

acid, one litre being used for every 10 grammes of powder, in order to dissolve out any salts of lime or other soluble compounds present. The mixture is then stirred occasionally for several hours and is allowed to settle, which it will do rapidly. It is then washed several times with water by decantation until it no longer settles rapidly, but remains in suspension for a considerable time. The operation of levigation now takes place, and this is facilitated by the addition of 2 c.c. of ammonium hydrate to each litre of water; this assists the finest particles to remain in suspension. Decantation is now resorted to at intervals of 15 minutes, 1 hour, 4 hours, 24 hours, and 8 days. The first deposit contains all the coarse particles unsuitable for polishing, the other four constituting an excellent series of polishing powders. Instead of waiting eight days for the last and finest deposit to settle, it may be thrown down quickly by neutralising the ammonia present with acetic acid, when the whole of the particles will be deposited in a few hours. The powders thus prepared are generally used on broadcloth mounted on revolving discs, and, for convenience in use, are often made into a paste kept in collapsible tubes, similar to those commonly used for oil paints. In order to prepare these pastes, the powders, obtained as above, are mixed with thin shavings of Castile soap, melted on a water bath, stirred thoroughly, and when the mass begins to thicken it is poured into the collapsible tubes. Other substances suitable for the preparation of polishing powders are chromic oxide, prepared by the ignition of ammonium bichromate, and ferric oxide, prepared by the ignition of oxalate of iron or by suitably washing the best jewellers' rouge. Other materials found useful in the preparation of various alloys are washed emery, tin oxide, diamantine powder, and globe polish, the latter being very suitable for brasses, bronzes, etc. The nature of the mount used for polishing has a considerable effect on the polished surface; for obtaining a perfectly smooth surface, a hard support such as glass is necessary, whereas, should relief polishing be desired, in which case the softer constituents are worn away, a soft support is necessary, such as a piece of rubber. For relief polishing, however, a rouge wheel is generally used, washed rouge being applied in the wet state on a revolving cloth-covered disc.

The amount of care and time devoted to the polishing operation will depend on the nature of the material, amount of etching possible, magnification required, etc. When unetched or heat-tinted specimens have to be photographed, very great care is necessary in order to eliminate all scratches.

In most cases, after the specimen has been suitably polished, the structure is developed, generally by one of the following methods:—

1. Simple attack by some solvent, such as nitric acid, sulphuric acid, hydrochloric acid, iodine solution, potassium cyanide,

ammonia, sodium hydrate, etc. Such a method may dissolve one component quicker than another; it may simply eat away the joints between adjacent grains or crystals, or it may colour one constituent differently to another and thus show up the structure.

2. Weyl's method consists of submitting the specimen to the action of a solvent under the influence of a feeble electric current. Charpy uses as poles the alloy under examination, and either platinum or an alloy very similar in composition to the specimen.

3. *Heat-tinting*.—In some cases the different constituents of an alloy may be differently tinted or coloured by gently heating the polished surface in air, the more oxidisable constituents being coloured by oxide tints. This method has been largely used by Stead, who has devised a special form of apparatus for heat-tinting under the microscope by means of an electric current. Some alloys, however, contain fusible constituents which melt before oxidation takes place properly; these may generally be tinted by slight heating in an atmosphere containing small quantities of bromine, iodine, or sulphuretted hydrogen.

4. Relief polishing, in which case the specimens are polished on a soft ground, such as cloth or leather, which causes the softer constituents to be worn away rapidly, leaving the harder constituents in relief.

5. *Polish Attack*.—This consists of finishing the polishing on a piece of wet parchment supported on a strip of wood and moistened with a 2 per cent. solution of ammonium nitrate, with which freshly precipitated calcium sulphate is used to assist the polishing.

*Mounting the Specimens*.—The specimens thus prepared for examination may be mounted on glass slips, or a mechanical or magnetic holder may be used. For temporary mounting, plasticine is best, a suitably sized true ring being used to mount the specimen absolutely flat. Hard canada balsam and lathe wax are also often used.

#### The Microscope and its Accessories.

Although quite possible to obtain very creditable photo-micrographs with simple apparatus, such as a microscope fitted with an adjustable camera placed on a perfectly steady support and illuminated by an incandescent gas-light or an acetylene lamp, yet for systematic research work or for the production of high-power photographs a well-appointed optical bench, fitted with a good heavy microscope stand, and a separately mounted horizontal camera, such as the Zeiss apparatus shown in fig. 104, is greatly to be preferred. Such an equipment should have at one end an arc lamp, A (20 or 30 ampères), fitted with an automatic feed arrangement to minimise the amount of adjustment required to keep the light central; after this should be placed a double

meniscus lens, B, to obtain parallel rays of light, followed by a cooling chamber, C, to absorb the heat and keep the microscope objectives and specimens cool. Next on the bench is placed a plano-convex lens, D, to produce convergent rays condensed on the specimen under examination. This condenser should be "aplanatic," that is, corrected for aberration, which is a deviation of the rays of light when refracted by a lens, by which they are prevented from uniting in one point. In position, this lens should be so adjusted as to give a well-focussed image of the

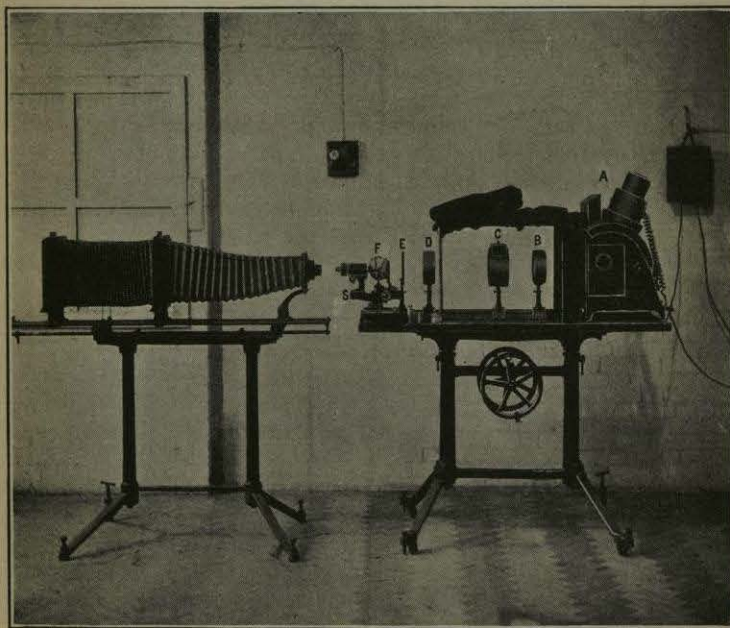


FIG. 104.—Microscopic Plant. A, lamp; B, double meniscus lens; C, cooling-chamber; D, plano-convex lens; E, iris diaphragm; F, mirror; S, stand.

crater of the arc-lamp on the window of the vertical illuminator. An iris diaphragm, E, is next placed on the bench, which should be arranged to give a very gradual variation of aperture; this is useful for exactly centring the light by closing down, and when in use must be adjusted so as to just illuminate the visual field. It is an advantage to use a green glass screen, as it renders the light monochromatic, cutting out the red rays, and increasing the contrast given by the specimen under observation.

For diverting the rays of light thus obtained on to the specimen a mirror, F, is required, and, when used in connection with the vertical illuminator, should be so placed as to give perfectly

horizontal rays, exactly at right angles to the main source of light.

There are several methods used for throwing the light on to the specimen, and the method will depend on whether "oblique" or "vertical" illumination is required, as the results obtained are quite different in the two cases: for example, if a perfectly flat surface be examined by oblique illumination, no rays will be reflected into the microscope, and such a surface will appear quite black; if, however, one constituent of the specimen be in relief, as the light falls upon one side of the projecting portion it will be reflected back into the microscope and will appear brilliantly illuminated, leaving the other side in shade.

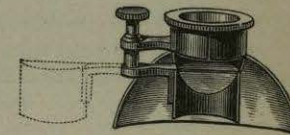


FIG. 105.—The Sorby-Beck Reflector.

For examination with low powers, the Sorby-Beck reflector is a useful type of illuminator, and by its use either oblique or vertical illumination may be obtained.

The construction of this illuminator is shown in fig. 105. It consists of a parabolic reflector, to which is attached a small

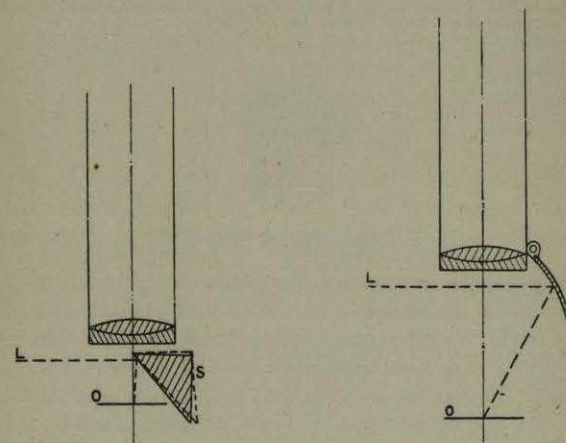


FIG. 106.

FIG. 107.

mirror with a face at an angle of  $45^\circ$ , which can be turned away from or under the object-glass by means of the milled head. When oblique illumination is required, the mirror is thrown outside into the position shown by the dotted lines, and the specimen is examined by light reflected from the silvered parabola. When direct illumination is required, however, the little mirror is turned back into the position shown in fig. 106, so that it partly eclipses the object-glass, but leaves room for the horizontal rays, L, reflected from the mirror on to the object, to be reflected

back from its surface into the microscope. In the case of oblique illumination, the horizontal rays of light, L (fig. 107), falling on to the parabola, are reflected at various angles upon the object below, and show up any of the constituents in relief. When vertical illumination is required for low-power work, it is not convenient to use the usual types of illuminator, as an insufficiently large field is illuminated, but a simple arrangement, suggested by Stead,<sup>1</sup> is more convenient for this purpose.

This arrangement is shown in fig. 108, and consists of a plain glass, G, placed at an angle of 45° between the specimen and the objective. The horizontal rays of light are partly reflected down on to the specimen, and then back from the object through the glass into the microscope. For high-power work direct illumina-

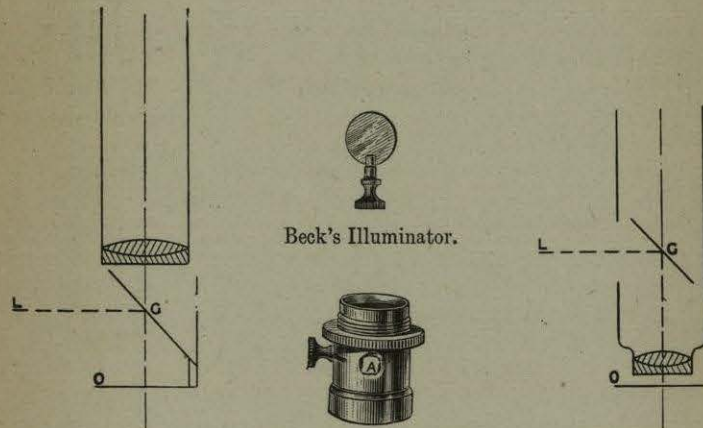


FIG. 108.

FIG. 109.—Reflector.

FIG. 110.

tion is always used, and Beck's illuminator is a useful form. It is exactly similar in principle to that just described, and consists of a metal collar or tube (fig. 109), in which is fixed on a pivot a cover-glass which acts as a reflector, and which can be rotated to any angle by the milled head shown, light being admitted to the reflector through an opening, A. The collar is screwed into the microscope tube, and the objective is then screwed on to the bottom of the collar, so that the reflector is in the tube of the microscope.

The reflector is turned to an angle of 45°, and the rays of light, L (fig. 110), admitted through the opening, A, fall upon the reflector, G, and are partly reflected down upon the object, and then up from its surface through the objective and reflector to the eyepiece.

Many workers now use a total reflecting right-angled prism

<sup>1</sup> "Practical Metallography," *Proceed. Cleveland Inst. of Engineers*, Feb. 26, 1900.

instead of the cover-glass reflector, as much better illumination of the field can thus be obtained. Figs. 111 and 112 show the form as supplied by Zeiss. In this case the rays of light, L, enter through a lateral opening in the mount of the apparatus, strike the hypotenuse surface of the reflecting prism, which covers one half of the aperture of the objective, and are thence totally reflected through the objective and concentrated upon the object, the image being produced solely through the open half of the objective. The diaphragms supplied for insertion in the vertical illuminator serve for two purposes:—

1. To prevent internal reflections of the mounts inside.

2. To cut off the very centre of the dioptric beam, known as the axial ray.

**Objectives and Eyepieces.**—Eyepieces should never be used with projection objectives or planar objectives.

The projection objectives usually used are listed as projecting aplanates, 35 mm. and 70 mm. in focal length.

For magnifications of about 50 diameters and for objects with considerable depth a 35 mm. planar objective is most useful; and if greater magnification is required, this is obtained by increasing the length of the camera. When using lenses with high focal length, the ordinary tube of the microscope is removed and a wider one inserted, to prevent the cutting out of some of the field.

For objects not possessing considerable depth long focus is not necessary, and a 16 mm. objective, together with a projecting eyepiece, either No. 2 or No. 4, is most useful.

For high magnifications, such as 1000 diameters, a 2 mm. oil immersion objective used in conjunction with a No. 4 eyepiece will be found satisfactory.

In order to calculate the magnification obtained in any case, the length of camera in millimetres is divided by the focal length of the objective, and multiplied by the magnifying power of the eyepiece.

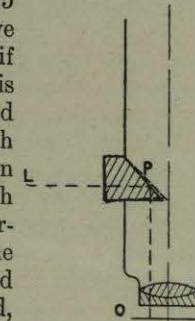
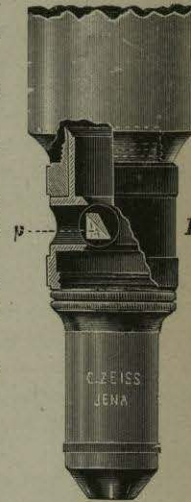


FIG. 111.



FIG. 112.

In order to calculate the visible field at any magnification, multiply the visible area of the objective by the magnification.

For oil-immersion lenses slightly thickened cedar oil is used, as this has practically the same refractive index as the glass from which the objectives are made.

### The Solution Theory of Alloys.

Our knowledge on subjects relating to alloys has advanced considerably of late years, owing for the most part to the combination of research by pyrometric and microscopic methods.

The methods of pyrometric examination have been considered in the previous chapter. The study of the molecular changes taking place during the solidification and cooling of metallic alloys has been greatly simplified by the adaptation of the solution theory, based on the similarity between the mode of solidification in alloys and in saline solutions.

Guthrie was the first to discover that the mixture of salt and water which had the lowest freezing-point contained about 23.5 per cent. of sodium chloride, and he came to the conclusion that this mixture was a hydrate of sodium chloride.

This and all similar bodies separating from saline solutions were called cryohydrates, meaning literally cold hydrates, or hydrates which could exist in the solid state at low temperatures only.

These cryohydrates have since been proved to be mechanical mixtures, and their counterpart in alloys are known as eutectics, which means literally "well-melting alloys." By taking a series of salt solutions containing successive additional amounts of salt and obtaining the points at which these solutions freeze, we shall have the necessary data for the construction of a freezing-point curve, from which valuable information can be obtained. Fig. 113 is such a curve for salt and water, and shows that each addition of salt to water, up to 23.5 per cent., depresses the freezing-point from 0° C. to -22° C., and also shows the existence of a freezing-point at -22° C. for all the mixtures, corresponding to the solidification of the cryohydrates. On further additions of salt being made the primary freezing-point rises, and in this case indicates the freezing out of salt, whereas below 23.5 per cent. of salt the primary freezing-point indicated the freezing out of pure water.

The maximum amount of salt soluble in water between 0° and 100° C. is just under 40 per cent., and fig. 113 is limited to this amount.

In freezing-point curves, the abscissæ represent composition and the ordinates represent the temperatures, and by following on the curves a substance of given composition we can ascertain the temperature at which freezing commences and at which solidifica-

tion is completed. Taking an example from the freezing-point curve of salt and water, fig. 113, suppose a solution containing 90 per cent. of water and 10 per cent. of salt be taken and placed in a cooling medium, when it reaches its freezing-point on the line ME ice will form, and there will be a retardation in the rate of cooling, denoting an evolution of latent heat; by this separation of ice the remaining solution becomes richer in salt, its freezing-point is lowered, and no further separation of

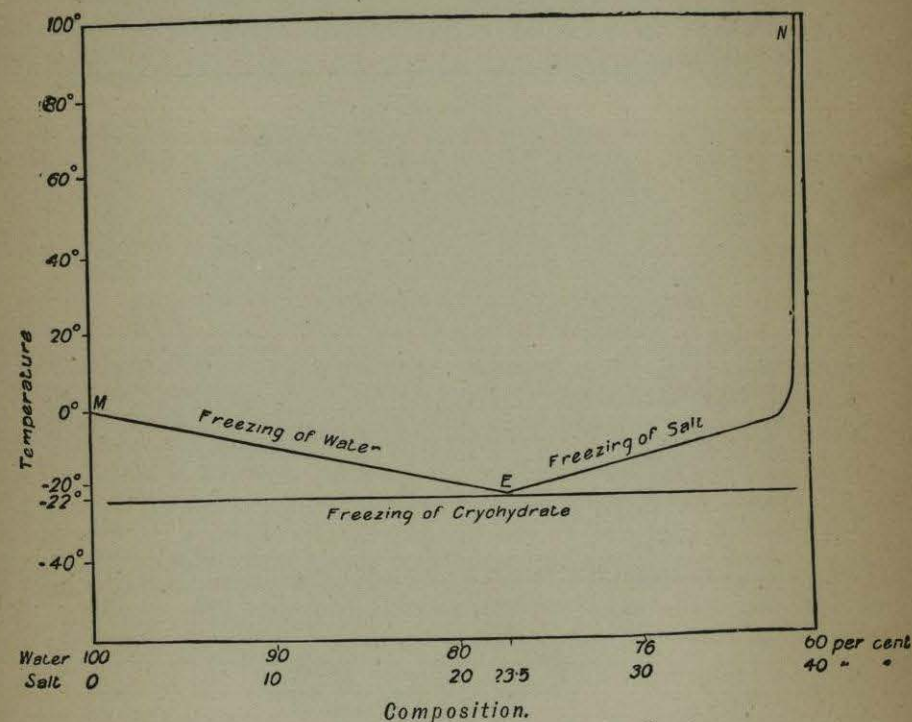


Fig. 113.—Freezing Curve of Solution of Common Salt.

ice will take place until its temperature is further lowered, when fresh formations of ice will take place along the line ME; when, however, a temperature of -22° C. is reached no further selective action will take place, and the remaining liquid portion, which will contain 23.5 per cent. of salt, will solidify as a whole.

Supposing we now take a solution containing 30 per cent. of salt: on cooling we first get a retardation at a point on the line EN, and during this retardation solid salt will separate out, because the whole bulk of solution contains more salt than the cryohydrate ratio, 23.5 per cent.; as the temperature is lowered

from the commencement of freezing, more and more salt will crystallise out, leaving the liquid poorer and poorer in salt, and therefore richer in water, until again a temperature of  $-22^{\circ}\text{C}$ . is reached, when the still liquid portion will have the composition corresponding to the cryohydrate, and will solidify as a whole, no further selective freezing taking place.

If we now pass from saline solutions to fused alloys we find the same phenomena exhibited; for example, the copper-silver series of alloys, of which fig. 114 approximately represents the freezing-point curve (not the equilibrium curve), is very similar

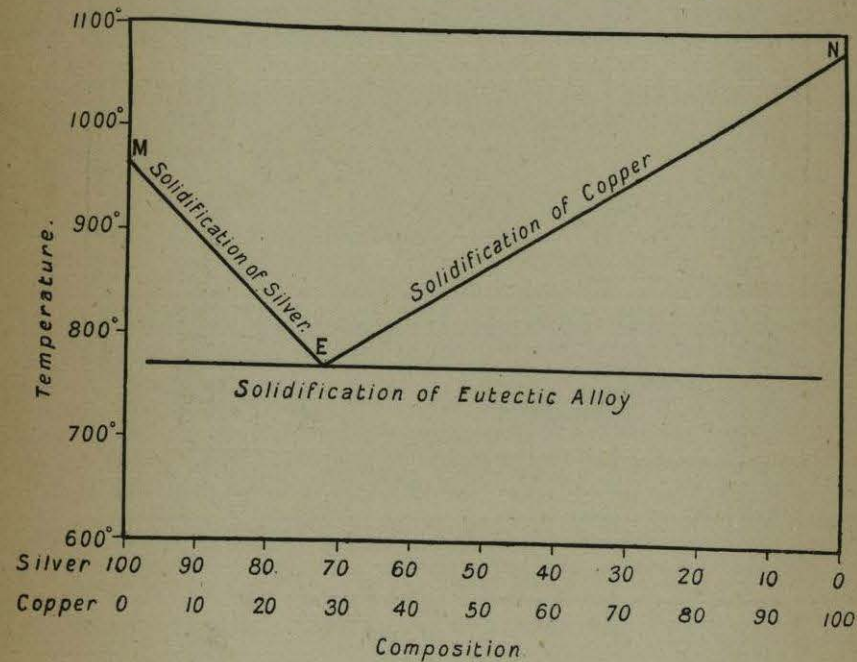


FIG. 114.—Freezing Curve of Copper-Silver Alloys.

to the salt-and-water curve given above. If we take an alloy containing 85 per cent. of silver and 15 per cent. of copper and cool down from a temperature of  $1000^{\circ}\text{C}$ . we shall again find a retardation at a temperature represented by a point on the line ME, where metallic silver, holding a certain amount of copper in solid solution, will first crystallise out; as the temperature is lowered from this point, silver will continue to crystallise out until a temperature of  $770^{\circ}$  is reached, at which temperature the portion remaining liquid will have become enriched in copper up to 28 per cent., and will solidify at this constant temperature; this is indicated at the point E on the diagram, and consists of

the eutectic alloy, which corresponds to the cryohydrate in the case of saline solutions.

The value of the combination of microscopic and pyrometric methods of examination will be evident on examination of fig. 115, which is a micro-photograph<sup>1</sup> of a silver-copper alloy of the same composition as the one taken above, that is, 85 per cent. silver and 15 per cent. copper; a polished surface of this alloy has been heated in the air, by which the copper portion has been oxidised and has been photographed at a magnification of 600 diameters. The white portions consist of metallic silver which has solidified

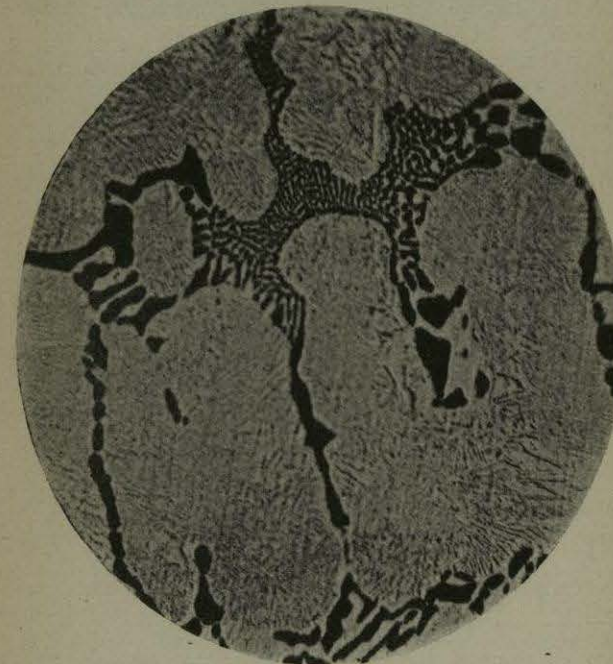


FIG. 115.

in advance of the eutectic, which can be seen in the darkened portions to consist of a conglomerate of copper and silver. If now an alloy of the eutectic composition be taken, it will be found that no retardation of temperature during cooling will take place until a temperature of  $770^{\circ}$  is reached, at which temperature the whole mass will solidify, forming a conglomerate of metallic silver and metallic copper. Fig. 116 is a micro-photograph of this alloy, prepared as above, and magnified 1000 diameters: it will be seen to be composed of alternate light and

<sup>1</sup> The three micro-photographs here reproduced are taken from Osmond and Stead's book.

dark portions, showing that it consists of alternate layers of silver and copper. If still another alloy of this series be taken and cooled from a high temperature—for example, one containing 65 per cent. of copper and 35 per cent. of silver—a retardation will be found at a point situated on the line E N, at which metallic copper will first crystallise out; and as the temperature is lowered, copper will continue to crystallise until  $770^{\circ}$  C. is reached, at which temperature the still liquid portion will have become enriched in silver up to 72 per cent.; and as this is the eutectic composition, the whole mass will now

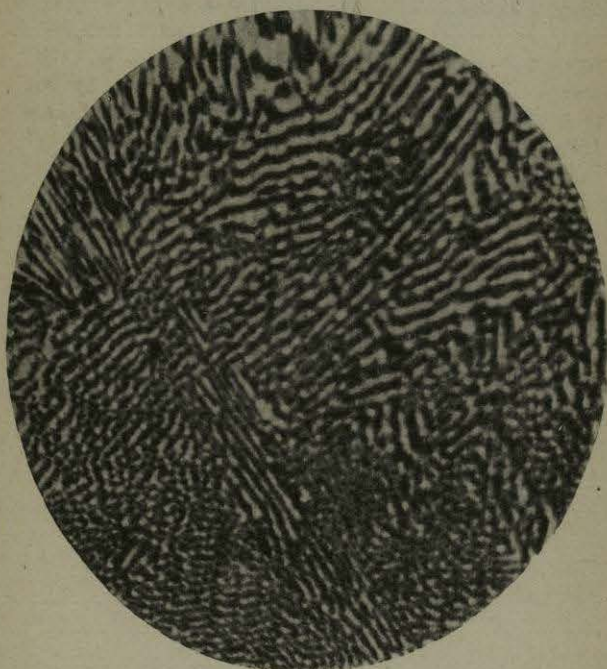


Fig. 116.

solidify into a conglomerate as before. Fig. 117 shows a photomicrograph of this alloy, magnified 600 diameters, in which the dark portions consist of the copper which has crystallised out along E N, and the lighter portions, which consist of solidified eutectic, will be seen to consist of a conglomerate of silver and copper as before.

The method of examination of alloy-series above indicated is now very largely used; but instead of merely noting the temperatures at which freezing commences and solidification is completed, every thermal change which takes place during the cooling of the alloy is noted, together with the duration of time these changes

occupy, and from the data thus obtained complete equilibrium curves are constructed. For obtaining perfect equilibrium many precautions are necessary, the most important being extremely slow cooling during the pyrometric observations.

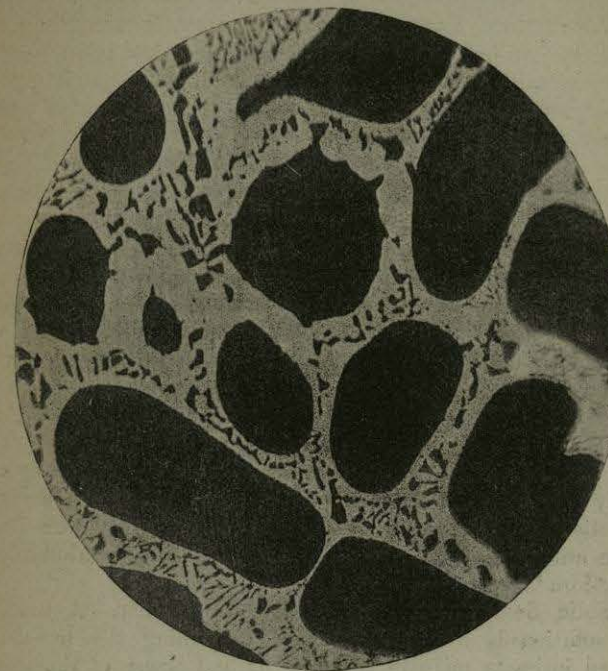


Fig. 117.

#### THE CONSTITUTION OF METALLIC ALLOYS.

As a result of the work carried out by modern methods of research, it is now recognised that the constituents of metallic alloys may consist of one or more of the following:<sup>1</sup>—

1. Free metals in the pure state.
2. Solid solutions of one metal in another.
3. Definite chemical compounds of metals with metals.
4. Definite chemical compounds of metals with non-metals.
5. Eutectic mixtures.
6. Solid solutions of chemical compounds in excess of metal.
7. Allotropic modifications.

1. **Free metals in the pure state.**—These are metals which fall out of solution or crystallise out during the cooling down of

<sup>1</sup> See Lecture by Stead, Cleveland Inst. of Engineers, Dec. 10, 1900.

a molten alloy. They are found in the solid alloys as crystallites (skeleton crystals minus their crystal faces) or as perfectly formed crystals, and when present in these forms they have generally formed in a fluid matrix; if the pure metal, however, has a lower freezing-point than that part of the alloys which first crystallises, it is found between the crystals, filling up the interstices. In order to ascertain whether a constituent consists of pure metal, it is sometimes possible to dissolve away by some suitable solvent everything except the apparently pure metal, and then make an analysis of it.

This method is not always possible, however, as sometimes it is difficult to obtain a reagent which will attack the portion not required, and at the same time remain inactive on the metal it is sought to isolate. In this case it is advisable to use a synthetical method by melting the metal with varying minute quantities of the second element in question, and cooling the product extremely slowly. If, now, the resulting metal be cut, polished, etched, and examined by the microscope, and if minute traces of the second substance be detected, it may be assumed that the second substance does not form a solid solution with the metal, and therefore that the metal crystallises out in the pure state. This latter method of examination may also be used to determine exactly what amount of one metal will remain in solid solution in another. Examples of this constituent in alloys are found in the antimony-lead,<sup>1</sup> zinc-cadmium,<sup>2</sup> gold-lead,<sup>3</sup> aluminium-magnesium<sup>4</sup> series, etc.

**2. Solid Solutions of one Metal in another.**—A metallic solid solution is a solid substance containing the metals in such an intimate mixture that the highest power of the microscope cannot detect a second constituent on properly prepared sections.

Oswald defined solutions as being homogeneous mixtures which cannot be separated by mechanical means; but it must be remembered that many mixtures, *e.g.* eutectics, cannot be separated by mechanical means, although they may, by heat-tinting, etching, etc., be shown under the microscope to be mixtures, and therefore not homogeneous. Many mixtures of metals which form liquid solutions do not remain in solution when they solidify, and these are known as solidified or congealed solutions; it is very important to distinguish between these terms.

The definition generally accepted by metallographists is the following:—

A solid solution is a homogeneous mixture of two or more

<sup>1</sup> H. Gautier, Roland-Gosselin, *Bull. Soc. d'Encour. pour l'Ind. nationale*, 1896.

<sup>2</sup> H. Gautier, *Contribution à l'étude des Alliages*, 1901, p. 93.

<sup>3</sup> Vogel, *Zeitschr. f. anorg. Chemie*, 1905, xlv. p. 11.

<sup>4</sup> Grube, *ibid.*, 1905, xlv. p. 225.

substances in the solid state. Solid solutions of metals are also called isomorphous crystals or mixed crystals.

As a general rule, solid solutions crystallise in a form identical with or very closely approximating to that constituent which predominates.

In certain cases, solid solutions may be heterogeneous, especially when solidification and cooling has taken place at such a rate that diffusion has not had sufficient opportunity to render the whole mass homogeneous. For example, in the gold-silver series of alloys there is a tendency for the central portion of the crystals to differ in composition from their outside boundaries. In this case the first crystals to form are richer in gold than the initial alloy because the alloys richer in gold have higher freezing-points and, as crystallisation proceeds, the mother metal will become richer and richer in silver, and so the successive layers of crystal tend also to become richer in silver. Now if this solid alloy be kept at a temperature only a little below its freezing-point for a long time, diffusion will be assisted, and this will tend to make the solid mass a homogeneous solid solution. Solid solutions are found throughout the series of antimony-bismuth,<sup>1</sup> gold-silver,<sup>2</sup> gold-platinum,<sup>3</sup> iron-manganese<sup>4</sup> alloys, etc., and to a limited extent in the series of alloys lead-tin,<sup>5</sup> lead-silver,<sup>6</sup> silver-tin,<sup>7</sup> silver-copper,<sup>8</sup> etc.

**3. Definite Chemical Compounds of Metals with Metals or Intermetallic Compounds.**—Many of the metals combine chemically with one another in atomic proportions. The resulting compounds were called metallo-metallic salts by Guthrie. These chemical compounds are quite homogeneous, and are recognised by having certain characteristics different from those of the metals combined. The methods of determining the presence of chemical compounds in alloy series have recently been reviewed by Dr Desch,<sup>9</sup> and consist of the following:—

(a) *Thermal Method.*—By the examination of the results of observation of freezing-points and other thermal changes which take place during the cooling of many individual alloys belonging to a series. This method has been greatly improved by Prof. Tammann<sup>10</sup> in his method of *Thermal Analysis*, in which observations are made of the time occupied by each arrest on the

<sup>1</sup> Gautier, *Bull. de la Soc. d'Enc. p. l'Ind. nationale*, 1896.

<sup>2</sup> Roberts-Austen and Rose, *Chemical News*, lxxxvii., 1903, p. 2.

<sup>3</sup> Doerinckel, *Zeit. anorg. Chem.*, 1907, liv. p. 345.

<sup>4</sup> Levin und Tammann, *Zeit. für anorg. Chemie*, xlvii. p. 136.

<sup>5</sup> Rosenhain and Tucker, *Phil. Trans.*, 1908, ccix. A. p. 89.

<sup>6</sup> Heycock and Neville, *Phil. Trans.*, 1897, clxxxix. A. p. 137.

<sup>7</sup> *Ibid.*

<sup>8</sup> Roberts-Austen and Rose, *Proc. Roy. Soc.*, lxxvii., 1900, p. 105.

<sup>9</sup> *Journ. Inst. Metals*, 1909, i. p. 227.

<sup>10</sup> *Zeit. anorg. Chem.*, 1906, xlix. 113; 1907, lv. 289, etc.

cooling curve of an alloy. Such arrests may be due to the primary separation of crystals, to the solidification of the eutectic, to a reaction between solid crystals and the portion still molten, or to a transformation in the solid state. By plotting the times thus obtained against the composition, the composition corresponding to the maximum development of heat is obtained, and by extrapolation the point at which the arrest vanishes is also found more accurately than by direct observation.

This method is particularly useful in giving evidence for the existence of compounds. In the pure state these completely freeze at a definite temperature, and when these compounds form maxima on the freezing-point curve they are comparatively simple to detect, but sometimes no maxima are shown, and the compounds are the result of reactions between solid and liquid portions; in these cases evidence is obtained by observing the position at which the reactions on either side of the supposed compound reach zero, and when this position coincides with the maximum evolution of heat due to the formation of the compound, then the composition of this compound can be obtained.

(b) *Microscopic Method.*—This is chiefly used as a control on the thermal analysis. Compounds should show a perfectly homogeneous structure, and the addition of small quantities of either of the component metals should give rise to a new constituent. In some cases, however, it is difficult to differentiate between compounds and solid solutions, especially when perfect equilibrium is attained.

(c) *Electro-motive Force Method.*—The measurement of the difference of potential between an alloy and one of its component metals is often of great value in determining the presence of compounds: it is very important, however, to obtain exact conditions of work before the results can be relied upon. Puschin<sup>1</sup> has shown that the most regular results are obtained when a solution of a salt of the less electro-positive metal is used as the electrolyte, and the difference of potential between that metal and the alloy is determined. If curves be plotted for composition and E.M.F., the form of the curve will be found to vary according to the nature of the series of alloys under examination.

In a series in which neither compounds nor solid solutions are formed, such as the gold-thallium series, the constant potential of thallium should be exhibited throughout, whereas in a series in which solid solutions are formed throughout, such as the antimony-bismuth series, a smooth curve is obtained in which the potential of the dissolved metal steadily falls with the increase of concentration of the second metal. On the other hand, when

<sup>1</sup> *J. Russ. Phys. Chem. Soc.*, 1907, xxxix. 13, 353, 528, 869.

compounds occur, the curve shows a sudden drop at the composition of the compound, as in the case of the silver-tellurium series which contains the compound  $\text{Ag}_2\text{Te}$ .

(d) *Chemical Examination of Residues.*—This method consists of attacking alloys of varying composition with reagents capable of extracting one or other of the components and analysing the residues. It is, however, liable to lead to inaccurate results; and before accepting these, the residue should remain unchanged in composition after repeated alternate treatment with two different reagents,<sup>1</sup> and should also be absolutely homogeneous.

(e) *Hardness.*—The hardness of a series of alloys may be determined by one of the methods described in Chapter II., and these figures, when plotted against composition, often give valuable results. Compounds are frequently harder than the constituent metals, but in a few cases are softer; for example, the compound  $\text{Cu}_2\text{Sb}$  is softer than antimony;<sup>2</sup> they give sharp maxima or minima on the curves. When solid solutions are formed throughout the series a smooth curve is obtained on plotting the results, this curve showing a maximum at an intermediate point between the metals, as in the case of the gold-silver series. The limit of solubility in any series is marked by a break in the curve; and when metals do not form solid solutions or compounds, that is, when they are eutectiferous throughout, the hardness is practically a linear function of the composition.

(f) *Electrical Conductivity.*—When a curve is plotted having as ordinates composition and electrical conductivity, the presence of compounds is indicated either as maxima or as minima; with series consisting of solid solutions a curve with a deep minimum is obtained, and with eutectiferous series a straight line. See Curves, etc., given in Chapter III.

Dr Desch has prepared the following tables to show the inter-metallic compounds which are well established, the pairs of metals which give no evidence of the formation of compounds, and also the doubtful cases.

<sup>1</sup> Guerther, *Metallurgie*, 1908, v. 184.

<sup>2</sup> Baikoff, *Bull. Soc. d'Encourag.*, 1903, civ. part 1, p. 626.



TABLE I.

The existence and formulæ of the following intermetallic compounds appear to be well established:—

Ag <sub>3</sub> Al, Ag <sub>2</sub> Al	Cu <sub>2</sub> Se
Ag <sub>3</sub> Hg <sub>4</sub> , and others	Cu <sub>2</sub> Te, Cu <sub>4</sub> Te <sub>3</sub>
Ag Mg <sub>2</sub> , Ag Mg <sub>3</sub>	Cu <sub>2</sub> Zn, Cu Zn, Cu <sub>3</sub> Zn <sub>3</sub>
Ag <sub>2</sub> Pt	
Ag <sub>2</sub> Sb	Fe Ni <sub>3</sub>
Ag <sub>2</sub> Se	Fe <sub>3</sub> Sb <sub>2</sub> , Fe Sb <sub>2</sub>
Ag <sub>2</sub> Sn	Fe Zn <sub>3</sub> , and another
Ag <sub>2</sub> Te	
Ag <sub>3</sub> Zn <sub>2</sub> , Ag Zn, Ag <sub>2</sub> Zn <sub>3</sub> , Ag <sub>2</sub> Zn <sub>5</sub>	Hg <sub>2</sub> K, Hg <sub>8</sub> K <sub>2</sub> , Hg <sub>3</sub> K, Hg <sub>2</sub> K
Al <sub>2</sub> Au, Al Au, Al Au <sub>2</sub> , Al <sub>3</sub> Au <sub>5</sub> , Al Au <sub>4</sub>	Hg Li <sub>3</sub>
Al <sub>3</sub> Ca	Hg <sub>4</sub> Na, Hg <sub>2</sub> Na, Hg Na <sub>3</sub> , and four others
Al <sub>5</sub> Co <sub>2</sub> , Al Co, and another	Hg <sub>2</sub> Tl
Al Cr <sub>3</sub>	
Al <sub>2</sub> Cu, Al Cu, Al Cu <sub>3</sub>	K Pb <sub>2</sub> , K Pb <sub>4</sub> , and another
Al <sub>3</sub> Fe	K Sn <sub>2</sub> , K Sn <sub>4</sub> , and two others
Al <sub>3</sub> Mg <sub>4</sub>	K <sub>2</sub> Tl, K Tl
Al <sub>3</sub> Ni, Al <sub>2</sub> Ni, Al Ni	
Al Sb	Mg <sub>2</sub> Ni, Mg Ni <sub>2</sub>
Al <sub>3</sub> Ti	Mg <sub>2</sub> Pb
As <sub>2</sub> Cd <sub>3</sub>	Mg <sub>3</sub> Sb <sub>2</sub>
As <sub>2</sub> Cu <sub>5</sub> , As Cu <sub>3</sub>	Mg <sub>3</sub> Sn
As <sub>2</sub> Fe <sub>3</sub> , As Fe <sub>2</sub> , and others	Mg <sub>3</sub> Tl <sub>3</sub> , Mg <sub>2</sub> Tl, Mg <sub>3</sub> Tl <sub>2</sub>
As Ni, As <sub>2</sub> Ni <sub>5</sub>	Mg Zn <sub>2</sub>
Au Cd <sub>3</sub> , Au Cd <sub>5</sub>	Mn <sub>3</sub> Sb, Mn <sub>3</sub> Sb <sub>2</sub>
Au <sub>2</sub> Pb, Au Pb <sub>2</sub>	Mn <sub>4</sub> Sn, Mn <sub>2</sub> Sn, Mn Sn
Au Sb <sub>2</sub>	
Au Sn, Au Sn <sub>2</sub> , Au Sn <sub>4</sub>	Na <sub>4</sub> Pb, Na <sub>2</sub> Pb, Na Pb, Na <sub>2</sub> Pb <sub>3</sub>
Au Te <sub>2</sub>	Na <sub>3</sub> Sb, Na Sb
Au Zn, Au <sub>3</sub> Zn <sub>5</sub> , Au Zn <sub>8</sub>	Na Se, Na <sub>2</sub> Se <sub>5</sub> , Na Se <sub>2</sub> , Na Se <sub>3</sub>
	Na <sub>4</sub> Sn, Na <sub>2</sub> Sn, Na <sub>4</sub> Sn <sub>3</sub> , Na Sn, Na Sn <sub>2</sub>
Bi <sub>2</sub> K, Bi <sub>2</sub> K <sub>3</sub> , Bi K <sub>3</sub> , and another	Na <sub>3</sub> Tl, Na <sub>2</sub> Tl, Na Tl
Bi <sub>2</sub> Mg <sub>3</sub>	Ni <sub>4</sub> Sb, Ni <sub>5</sub> Sb <sub>3</sub> , Ni Sb, and another
Bi Na, Bi Na <sub>3</sub>	Ni <sub>3</sub> Sn <sub>2</sub> and others
Bi <sub>3</sub> Ni, Bi Ni	Ni Zn <sub>3</sub>
Ca Cd, Ca Cd <sub>3</sub> , and another	Pb <sub>2</sub> Pd, Pb Pd, Pb Pd <sub>3</sub> , Pb Pd <sub>3</sub>
Ca Pb <sub>3</sub>	Pb Pt, and two others
Ca Sn <sub>3</sub>	Pb Te
Ca Tl <sub>3</sub> , and another	Pb Tl <sub>2</sub>
Ca <sub>2</sub> Zn <sub>3</sub> , Ca Zn <sub>4</sub> , Ca Zn, and another	Pt <sub>3</sub> Sn, Pt Sn, Pt <sub>2</sub> Sn <sub>3</sub> , and another
Cd <sub>3</sub> Cu <sub>2</sub> , Cd Cu <sub>2</sub>	
Cd Mg	
Cd <sub>5</sub> Na, Cd <sub>2</sub> Na	Sb <sub>2</sub> Se <sub>3</sub>
Cd <sub>3</sub> Sb <sub>2</sub> , Cd Sb	Sb <sub>2</sub> Te <sub>3</sub>
Cd Sn <sub>4</sub>	Sb Tl <sub>3</sub>
Co Sb, Co Sb <sub>2</sub>	Sb Zn, Sb <sub>2</sub> Zn <sub>3</sub>
Co <sub>2</sub> Sn, Co Sn	Sn Te
Co Zn <sub>4</sub>	
Cr Sb, Cr Sb <sub>2</sub>	
Cu <sub>2</sub> Mg, Cu Mg <sub>2</sub>	Also two ternary compounds—
Cu <sub>3</sub> Sb, Cu <sub>2</sub> Sb	Cd HgK
Cu <sub>4</sub> Sn, Cu <sub>3</sub> Sn, and perhaps others	Hg <sub>2</sub> KNa

TABLE II.

The following pairs of metals do not give evidence of the formation of a compound under the conditions of the investigations:—

Ag-As	Au-Bi	Cd-Tl	Fe-Pb
Ag-Au	Au-Cu	Cd-Zn	Fe-Pt
Ag-Bi	Au-Fe	Co-Cr	Fe-Tl
Ag-Co	Au-Ni	Co-Cu	Fe-V
Ag-Cr	Au-Pd	Co-Fe	Hg-Pb
Ag-Cu	Au-Pt	Co-Ni	Hg-Sn
Ag-Fe	Au-Tl	Co-Pb	Hg-Zn
Ag-Mn		Co-Tl	
Ag-Ni	Bi-Cd	Cr-Cu	Mg-Na
Ag-Pb	Bi-Co	Cr-Ni	Mn-Ni
Ag-Pd	Bi-Fe	Cr-Pb	Mn-Pb
Ag-Tl	Bi-Hg	Cr-Sn	
Al-Bi	Bi-Mn	Cu-Fe	Ni-Pb
Al-Cd	Bi-Pb	Cu-Mn	Ni-Tl
Al-Na	Bi-Sb	Cu-Ni	Pb-Sb
Al-Pb	Bi-Zn	Cu-Pb	Pb-Sn
Al-Si		Cu-Pd	Pb-Zn
Al-Sn	Ca-Fe	Cu-Pt	
Al-Tl	Cd-Fe	Cu-Tl	Sn-Tl
Al-Zn	Cd-Hg		
As-Pb	Cd-Pb	Fe-Mn	Tl-Zn

TABLE III.

The following pairs of metals enter into combination, but the formulæ of the compounds formed have not yet been satisfactorily determined:—

Ag-Cd	Bi-Ca	Cr-Fe	Hg-Sr
Al-Hg	Bi-Cu	Cr-Si	K-Na
Al-Mn	Bi-Tl	Cu-Hg	K-Zn
Al-Pt			
Al-Th	Ca-Sb	Fe-Mo	Na-Zn
Al-Ti	Cd-Co	Fe-Sn	
Al-W	Cd-K	Fe-W	Sb-Sn
	Cd-Ni		Se-Sn
	Co-Cr	Hg-Rb	Se-Tl
Ba-Hg			

#### 4. Definite Chemical Compounds of Metals with Non-metals.

—In exactly the same manner that certain metals combine with one another to form intermetallic compounds which act as constituents in certain alloys, so also compounds are formed between some metals and non-metallic elements, and a few of these are most important constituents in certain classes of alloys. Undoubtedly the most important of these compounds is the carbide of iron, Fe<sub>3</sub>C, on the amount and condition of which in carbon-steels most of the valuable properties of the steels depend. Phosphorus and silicon also form important compounds.

The following table gives a list of the most important com-