke per cwt. of gun-metal melted has been reduced from 107lbs. to 44lbs. Also it is found that five furnaces can now do as much as 14 could formerly do under the old conditions. The loss of metal is also found to be considerably less than before, while there is practically no danger of overheating the metal. No forced draught of any kind is required, and the cost of the alteration is very slight.

#### FUEL.

The fuel used in crucible furnaces is always coke, and for good work a good coke must be selected. In selecting a coke, three points must be attended to: (1) The percentage of fixed carbon, because on this the heating power of the coke depends. It is only the fixed carbon that is of any use, any volatile carbon simply escapes with the waste gases, or, if it burns, is burnt at the top of the furnace, where it is of no use. (2) The percentage and quality of the ash left when the coke is burned. The percentage of ash will usually vary inversely as the quantity of fixed carbon, because a good coke will consist essentially of fixed carbon and ash. The quality of the ash may, however, vary very considerably. When a furnace has been in use a little time, it becomes much enlarged by the fluxing away of the bricks. The temperature is, of course, never up to the melting point of the bricks, and the corrosion is due to the action of the

coke ash. The ash of some cokes is much more corrosive than that of others. In general, the less ash in a coke and the less basic material in the ash, the better it will be.

The efficiency of crucible furnaces is always very low. In round numbers about 100lbs. of coke will be required to melt 100lbs. of brass. The amount of heat theoretically required can be calculated. Assume, for convenience, that it is copper which is to be melted.

The melting point of copper is 1,085° C.

The specific heat of copper is, according to Frazer and Richards,  $0.0939 + 0.00001778t$ , so that the heat required to raise 1lb. of copper from 0° to its melting point, 1,085° C., will be  $1085 \times (0.0939 + 0.00001778 \times 1085) = 1085 \times (0.0939 + 0.1923) = 1085 \times 0.2862 = 310.127$ , say, 122 units. Taking the latent heat of fusion to be 45, the heat required to raise 1lb. of copper to its melting point and to melt it would be about 167 units, or for 100lbs., 16,700. As coke may be taken as having a calorific power of, say, 6,400 units, 2 6lbs. of coke would be sufficient to melt 100lbs. of copper. Taking the amount of fuel given above, the efficiency of the furnace will be 2.6 per cent.

It is easy to see the sources of the loss : (1) The coke is not completely burnt to carbon-dioxide, but a considerable portion escapes as carbon-monoxide ; (2) the products of combustion must leave the furnace at a high temperature in order to produce a draught. These sources of loss cannot be avoided, but owing to faulty furnace construction, the actual loss is often much higher than it need be.

Mr. J. F. Buchanan gives the following table of fuel consumption in certain cases in making bronze :—

No.	Metal Melted. Lbs.	Method.	Kind of Fuel.	FUEL.		
				Quantity Used. Lbs.	Losses in Melting. Per cent. of Fuel.	Melting Ratio per lb.
1.....	400.....	Crucibles	N.O.....Charcoal	318.....	89.....	1.25
2.....	400.....	„	„.....Prepared Coke...	300.....	1.22.....	1.33
3.....	400.....	„	F.D.....Coke	348.....	2.18.....	1.12
4.....	400.....	„	N.D.....Coke	325.....	1.04.....	1.20
5.....	1750.....	Cupola	.....Coke	2184.....	7.93.....	7.91
6.....	2240.....	Reverberatory	.....Coal.....	1768.....	3.57.....	1.26

**Tilting Furnaces.**—With all ordinary forms of crucible furnace, the lifting of the crucibles out of the hot fire into the cold air is a source of danger, and seriously diminishes the life of the pot. Not only so, but the handling of the pot weakens it, and there is always the danger that the pot may break in the tongs. The use of graphite (plumbago) crucibles reduces these dangers, as such crucibles will stand alternations of temperature and handling much better than clay crucibles. Still, they would last much better if the exposure to the cold air could be avoided.

This difficulty is overcome in the Piat oscillating furnace. This consists of a circular iron shell lined with firebrick, which is provided with a grate, and which stands over an air chamber into which the air is supplied under pressure. The crucible stands on a block within the furnace, and is provided with a spout passing through the casing, by which the metal can be poured off. When the charge is to be poured, the chimney is disconnected, the whole furnace is lifted by means of a crane, and the metal is poured into the moulds. As there is no cooling, once the furnace is hot, the melting is very quick, and the life of the crucibles is much prolonged.

Many other types of tilting furnace have been designed, but in spite of their advantages none of them have come largely into use.

One of the latest, and probably the best, of the tilting furnaces for solid fuel, is that recently introduced by the Morgan Crucible Company. It is made in several types and sizes, and with a melting capacity of from 400lbs. to 1,000lbs. It is made either in the fixed form here described, in which the metal is poured into movable moulds or into a ladle, or in a movable form in which the body of the furnace can be carried by an overhead crane to the moulds.

In the fixed type, the body is an octagonal steel casing hinged to a solid framework in such a way that the spout is the centre of rotation. In the movable type the body is carried on trunnions in the usual way. The casing is lined with refractory firebrick, so as to make a cylindrical fuel chamber, and the crucible

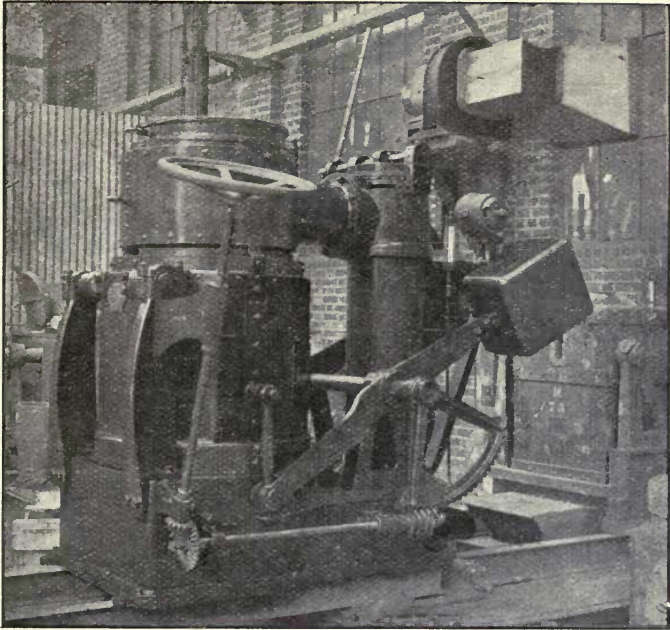


FIG. 126.—MORGAN CRUCIBLE TILTING FURNACE.

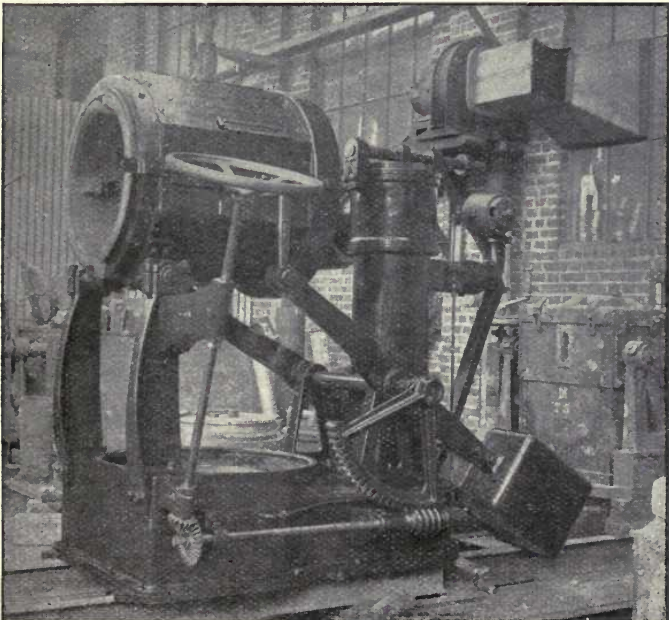


FIG. 127.—MORGAN CRUCIBLE TILTING FURNACE.

is, of course, fixed in this so that it is not removed until it is worn out. At the bottom of the casing is fixed the grate. A double casing is also provided round the lower portion of the furnace, from which air holes communicate with the interior. When at work the body rests on an iron base forming an air chamber, into which the air is blown, and thence finds its way through the bars and through the openings in the furnace wall. The furnace is covered with a movable hood, and the products of combustion are carried away by an iron pipe. This pipe is surrounded by another pipe, and the air to be supplied is passed through the annular space between the two pipes, thus becoming heated to 300° C. before entering the furnace.

The combustion is very complete, as much as 17 per cent. of carbon dioxide having been found in the products of combustion, and therefore a very high temperature can be obtained. The air should be supplied at a pressure of 1½ in. to 2 in. water gauge, and about 250 ft. of air is required per minute.

The following figures are quoted by the Morgan Company as examples of the work that can be done.

Two days' work, starting cold, and working on gun metal, five heats being worked each day :—

	First Day.	Second Day.
Total pounds of metal melted . . . . .	2191	2102
„ „ coke used . . . . .	400	386½
Time under blast . . . . .	6 hrs. 52min.	6hr. 21min.
Average pounds of metal per pound of coke (including first heat) . . . . .	5.48	5.44
Pounds of metal melted per hour . . . . .	320	330

One day's work on cast iron starting cold, four heats being worked :—

Total pounds metal melted . . . . .	1360
„ „ coke used . . . . .	383
Time under blast (including first heat)	6 hrs. 10 mins.
Average pounds of metal per pound of coke . . . . .	3.55
Pounds of metal melted per hour . . . . .	220



## GAS AND LIQUID FUEL FOR CRUCIBLE FURNACES.

There are many objections to the use of solid fuel where a high temperature is required: (1) The frequent addition of cold fuel is necessary, so that it is impossible to maintain a uniform temperature over any long period; (2) the presence of ash in the fuel constantly tends to corrode the furnace and the crucibles; (3) the loss of fuel through the fire-bars by poking may be considerable.

To overcome these objections, the use of gas and oil fuel has frequently been suggested.

**Gas-fired Furnaces.**—Gas furnaces have never come largely into use. As usually used, gas made in gas producers is not economical for work on the small scale required for melting

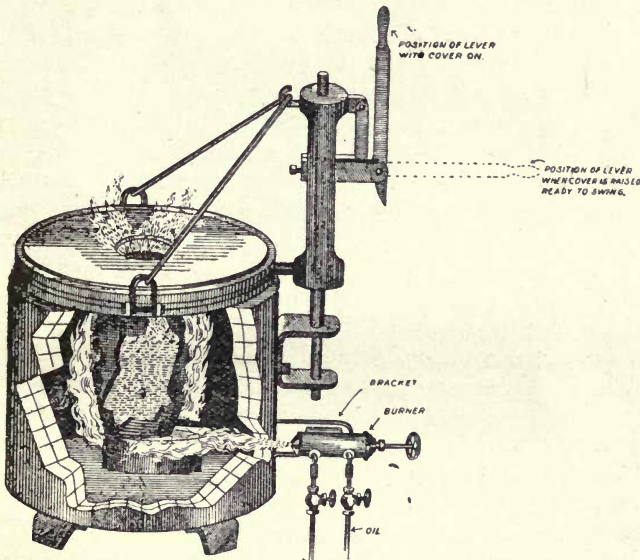


FIG. 128.—MONARCH NON-TILTING CRUCIBLE FURNACE FOR USE WITH OIL OR GAS.

alloys in crucibles, and though it has been tried in Sheffield for melting crucible cast steel, which is done on a much larger scale, even there it has never become general.

Gas furnaces may be of the usual crucible type, the gas and air being supplied into the melting chamber, or they may be of much larger size,

capable of holding many crucibles, in which case they are practically gas reverberatory furnaces of the ordinary type, with holes in the roof, by which the crucibles can be let down on to the hearth. But little attention seems as yet to have been given to the use of gaseous fuel for foundry work; probably when more attention is given to it, it may be found to be not only practicable but economical to use gaseous fuel in large foundries. Of course, it is only producer gas of some form that can be used economically. Coal gas, whilst an excellent fuel, is far too expensive.

**Oil Furnaces.**—The use of oil as a fuel has many advantages. It is cleaner than solid fuel, does not yield any ash to corrode the furnace and crucibles, and it has the advantage over gas that it does not need a plant to be continually going for its production. The oils used are always heavy oils, which are comparatively cheap, and they are blown into the furnace in the form of spray by means of a blast of air, so that air under pressure is necessary. Oil has been little used for crucible furnaces, but the recently introduced Steele-Harvey furnace seems to promise success, and in the few works in this country where it has been introduced it has been successful. It consists of a circular steel shell, lined with two layers of firebrick; the size of the inner cavity is such as to leave a combustion space round the crucible.

The furnaces are of two types. In the fixed type, the crucible is supported on a block of refractory material, and the furnace is worked exactly in the ordinary way. In the tilting furnace the crucible rests on a block of refractory material, and is so supported by side blocks that it does not move when the furnace is tilted. The casing is carried on trunnions, so that it can be tilted to pour out the metal, or it may be arranged so that it can be lifted away bodily by means of a crane and carried to the moulds exactly as a large crucible might be carried. As the crucibles are not handled, they can be made of much larger size than when they have to be used in ordinary furnaces. As in the case of other tilting furnaces, neither the furnace nor the crucible need cool much between the heats, and therefore the melting may be rapid.

These furnaces are made up to a capacity of 750lbs. per heat. The lining is said to stand about 500 heats, and the crucible may stand 30 heats or more. As the air is supplied under pressure no chimney draught is needed.

The air is required at a pressure of about 40lbs. In a paper read before the Pittsburgh Foundrymen's Association in 1905, Mr. T. W. Krause gave some details as to

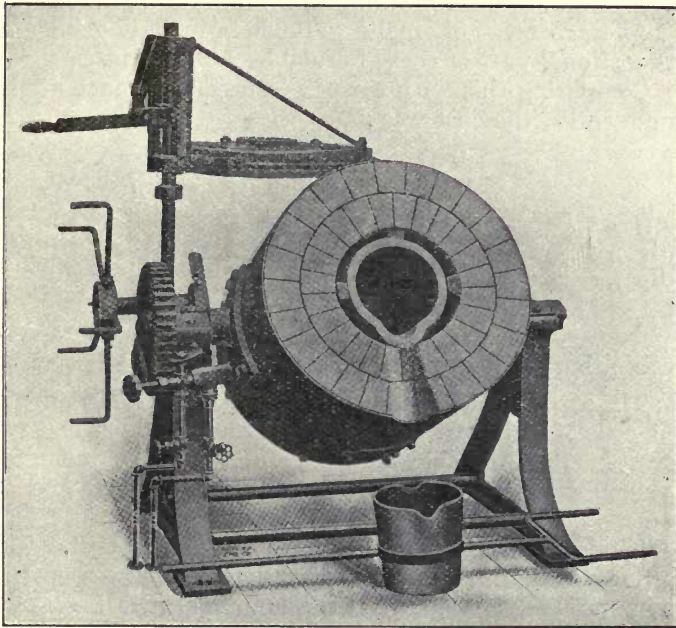


FIG. 129.—STEELE-HARVEY FURNACE IN POURING POSITION.

experiments with this furnace at the works of the Maryland Steel Company.

Taking one day's work as an example, he gives :—

Charge.	Time of Melting.	Oil Consumed,
1st, 750lbs. ...	2 hrs. 30 min. ...	...
2nd, 738lbs. ...	2 hrs. 30 min. ...	32 gals.
<hr/>	<hr/>	
1,448lbs.	5 hrs. 20 min.	

The loss in melting was 1·06 per cent.

On a four days' test the figures were:—

	Metal—Pounds.	Oil—Gallons.	Cost.	Loss.
1st day	1,488	32	\$0.80	1.06
2nd „	2,252	56	1.40	1.19
3rd „	2,579½	65	1.62	1.96
4th „	2,534	62	1.55	1.03
	8,853½	215	\$5.37	1.06 average %

Average cost of melting 100lbs., including oil and proportional part of cost of crucible, 1 34 cents.

Comparing this with a work in a coke furnace at the same works, the cost was:—

	Pounds of Metal.	Cost of Coke.	Loss.
1st day	1,465½	1.98	2.7
2nd „	975	1.24	2.8
3rd „	1,547	1.89	2.8
4th „	534	1.29	2.0
	4,521½	\$6.40	2.80 average %

Melting 100lbs. of metal cost 33.3 cents.

The life of the crucibles was on an average 24 heats; in one case Mr. Krause states that a crucible which had run seven heats in the coke furnace, and which was put aside as done with, was put into the oil furnace and lasted 22 heats.

The great question, of course, is that of cost. The furnace for the oil is more costly and air under pressure has to be supplied, but against this has to be set the larger output and greater cleanliness and convenience, and the longer life of the crucibles, always a large item of expense. The principal point which will determine the economy will be the cost of fuel.

The oil will have a specific gravity of about .87, so that a gallon will weigh about 7.27lbs. It will have a calorific power of about 20,000 B.Th.U., so that the heat evolved by the combustion of 1 gal. will be about 145,400 units. A good coke will have a calorific power of about 13,000 B.Th.U., so that 1 gal. of oil will be equivalent in actual heating power to about 11lbs. of coke. It will be seen, therefore, that the oil must be very cheap to compete with coke. It must be remembered that the oil can be

much more economically burned than the coke, and the incidental expenses are all in favour of the oil. It is generally said that in this country oil can compete with solid fuel when it can be obtained for about 1d. a gallon. Of course many other points besides the actual cost of the oil have to be taken into account.

#### REVERBERATORY FURNACES.

The reverberatory furnace is usually used when large quantities of metal have to be cast, as it avoids the use of a large number of crucibles. Such furnaces have advantages

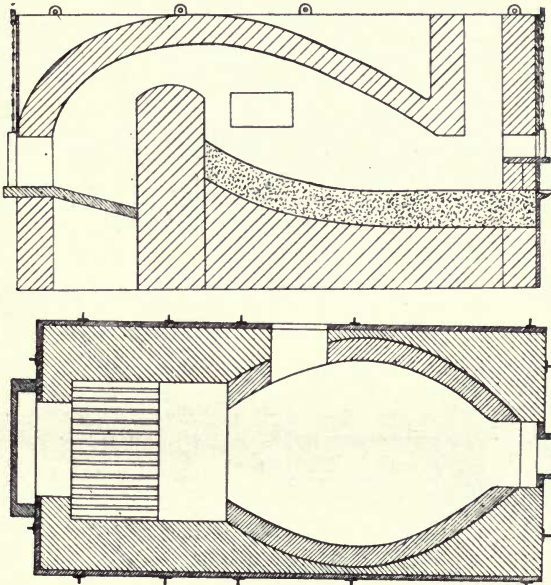


FIG. 130.—REVERBERATORY FURNACE FOR THE PREPARATION OF ALLOYS.

and disadvantages. They are not economical in fuel, but coal can be used which is much cheaper than good coke. There is usually a much greater loss by oxidation, and in general the reverberatory furnace is not suited for melting easily oxidisable metals. As the metal is in contact with the products of combustion, and these will usually contain sulphur from the fuel, sulphur may be taken up by the metal. The metal may be kept melted any required time (in the case of brass it will be constantly losing zinc),

and it should be kept covered with a layer of charcoal to prevent oxidation, or sand may be added, so as to form with the oxides produced a layer of fusible slag, which is

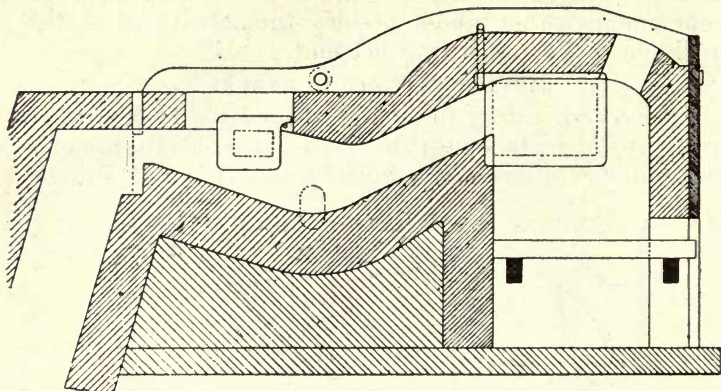


FIG. 131.—SMALL REVERBERATORY FURNACE FOR PREPARATION OF ALLOYS, TO MELT  $1\frac{1}{2}$  CWTs. SCALE ABOUT  $\frac{1}{17}$ . (LONGITUDINAL SECTION).

a much better protection against oxidation. The reverberatory furnace is very convenient for melting down scrap and casting it into ingots, so as to obtain ingots of definite and fairly uniform composition.

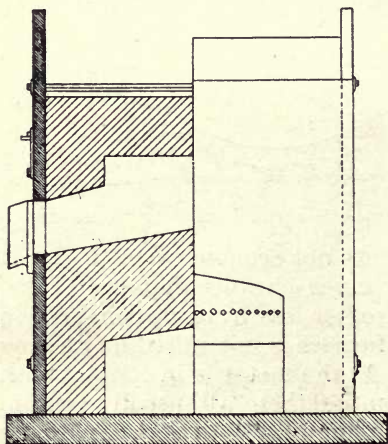


FIG. 132.—SMALL REVERBERATORY FURNACE (HALF CROSS-SECTION AND HALF ELEVATION.)

**Solid Fuel Furnaces.**—The furnaces used in the brass foundry are usually fed with solid fuel, and are simply ordinary reverberatory furnaces. The bed must slope towards a tap hole, so that the metal may accumulate ready for tapping; the hearth may slope downwards from the fire bridge to the flue, or it may dip in the centre and rise again. The bed is usually of sand well

rammed, laid over a layer of firebrick set on edge, or sand or firebrick alone may be used. As a high temperature is required, the area of the fireplace must be large, usually about one-fourth or one-fifth of the area of the hearth.

The furnace should be cased with iron, and held by vertical stays tied by cross ties, which can be loosened as the furnace is heated, and tightened up when it cools, so as to allow for the expansion and contraction of the roof. The charging door is usually near the fire bridge, and the tap hole may be either at the side or at the end. This is stopped with clay when the charge is melting, and is opened by means of an iron rod for tapping. Whilst as a rule the air furnaces are of large size, in some works small furnaces are used quite successfully. The amount of coal consumed will vary with the size of the furnace. As a rule, the larger the furnace the more economical it will be. About 50lbs. of coal will be required to melt 100lbs. of metal, but with a five-ton furnace working at its full capacity the amount may be reduced to 33lbs. The melting down is much more rapid than in a crucible furnace.

**Gas Furnaces.**—For large reverberatory furnaces gas may be satisfactorily used.

**Oil Furnaces.**—Many oil-fired reverberatory furnaces have been introduced. These consist as a rule of iron cylinders lined with refractory material, and carried on trunnions so that they can be tilted to pour out the metal, the oil being sprayed in by means of an air blast at one end. The best known of these is the Rockwell furnace, though there are many others on the market. This furnace is frequently built double, consisting then of two independent chambers, the oil being blown into them alternately. It is obvious that two different alloys could be melted at the same time and the furnace could be worked continuously in one direction if preferred. The furnace body is lined with ganister, which is rammed round a core.

The shell is made in two halves, which are hinged together. These furnaces may be made of any size,

but the usual capacity is about 500lbs. to 1,000lbs. for each furnace.

Some experiments were made by Mr. W. S. Quigley, and are described in a paper read before the Pittsburg

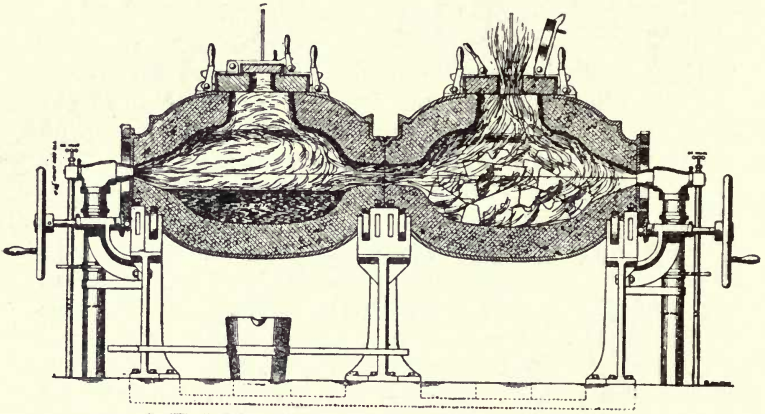


FIG. 133.—ROCKWELL OIL FURNACE.

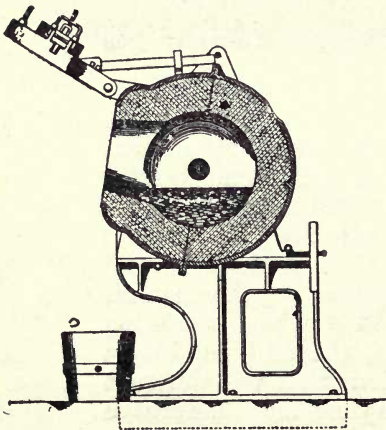


FIG. 134.—VIEW SHOWING POURING POSITION.

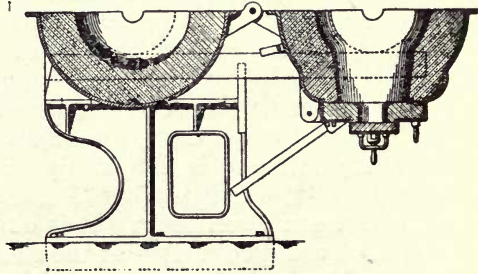


FIG. 135.—VIEW SHOWING FURNACE OPENED FOR RELINING.

ROCKWELL OIL FURNACE.

Foundrymen's Association in 1905, and the following figures were published :—



Metal charged .. .. .	7,000lbs.
Oil used in melting, including that used in heating up .. ..	93 gals.
Oil used per 100lbs. of metal melted	1·3 gals.
Time required to heat up furnace, starting cold .. .. .	27 mins.
Oil consumed in heating up ..	8 gals.
Actual time furnace was in blast, including heating up .. ..	7 hours 58 mins.
Time per 100lbs. of metal made ..	6·8 mins.
Weight of metal per minute ..	14·6lbs.
Average time per heat of 500lbs.	34 mins.

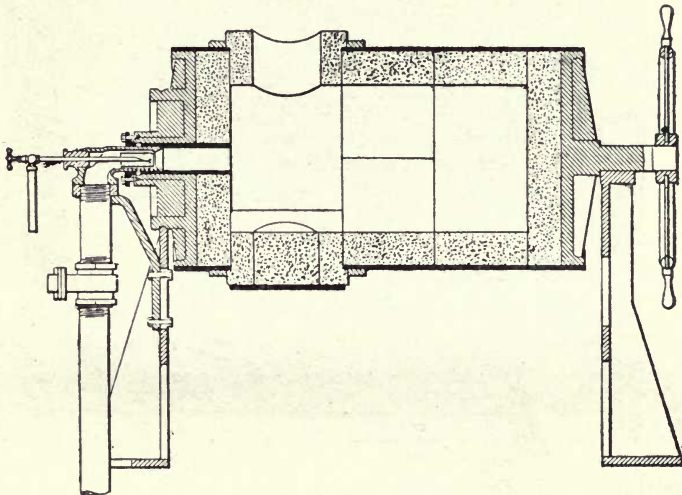


FIG. 136.—SECTION, LUNKENHEIMER FURNACE.

Another excellent furnace is the Lunkenheimer, made by the Lunkenheimer Foundry Company. The furnace consists of a steel drum lined with firebrick. There are two openings through the shell, only one of which is in use at a time, the other being closed with a brick. The cylinder is carried on trunnions so that it can be turned over to pour the metal, and the oil for combustion is supplied through one of these trunnions. When the pouring hole is badly worn it is closed by means of a tile and clay; the furnace is reversed and

the brick is removed from the other opening in the shell.

From six to seven heats per day of ten hours are said to be made in these furnaces (each heat 550lbs.), with a consumption of 2 gals. to 2½ gals. of oil per 100lbs. of metal melted. The linings are said to last 300 or 400 meltings.

**Cupolas.**—Cupolas are rarely used for melting alloys. Mr. J. F. Buchanan says, "In the cupola the fuel is in

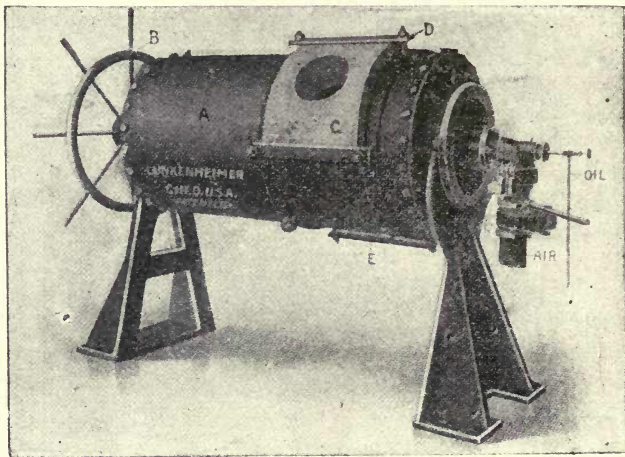


FIG. 137.—LUNKENHEIMER FURNACE.

contact with the bronze, and gases and impurities are absorbed by the molten metal from the waste products of combustion." "To obtain satisfactory results, the pressure of the blast must be lowered, and the more fusible metals—tin, lead, zinc—must be mixed in the ladle instead of passing through the cupola to form the alloy." The alloy is therefore not likely to be as homogeneous as when it is melted in crucibles.

#### OTHER METHODS FOR THE PREPARATION OF ALLOYS.

ALLOYS are always made on the large scale by the methods already described, but they can be prepared by other methods which are of interest or of practical utility.

**Preparation of Alloys by Pressure.**—As early as 1878 Prof. Spring, of Liege, succeeded in alloying metals by pressure. The metals, in a fine state of division, were mixed, and then were subjected to a pressure of some thousands of atmospheres. Under a pressure of about 2,000 atmospheres, or 13 tons on the square inch, lead is compressed into a solid block, whilst bismuth, though a very brittle metal, unites under a pressure of 6,000 atmospheres. Under similar pressures the metals can be made to unite to form alloys which have all the properties of alloys formed in the usual way by fusion. For instance, finely-divided bismuth, lead, tin, and cadmium, mixed in the proper proportions and subjected to pressure, produced a fusible alloy, the melting point of which was below  $100^{\circ}$  C. The alloys have to be broken up, and again subjected to pressure in order to ensure uniformity.

Only the metals which flow at a moderately low pressure, such as tin, lead, cadmium, bismuth, &c., have as yet been alloyed by pressure.

**Preparation of Alloys by Cementation.**—In some cases metals when heated in contact to temperatures far below their melting point will unite, the one metal slowly diffusing into the other. This process, however, is always very slow.

**Production of Alloys by Electro-deposition.**—It is well known that when an electric current is passed through a fused metallic salt, or the solution of a metallic salt in water, the salt is broken up into two portions or ions, the one, the metal, being deposited on the electro-negative plate or cathode, whilst the other, which may either be an element or group of elements, is liberated at the electro-positive plate or anode. This constituent may escape, if it is an element and the anode is not attacked by it, or if it is a complex group it may be broken up.

Thus, for instance, if a solution of copper chloride be electrolysed, copper is deposited at the cathode and chlorine is liberated at the anode. If a solution of copper sulphate is used, copper is still liberated at the cathode, but the group  $\text{SO}_4$  which is liberated at the anode cannot exist in the free condition, but at once combines with water, forming sulphuric acid and liberating oxygen.

When the anode is the same metal as that which is being deposited, it is attacked and dissolved, so that the solution retains its strength practically unchanged, and the energy given out by the dissolving anode exactly compensates for that used in depositing the metal at the cathode. Advantage is taken of these facts in the electro-deposition of the metals, which is now carried on on a very large scale, gold, silver, nickel, and copper being the principal metals deposited.

The metal may be thrown down in the form of a very thin layer for ornamental or protective purposes, as in the case of gold in electro-gilding, silver in electro-plating, nickel in electro-nickelling, or other metals; or in larger quantities when articles of small size, such as medals, medallions, plaques of silver or copper are prepared by electro-deposition.

Whether a metal will be deposited or not depends on the solvent present. If the solvent be of such a nature that the liberated metal would dissolve in it, it is obvious that the metal will not be precipitated unless the precipitation be much more rapid than the solution, and then only a small portion of the metal would be obtained.

Sir H. Davy obtained the alkali metals by decomposing fused chlorides by means of an electric current, but the metals cannot be obtained from aqueous solutions of the salts, because the liberated metal is at once dissolved in the water, and hydrogen is liberated; so similarly zinc is not deposited in an acid solution because it is dissolved by the acid, hydrogen being evolved.

In order to obtain a pure metal by electrolysis, the solution or electrolyte is kept as pure as possible, and of such a character that any impurities present are not likely to be thrown down. In the case of electro-deposition, it is usually quite easy by using a pure solution to start with and an anode of a pure metal, to have a solution in which there is no metal except that to be precipitated. Even in this case, however, the current must not be too strong, or the water present may be decomposed and hydrogen be liberated with the metal, thus tending to make the deposit unsound, and at the same time to waste energy.

In the electro-refining of copper, where an impure blister copper is used as the anode, the electrolyte is always a solution of copper sulphate acidified with sulphuric acid; in this some of the constituents of the blister copper, such as gold and silver, will not dissolve, and others, such as zinc and iron, which do dissolve, are not precipitated, so that though there are impurities present in the blister copper, the electro deposited copper is nearly pure.

When a current is passed through a solution which contains two or more metals which can be deposited under the conditions of the experiment, all the metals may be thrown down, but the proportions in which they will be deposited will depend on at least three conditions: (1) The proportions in which the metals are present in the solution, (2) the chemical character of the metals, and (3) the strength of the current. So that when it is desired to deposit two or more metals at the same time, all these conditions must be carefully considered and arranged. When two metals which alloy easily are thrown down together they tend to form alloys.

The principal alloys prepared electrolytically are brass, bronze, German silver, and gold alloys.

**Electro-deposition of Brass.**—Of all the alloys, brass is that most largely deposited. Articles of zinc, white metal, &c., are frequently coated with brass to give them the appearance of brass articles. Such articles are much more easily made, and are therefore much cheaper than those of real brass.

The electrolyte solution must, of course, contain both copper and zinc. It must be of such a character that both metals can be precipitated together, and it must contain the metals in the proportions in which they are to be deposited, otherwise its composition would vary as the deposition goes on. Obviously, the solution must not be acid, or at least not strongly so, or the deposition of the zinc would be prevented. Very many solutions have been suggested, but that which is always used in practice is a double cyanide of the metals, which may be made in various ways, and which always contains

an excess of cyanide. It is usually used cold. The solution may vary in strength by irregular deposition, and its strength is brought up to the required point by the addition of copper or zinc as the case may be.

The anode is usually of brass or as nearly as possible the composition it is intended to deposit, or in rare cases it is composed of plates of copper and zinc. The former is, however, much preferable.

The deposit depends much on the strength of the current. As a rule, copper is much more readily deposited than zinc, and this difference becomes greater the weaker the current, so that with a very weak current nearly pure copper might be deposited, whilst the stronger the current the more nearly will the rate of deposition of the zinc approach that of the copper. As the deposition goes on the colour of the deposit is carefully watched. If it becomes too red either the current is made stronger or more zinc is added to the solution. If it becomes too white, either the current is reduced or more copper is added to the solution. The limits between which the current can be varied is not very large, because it is essential to produce a close adherent deposit, which can only be done by a current which has approximately definite strength. As variations in the strength of the solution might cause change in the colour of the deposit, and if the solution were left at rest, local changes might take place which would be only slowly rectified by diffusion, the solution is kept continually stirred or circulated.

**Electro-bronzing.**—Electro-bronzing is not very frequently used, it being usually easier to deposit a layer of copper and then to colour it to imitate bronze. Bronze is usually precipitated from alkaline solutions.

**German Silver.**—German silver may be precipitated from a cyanide solution of copper and nickel, with or without the addition of zinc. It is, however, rarely used, since nickel itself is much more easily precipitated, and answers most purposes quite as well. It is recommended by Watt for certain purposes, as the colour is more pleasing than the silver white of pure nickel. This is, of course, a matter of taste.

**Coloured Gold.**—Pure gold has too pale a colour for many tastes, and the gold used in gilding is therefore often coloured by the addition of a little copper; that is, in place of pure gold, an alloy of gold and copper is thrown down. The deposit can be made of any composition so as to imitate gold of any carat required. Even gold articles are frequently electro-gilded to give the surface the desired shade.

The alloys thrown down by an electric current do not seem to differ essentially from those prepared by fusion, but they are usually highly crystalline and porous.

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This is a very valuable book.

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## THE REPORTS OF THE ALLOYS RESEARCH COMMITTEE OF THE INSTITUTION OF MECHANICAL ENGINEERS

are invaluable. Eight reports have now been issued, of which the fifth and sixth treat of Iron and Steel Alloys

These reports should be studied by all interested in the subject. The eighth report, which deals with the Alloys of Copper and Aluminium, is a model of how such work ought to be done.

Reference is made in the text to various papers to which reference may be made, but as the number of these is constantly and rapidly increasing, a list of them would be of little value.



# INDEX.

A	PAGE
Admiralty Brass .....	105
“ Ajax ” Plastic Metal .....	153
— Standard Metal .....	153
Alloys, Colour of .....	8
— Micro-structure of .....	61
— Nature of .....	1, 3, 7
— Preparation of .....	244, 279
Allotrimorphic Crystals .....	57
Aluminium .....	85, 197
— Alloys, Preparation of .....	254, 257
— Bronze .....	155, 168
— — Alternating Stress Test .....	163
— — Colour .....	155
— — Comparison with Steel .....	167
— — Containing Other Elements .....	168
— — Cooling Phenomena .....	163, 164
— — Corrosion of .....	166
— — Ductility .....	161, 162
— — Hardness .....	156
— — Heat Treatment .....	165
— — Microstructure .....	165
— — Specific Gravity .....	155, 156
— — Tensile Strength .....	157-160
— — Torsional Strength .....	163
— — Uses of .....	168
— Copper Alloys .....	198, 199
— — Zinc Alloys .....	202
— Iron Alloys .....	205, 204
— Magnesium Alloys .....	201
— Nickel Alloys .....	202
— Tin Alloys .....	181, 204
— Tungsten Alloys .....	205
— Zinc Alloys .....	205
— in Bearing Metal .....	186
— in German Silver .....	212, 213
Amalgams .....	239-243
— Preparation of .....	258
Analyses of “ Ajax ” Metals .....	153
— — Aluminium, Copper, Zinc Alloys .....	202
— — Aluminium, Tin, Silicon Alloys .....	204
— — Arsenical Bronzes .....	153, 154
— — “ Babbitt’s ” Metal .....	187
— — Bearing Metals .....	154

	PAGE
Analyses of Bell Metals .....	138
— — Brasses .....	90-93, 104-106
— — Britannia Metal .....	181
— — Bronzes .....	123, 124, 139
— — Cooper’s Gold, &c. ....	237, 238
— — Commercial Antimony .....	84
— — — Bismuth .....	85
— — — Copper .....	81
— — — Lead .....	84
— — — Nickel .....	210
— — — Tin .....	83
— — Fusible Alloys .....	206, 208
— — German Silver .....	214, 215
— — Gold Solders .....	227
— — Hensler’s Magnetic Alloy .....	171
— — Hoyle’s Alloy .....	194
— — Jacana Metal .....	194
— — Machinery Brasses .....	148
— — Plastic Metals .....	152, 153
— — Silver Solders .....	233, 234
— — Specula Metals .....	140
— — Type Metal .....	183
— — White Bearing Metals .....	188
— — White Metal Patterns .....	196
Annealing .....	68, 69
— Temperature of .....	70
Anti-friction Metals, White .....	184
Antimony .....	84
— Copper Alloys .....	170
— Lead Alloys .....	181, 190
— Silver Alloys .....	234
— Tin Alloys .....	177
Atomic Volume, Definition of .....	11

## B

Babbitt’s Metal .....	187
Banca Tin .....	81
Bearing Metal .....	148
— Bronze .....	149
Bell Metal .....	138
Benedick’s Formula for Hardness ..	157
Bismuth .....	85
— in Bearing Metal .....	186
Blowholes .....	39
— Prevention of .....	40
Brasses .....	87

	PAGE		PAGE
Brasses, Aluminium in.....	107	Bronze, Rate of Solidification ....	131
— Antimony in .....	109	— Silicon .....	145
— Arsenic in .....	110	— Specific Gravity of .....	123, 124
— Bismuth in .....	112	— Statuary .....	139
— Calamine .....	254	— Tenacity of .....	124
— Classification of .....	103-106	— Varieties of .....	137-140
— Colour of the .....	90	— Wear of Lead .....	151, 152
— Extensibility of the .....	95	— Wear of Plastic .....	153
— Foreign Constituents in.....	106	Burning .....	74
— Fracture of ..90, 102, 109, 111, 113			
— Freezing Point Curves .....	96, 103		
— Fusibility .....	95		
— Hardness .....	95		
— Impurities in .....	87		
— Iron in .....	113		
— Lead in .....	114		
— Machinery .....	147		
— Manganese in .....	117		
— Microstructure of .....	98, 99, 100		
— Naval .....	118		
— Nickel .....	118		
— Oxygen in .....	118		
— Phosphorus in.....	118		
— Preparation of.....	248		
— Properties of the.....	89		
— Range in Composition of.....	88		
— Specific Gravity of the .....	91		
— Sulphur in .....	87		
— Tenacity of .....	92		
— Tin in .....	118		
Brazing Metal .....	104, 106		
Brinell's Test for Hardness .....	156, 157		
Britannia Metal .....	180		
Bronze .....	120		
— Aluminium .....	155-168		
— Bearings .....	148, 149		
— Castings .....	147		
— Coinage .....	138		
— Colour of .....	123		
— Ductility of .....	125		
— Electric Conductivity of .....	126		
— Freezing Point Curves ..121, 122, 132			
— French (Brass) .....	106		
— Friction of Lead.....	151		
— Heat Treatment of.....	133-137		
— Lead in .....	150-153		
— Manganese .....	145, 146		
— Medal .....	138		
— Mirror .....	123, 140		
— Microstructure of .....	126-134		
— Nickel .....	152		
— Oxides in .....	140, 141		
— Phosphor .....	141, 143, 144		
— Preparation of.....	247		
— Quenching of .....	135-137		
— Range of Composition .....	120		
		<b>C</b>	
		Carr's Crucible Furnace .....	263
		Castings, Bronze .....	147
		— Under Pressure .....	41
		Cementation, Preparation of Alloys	
		by .....	279
		Changes During Cooling .....	64
		Chemical Analysis, Limits of .....	4
		Chemical Compounds, Alloys of	
		Metals Forming .....	31
		— of Copper and Zinc.....	97
		— of Copper and Tin.....	131
		— Nature of .....	2
		Coinage, Bronze .....	138
		— Gold .....	220
		— Silver .....	231
		Colour of Alloys .....	8
		— Aluminium Bronze.....	155
		— of Brass .....	90, 102
		— of Bronze .....	123
		— of Gold-silver Alloys .....	221
		— of Nickel-copper Alloys.....	210
		— of Silver-copper Alloys .....	229
		Colouring Silver .....	232
		Comparison of Aluminium Bronze	
		with Steel .....	167
		Composite Cooling Curves (see	
		Freezing Point Curves).	
		Composition, of the Brasses, Range	
		of .....	88
		— — — Bronzes .....	120
		Compression Strength of Tin-lead	
		Alloys .....	175
		— Tests on Bearing Metals ....	187, 193
		Conductivity, Electrical....	12-15, 126
		— Heat, of Bronzes .....	126
		Cooling, Effect of Slow.....	72
		— Internal Changes During .....	64
		— Phenomena of Aluminium-Bronze	
		.....	160-164
		Cooling Curves of Water .....	21
		— Water and Salt .....	24
		Cooper's Metals .....	237, 238
		Copper .....	75
		— Admiralty Test for.....	79

	PAGE
Copper Aluminium .....	155
— Amalgam .....	241
— Analysis of Commercial.....	78
— Antimony Alloys.....	170
— Chili Bar .....	80
— Commercial .....	78
— Gold Alloys .....	222
— Iron Alloys .....	170
— Lead Alloys.....	168
— Magnetic Alloys .....	171
— Manganese Alloys .....	170
— Nickel Alloys .....	210
— Platinum Alloys .....	237
— Properties of .....	75
— Silver Alloys .....	227
— Tin Alloys (see Bronze).....	120
— Zinc Alloys (see Brass) .....	87
— Zinc-aluminium Alloys .....	202
Corrosion of Aluminium Bronze....	166
— Aluminium-copperAlloys .....	200
Coulomb's Law of Friction .....	184
Crucible Furnaces .....	259-273
Crystals, Growth of .....	22, 35
— — at High Temperature .....	68
Cupellation .....	236
Cylindrical Crucible Furnace .....	262

**D**

“ Diamantine ” for Washing .....	47
Diffusion .....	71
Ductility.....	11
— of Aluminium Bronze.....	161
— of Brass .....	95
— of Bronze .....	125
Dutch Metal .....	104

**E**

Effect of Slow Cooling.....	72
— Slow Solidification .....	72
— Work .....	73
Electrical Properties of Alloys....	12
— Conductivity of Alloys .....	12
— — of Bronzes.....	126
Electro-bronzing .....	282
— Deposition of Alloys .....	279, 280
— — Brass .....	281, 282
— — Bronze .....	282
— — German Silver .....	282
Electromotive Force .....	16
— — — Curves .....	17, 18
Electrotype Copper .....	78
Electrolysis, Nature of.....	16
Electrum .....	221
Elongation (see Ductility) .....	11

	PAGE
Elongation Curves ..108, 116, 117,	118, 125, 158, 159
— (see also Extensibility)—	161, 162, 175, 198, 199
Emery for Polishing.....	47
Etching of Micro-sample.....	47
Eutectic Alloys of Copper Tin	121, 127-129
— — Copper Zinc .....	96, 97, 99
— — Gold Copper.....	223-225
— — Iron Phosphorus .....	61, 62
— — Lead Antimony.....	181
— — Lead Tin .....	173
— — Silver Copper.....	228
— — Silver Antimony .....	234
— — Tin Antimony .....	177
Eutectic, Definition of.....	26
— Stead's Classification of.....	60
— Under Microscope .....	58
Expansion by Heat .....	12
Extensibility Curves :—	
— Aluminium Brass .....	108
— Bronze .....	158-162
— Copper .....	198, 199
— Brass .....	94
— Bronze .....	125
— Lead Brass.....	116
— Manganese Brass .....	117
— Tin Brass .....	119
— Tin Lead .....	175

**F**

Fracture of Metals .....	43
Freezing Point Curves of Brass..	96, 103
— — Bronze .....	127, 132
— — Copper Gold .....	222
— — Copper Silver.....	228
— — Copper Tin.....	121, 132
— — Copper Zinc.....	96, 103
— — Lead Tin .....	31, 173
— — Salt Solution.....	25
— — Silver Gold .....	29
— — Typical .....	30, 32
French Bronze (Brass).....	106
— Gold (Brass) .....	104
Friction .....	184
Frictional Resistance .....	186
Fuel for Crucible Furnaces .....	264
— Gas for Crucible Furnaces .....	269
— Liquid for Crucible Furnaces....	270
Furnaces .....	259-278
— Carr's .....	263
— Crucible .....	259-273
— Cupola .....	259, 278
— Gas Fired.....	269

	PAGE		PAGE
Furnaces, Lunkenheimer .....	277, 278	Impurities in Commercial Brass ..	87
— Monarch Non-tilting .....	269	— — — Copper .....	78
— Morgan's Tilting .....	267	— — — Lead .....	84
— Oil Fired ..	271, 272	— — — Tin .....	83
— Piat Oscillating .....	266	— — — Zinc .....	82
— Reverberatory .....	273-277	Insolubility, Mutual, of Metals....	27
— Rockwell .....	275	Investigation, Methods of .....	4
— Steel-Harvey .....	270-272	Iron and Aluminium .....	203
— Tilting .....	266	— in German Silver.....	214
— Weir's .....	264		
Fusible Alloys .....	206-208	<b>J</b>	
Fusibility .....	12	Jacana Metal.....	194
— of Brasses.....	95	Jewellery Gold .....	224
— of Bronzes .....	121		
<b>G</b>		<b>K</b>	
Gas-Fired Crucible Furnaces.....	269	Kalchoids .....	147
— Reverberatory Furnaces .....	275		
Gases, Evolution in Metals, Result of	39	<b>L</b>	
— Solution of, in Metals.....	38	Lead .....	84
German Silver .....	212, 213	— Alloys (Minor).....	181
— — Iron in .....	214	— Antimony Alloys .....	182, 190
— — Varieties of .....	215	— Arsenic Alloys.....	183
Gold .....	217	— in Bronze.....	151, 152
— Alloys (minor).....	226	— Copper Alloys .....	168, 169
— Amalgam .....	239	— Silver Alloys .....	235
— Coinage .....	220	— Tin Alloys .....	172-177
— Colouring .....	283	— Tin, Antimony Alloys .....	182, 190
— Electro Deposition of .....	283	Light Alloys .....	197
— Fineness of .....	218	Liquation .....	37
— Silver Alloys ..	220, 221	Liquid Fuel .....	269, 270
— Solders .....	226, 227	Lunkenheimer Furnace .....	277, 278
Gun Metal .....	137, 138		
<b>H</b>		<b>M</b>	
Hardness of Aluminium Bronze....	156	Machinery, Brasses .....	147
— of Brasses.....	95	— Bronzes .....	147
— Brinell's Test for.....	156	— — Lead in .....	151
Heat Conductivity of Bronze.....	126	Magnesium-aluminium Alloys 201,	202
Heat, Expansion of Alloys by .....	12	Magnetic Alloys.....	171
— Treatment of Alloys .....	64	Magnolia Metal .....	191
— — of Aluminium Bronze..	165, 166	Manganese Bronze .....	145, 146
— — Brass .....	65-69	— Copper Alloys .....	170, 171
— — Bronze .....	133-137	Mechanical Mixtures.....	2
Hensler's Magnetic Alloy.....	171	Medal Bronze .....	138
Homogeneity, Conditions of .....	33	Melting Points of Copper-aluminium	
<b>I</b>		Alloys .....	164
Illumination .....	51	— Lead-tin Alloys .....	174
— Kinds of .....	52	— Tin-aluminium Alloys .....	205
Illuminators, Vertical .....	50	Mercury .....	239
Impurities in Commercial Antimony	84	Metals, Crystalline surface of .....	55
— — — Bismuth .....	85	— Evolution of Gas from Cast ....	39
		— Forming Definite Chemical Com-	
		pounds .....	31
		— Impurities in .....	78, 82-87

	PAGE
Metals Insoluble in One Another ..	28
— Partly Soluble in One Another ..	27
— Soluble in One Another .....	30
— Solution of Gases in .....	38
— Treatment for Sound Castings.40,	41
— Used for Alloys ...75-85, 209,	236
Microscope, Aid to Investigation ..	4
— Chemical Compounds Under....	57
— Examination .....	51
— Eutectics Under the .....	60
— Metallurgical .....	49
— Preparation of Samples for ....	45
— Principle of Methods used for ..	44
— Pure Metals Under .....	56
Microstructure of Alloys .....	61-63
— Aluminium Bronze .....	165
— Aluminium-copper Alloys .....	201
— Brasses .....	98-100
— Bronzes .....	126-133
— Copper-nickel Alloys .....	210
— German Silver .....	215, 216
— Lead, Tin, Antimony Alloys .192,	193
— Silver-antimony Alloys .....	235
— Tin-antimony Alloys .....	178
— Tin-lead Alloys .....	174
— White Bearing Metals.....	189
Mirror Metal .....	123, 140
— — Cooper's .....	237
Molecular Mobility .....	65, 71
Muntz Metal .....	105
Mystic Metal .....	191
<b>N</b>	
Naval Brass (for Condenser Tubes)..	118
Nickel .....	209
— Alloys: Preparation of .....	258
— Aluminium Alloys .....	202
— in Bronze .....	152
— Commercial .....	210
— Copper Alloys .....	210
— Silver Alloys.....	235
<b>O</b>	
Oil-fired Crucible Furnaces ....270-272	
— Reverberatory Furnaces ..	275-278
Overheating .....	68
<b>P</b>	
Pewter .....	172, 176
Phosphor Bronze.....	141, 143-144
— Copper .....	141
— Phosphor Tin .....	142
Photo-micrographs, Al. Bronze..163,	164
— Aluminium Copper .....	200
— Antifriction Alloys .....	189-195
— Bearing Bronze .....	149
— Brasses .....	65-69, 98-100

	PAGE
Photo-micrographs, Bronzes ..	127-131
— Cementite .....	60
— Copper-gold Alloys .....	224, 225
— Copper-lead Alloy .....	169
— — Nickel Alloy .....	211
— — Zinc Alloy .....	216
— — Silver Alloy .....	228, 229
— Ferrite .....	56
— German Silver .....	216
— Gold-copper Alloys .....	224, 225
— Graphite and Ferrite .....	61
— Iron Phosphide .....	61, 62
— Jacana Metal .....	194
— Lead-antimony Alloy.....	182
— — Arsenic Alloy .....	183
— Magnolia Metal .....	191
— Manganese Bronze .....	146
— Pearlite .....	59
— Phosphor Copper .....	141
— — Tin.....	142
— Silicon Ferrite .....	57
— Silver-antimony Alloy .....	235
— — Copper Alloy .....	228, 229
— — Lead Alloy .....	59
— Standard Gold Alloy .....	224
— Tin-antimony Alloys .....	178-180
Physical Properties of Alloys .....	5-12
Plastic Bronze .....	152, 153
Plasticity of Bearing Metal .....	185
Platinum .....	236
— Alloys (Minor) .....	239
— — Preparation of .....	258
— Copper Alloys .....	237
— Iridium Alloys .....	238
— Rhodium Alloys .....	238
— Silver Alloys .....	238
Polishing Agents .....	47
— Machines .....	43, 45, 46
Potential Difference .....	76
Preparation of Alloys .....	244
— — — by Cementation .....	279
— — — by Electro-deposition, 279,	280
— — — by Pressure .....	279
— — — of Low Melting Point....	246
— — Aluminium Alloys ....	254-257
— — Amalgams .....	258
— — Brass .....	248, 254, 281, 282
— — Bronze .....	247, 282
— — Calamine Brass .....	254
— — Coloured Golds .....	283
— — German Silver .....	282
— — Micro-sample .....	45
— — Nickel Alloys .....	258
— — Platinum Alloys .....	258
Pressure, Casting under .....	41
— Preparation of Alloys by.....	279

	PAGE		PAGE
<b>Q</b>			
Quenching of Bronzes .....	134-137	Standard English Brass .....	104
<b>R</b>			
Reduction Area Curves. Al. Bronze	162	— Gold .....	224
— — — Bronze .....	134-136	— Silver .....	230
Regulus of Venus .....	170	Statuary Bronze .....	139
Research, Methods of .....	5	Stead's Polishing Machine .....	46
Reverberatory Furnaces .....	273, 274	Structure of Pure Metals .....	54
Rockwell Furnace .....	275-277	<b>T</b>	
<b>S</b>			
Scorification .....	235	Tenacity .....	11
Segregation .....	36	— of Aluminium Bronze .....	159-162
— of Bronze .....	137	— — Brass .....	92
— Prevention of .....	37	— — Bronze .....	124
Silicon Bronze .....	145	Tensile Strength: Curves of—	
— in Aluminium Bronze .....	168	— Aluminium Brass .....	107, 108
Silver Alloys .....	227	— — Bronze .....	107, 158
— Amalgam .....	243	— — Copper .....	198, 199
— Coinage Alloys .....	231	— Brass .....	94
— Colouring .....	232	— Bronze .....	125
— Copper Alloys .....	227, 228	— Lead Brass .....	116
— Lead Alloys .....	235	— Manganese Brass .....	117
— Nickel Alloys .....	235	— Tin Brass .....	119
— Platinum Alloys .....	238	— — Lead .....	175
— Solders Alloys .....	233	Ternary Alloys ..	148, 191-196, 208, 212
— Standard Alloys .....	230	Tin .....	83
— Tin Alloys .....	234	— Aluminium Alloys .....	181, 204
Sodium Amalgam .....	243	— — Silicon Alloys .....	204
Solder .....	176-7	— Amalgam .....	242
— Brazing .....	105, 106	— Antimony Alloy .....	177
— Gold .....	226, 227	— Lead Alloys .....	172
— Nickel .....	216	— Silver Alloys .....	234
— Silver .....	233	Tombac .....	104
Solid Diffusion .....	71	Tungsten Aluminium Alloys ..	205, 206
Solid Fuel for Furnaces .....	259-261, 274	Type Metal .....	183
Solidification, Conditions of .....	33-35	<b>U</b>	
— Effect of Slow .....	72	Uses of Aluminium Bronze .....	168
— of Metallic Alloys .....	27	<b>W</b>	
— Mode of .....	35	Wear in Bearing Metals .....	151
— Phenomena of .....	5, 20, 33	Weir's Crucible Furnace Modification	265
— of Salt Solutions .....	23	White Alloys .....	172
— — Solutions .....	22	— Antifriction Alloys .....	184
— — Pure Substances .....	21	— Metal Patterns .....	196
Solubility, Mutual, of Metals .....	28-33	Wolframium .....	206
Solutions, Character of .....	3	<b>Y</b>	
— Essentials of .....	20	Yield Point Curves: Al. Bronze..	158-162
— of Gases in Metals .....	38	— — — Aluminium Copper..	198, 199
— Solid .....	3	<b>Z</b>	
— — under the Microscope .....	58	Zinc .....	81
Specific Gravity .....	9	— Aluminium Alloys .....	205
— of Aluminium Bronze .....	155, 156	— Cadmium, Antimony Alloys	194, 195
— Brass .....	91	— Copper, Aluminium Alloys .....	202
— Bronze .....	123, 124	— Impurities in .....	82
— Tin-lead Alloys .....	172	— Tin Alloys .....	181
Speculum Metal .....	123, 146	Ziskon .....	205

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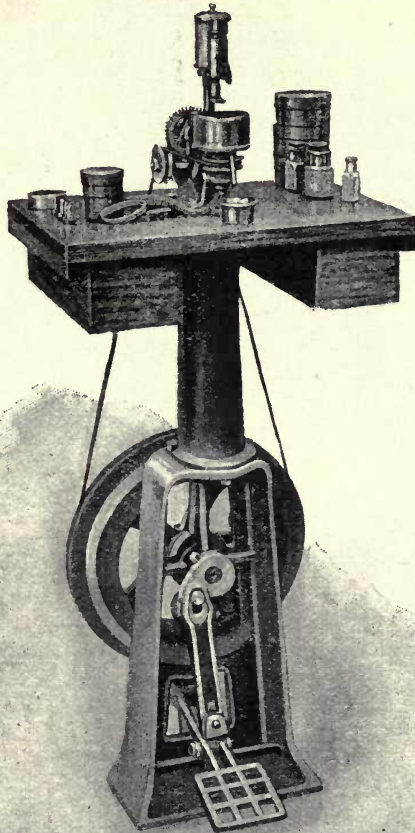


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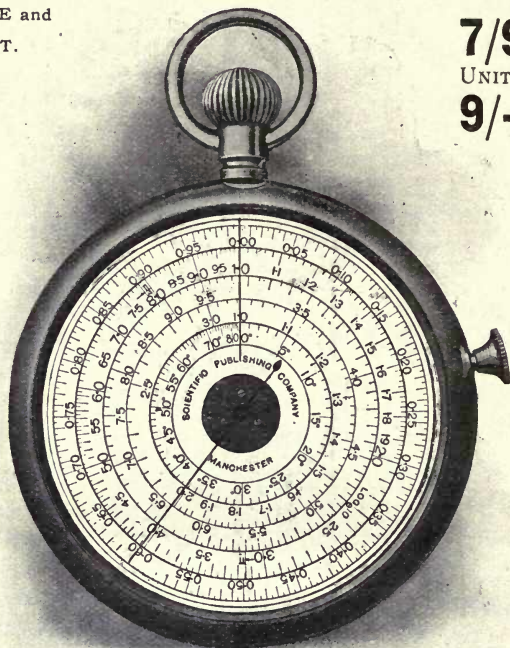
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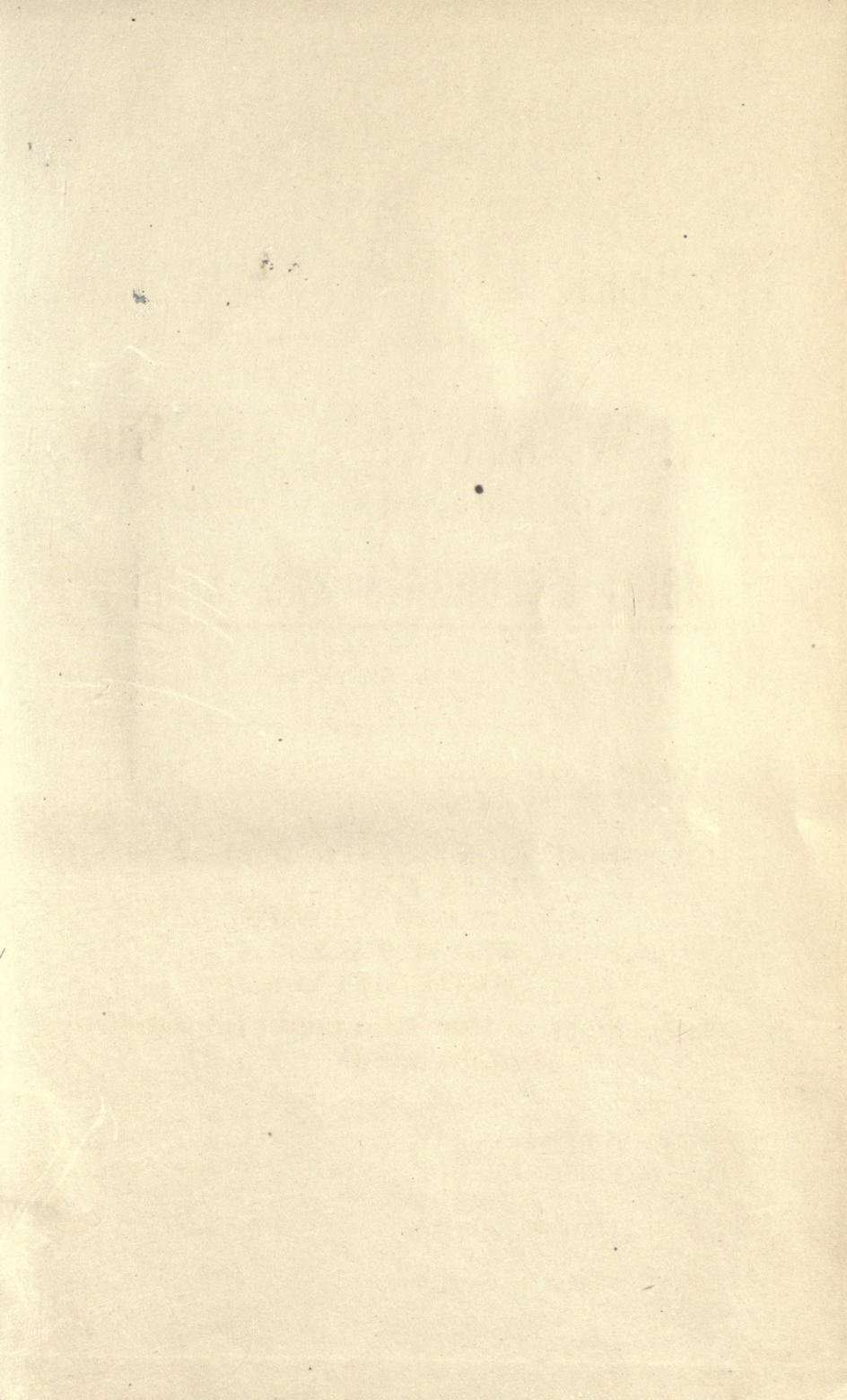
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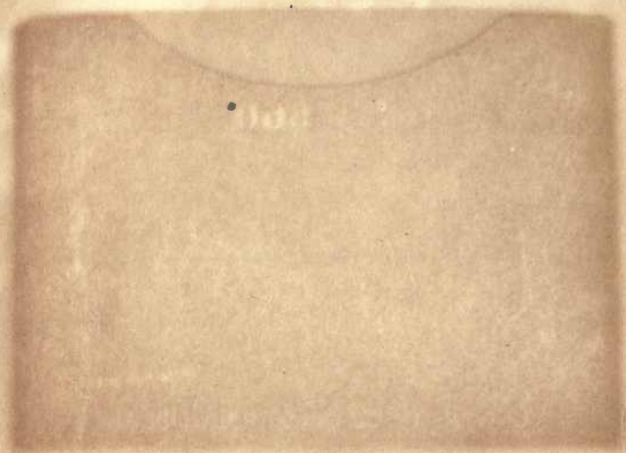
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