

## THE PLANIMETRIC ANALYSIS OF ALLOYS, AND THE STRUCTURE OF PHOSPHOR-COPPER.

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In the microscopic examination of metallic alloys, a smooth surface prepared by grinding and polishing is treated chemically in such a way as to differentiate between the structural constituents, and so to render the arrangement visible to the eye. This differentiation may be brought about by means of an attack by a solvent, which, dissolving one constituent more than another, produces differences of level which become visible on illumination, or by means of a reagent forming surface films of oxide or sulphide, so that differences of colour are produced. In both cases the contrasts of light or colour make visual and photographic examination of the specimen possible. Valuable qualitative information is thus obtained as to the number, character, and arrangement of the structural constituents of the alloy, and in many cases the previous mechanical and thermal treatment of the specimen may be inferred. But in certain cases the examination may be carried a stage further, and may be utilised to yield quantitative information, so as to indicate the proportions in which the component metals are present, the nature of those metals being supposed to be known.

On examination of the polished and etched section one or other of the following conditions may present itself :

1. The section exposed is homogeneous, containing only one structural constituent. This may show division into crystal grains, without, however, any intercrystalline cementing material. Owing to differences in the orientation of neighbouring grains, contrasts may appear under oblique illumination, but after a little experience there is no danger of confusion with the case of more than one micrographic constituent. The specimen may be :
  - a. A pure metal ;
  - b. A definite intermetallic compound ; or
  - c. A homogeneous solid solution.

In case *a*, the information obtained is definite. Thus in the alloys of lead and tin, or of gold and thallium,\* which do not form either compounds or solid solutions with one another, the only members of the series which present a homogeneous appearance under the microscope are the pure metals. The addition of even a small quantity of the second metal brings about the appearance of a second micrographic constituent, the absence of which is a proof of the purity of the metal.

In case *b*, the composition is also definite. For instance, magnesium

\* Levin, *Zeitsch. Anorg. Chem.* 1905, **46**, 49.

forms with tin the compound  $\text{Mg}_2\text{Sn}$ ,\* which does not form solid solutions with either magnesium or tin. An alloy, therefore, containing 29 per cent. Mg and 71 per cent. Sn, corresponding with the formula  $\text{Mg}_2\text{Sn}$ , is homogeneous, and an increase in the proportion of either tin or magnesium brings about the appearance of a second constituent.

In case c, the composition is indeterminate. When the two metals are isomorphous, the entire series of their alloys is homogeneous, and microscopic examination gives no clue to the composition. Such pairs of metals are gold and silver, iron and manganese, and cobalt and nickel. When, however, the solubility of one component in the other in the solid state is limited, so that there is a gap in the series of mixed crystals, a homogeneous structure indicates that the composition of the alloy falls within certain limits, which may in some cases be very narrow. Thus silver dissolves aluminium at the ordinary temperature up to a limit of 4 per cent. Al, any further increase of aluminium becoming apparent by a separation into two constituents.† In the case of the cadmium-gold alloys, between the compounds  $\text{Au}_4\text{Cd}_3$  and  $\text{AuCd}_3$ , a series of solid solutions is formed containing from 51 to 63 per cent. Cd.‡

2. Two solid constituents are visible in the same section. If the composition of the two phases is known, a measurement of the relative areas occupied by them, in the manner described below, gives by calculation the proportions in which the two components are present. A good example of this case is presented by the copper-zinc alloys containing from 36.5 to 46.5 per cent. Zn, sections of which exhibit two micrographic constituents, the so-called  $\alpha$  and  $\beta$  solutions.
3. The alloy is a eutectic mixture. Two solid phases are then present, mechanically intermixed in an intimate fashion, and since the eutectic formed by any given pair of phases has always the same composition, the composition of the alloy is known.
4. Crystals of a solid constituent are surrounded by a eutectic. The composition of the eutectic being constant, it may, although heterogeneous in structure, be treated as a single constituent, with certain exceptions to be discussed later. Measurements of the relative areas occupied by crystals and eutectic may then be made as in case 2.

It is essential to the application of this method that the alloys shall be in a known condition of equilibrium, that is, they must either have been cooled so slowly that sufficient time has been allowed for equilibrium to have been established between the solid phases, or if quenched, the conditions of equilibrium at the temperature of quenching must be known. The method of quantitative microscopic measurement is therefore only applicable to alloys of which the freezing-point and transformation curves have been accurately determined. In general, this is only true of alloys which have been investigated by Tammann's method of thermal analysis,§ the mere determination of the liquidus curve being insufficient. This method consists in observing the time occupied by each arrest in the cooling curve of an alloy. Thus, in an alloy containing a eutectic, there will be an arrest in the cooling curve at the temperature of solidification of the eutectic, and the duration of that arrest will depend on the proportion of eutectic present.

\* Grube, *Zeitsch. anorg. Chem.*, 1905, **46**, 76; Kurnakoff and Stephanoff, *ibid.*, 177.

† Petrenko, *Zeitsch. anorg. Chem.*, 1905, **46**, 49.

‡ Vogel, *Zeitsch. anorg. Chem.*, 1906, **48**, 333.

§ Tammann, *Zeitsch. anorg. Chem.*, 1903, **37**, 303; 1905, **45**, 24.

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On plotting the duration of the arrest for a series of alloys of varying composition against the composition, the maximum time, obtained either directly or by interpolation, corresponds with the eutectic composition. In the same way, when a heat evolution is due to the enantiotropic change of a compound, the composition of the compound may be arrived at by plotting the duration of that heat evolution against the composition of a series of neighbouring alloys. It is in this way that the presence of definite compounds in a series of solid solutions may be detected. It must be remembered that equilibrium in solid alloys is often only gradually attained, the processes of diffusion and segregation being very slow, so that long annealing at a definite temperature may be necessary in certain cases.

In the actual carrying out of the method in cases 2 and 4 mentioned above, it is found that the ordinary photo-micrographs are on too small a scale to allow of accurate measurement. It is therefore necessary to enlarge them, or, more simply, to project the magnified image of the section by means of a horizontal photo-micrographic apparatus on to a sheet of paper pinned to a drawing-board placed vertically, and to trace the outlines of the constituents with a pencil. When, owing to the low reflecting power of the surface of the alloy, the illumination is insufficient for this purpose, or when a vertical camera is employed, it is better to replace the ground-glass screen of the camera by tracing paper laid on clear glass, and

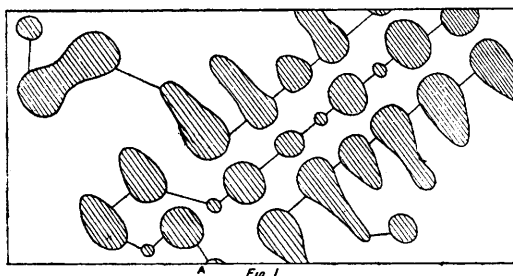


Fig. 1

to trace the outlines in that way. It is of course essential that the field chosen for projection shall be typical of the structure of the whole specimen, or, where the structure varies from one part of the specimen to another, several fields must be measured and the results averaged.

A tracing having been obtained by one or other of these methods, a boundary line is ruled so as to enclose the pattern to be measured. It will be found to facilitate measurement if the crystals of that constituent which has the most clearly developed outlines be shaded with pencil. The area of the shaded portions is then measured by means of a planimeter. A starting-point is marked on the margin as at A (Fig. 1) and the outline is then followed clockwise with the tracing point of the planimeter, passing from one detached outline to another along a straight line as shown in the figure, care being taken that the return journey is made over the same line. It is advisable to check the result, after taking the final reading of the planimeter, by retracing the outline in the opposite direction (counter-clockwise), when the dial of the planimeter should of course return to the initial reading.

When the pattern is very complicated, or made up of many small and detached portions, or when the outlines of the crystals are unusually intricate, the errors of the planimetric method may become greater than is permissible. In such cases, better results are obtained by ruling lines 1 cm.

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apart on the tracing, so as to divide the whole field into 1 cm. squares. After a little practice, it is not difficult to estimate the relative proportions of the shaded and white areas in any square, and the results are set down in order. Thus 0·7 indicates that the square is estimated to be shaded over seven-tenths of its area and white over three-tenths. The readings are added up separately and divided by the number of squares in the column, and the mean of all the results so obtained is taken. In this way a very close approximation to the true proportions may be obtained.\*

Two other methods of obtaining the superficial areas of the constituents were met with when we had nearly completed this work, and may be mentioned here for the sake of completeness, although they are much less convenient than those described above. The first consists in cutting out the shaded portions of the tracing, either on paper alone or on paper with a tinfoil backing, and weighing the separated portions. This method was introduced by Delesse in 1847 for the purpose of determining the volume composition of igneous rocks, but is obviously not susceptible of as great accuracy as measuring with the planimeter. The second method, also employed by petrologists in the study of igneous rocks,† consists in drawing straight lines through typical fields, and measuring the intercepts of the different constituents upon these lines. Although this method gives sufficiently accurate results in the case of rock-sections, in which the minerals present usually form fairly compact and regular areas, it is less applicable to the more complex patterns which characterise the micro-sections of metallic alloys. It is easy to show that either of these methods, depending on the measurement of superficial areas or of linear intercepts, gives the true volume ratios of the constituents.

The examination of an alloy by this method occupies very little time. With practice it is possible to grind, polish, and etch a Muntz metal, for instance, in five minutes, using a Stead polishing machine driven by an electric motor, and the projection and planimetric measurement may be completed in half an hour. The method therefore possesses the advantage of great rapidity.

The proportions of the component metals corresponding with the areas exposed may be calculated from a knowledge of the densities of the constituents. It is possible, however, to dispense with this calculation by employing a graphical method already in use for metallographic purposes, and shown in Fig. 2. The diagram is constructed by taking as abscissæ the percentages of the component metals and as ordinates the percentage of the area occupied by any micrographic constituent. The diagonal lines are obtained by joining up points corresponding with the composition of each

\* COMPARISON OF PLANIMETRIC MEASUREMENTS WITH MEASUREMENTS BY THE METHOD OF SQUARES.

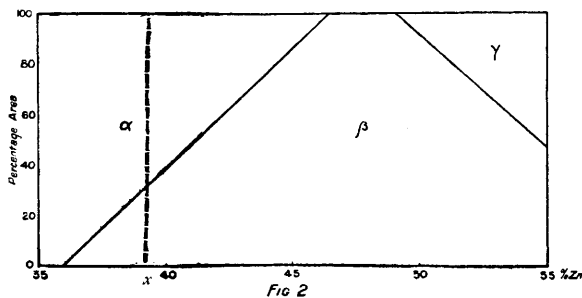
No. of Specimen.	Condition.	Area of Crystals.		Phosphorus per cent.		
		Planimeter.	Squares.	Planimeter.	Squares.	Analysis.
403	As cast	31·4	28·6	10·08	9·9	9·89

Areas of crystals from about 25 per cent. to about 75 per cent. can be fairly accurately judged by the eye, *e.g.*, No. 403 given above was originally estimated at about 30 per cent.—the exact mean between the readings from the planimeter and from the method of squares.

† See J. W. Evans, *Quart. J. Geol. Soc.*, 1906, **62**, 116.

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micrographic constituent in order, the points being taken alternately on the top and bottom line. An ordinate erected at the composition of any given alloy will therefore, by its intersection with the diagonal, give at once the percentage area occupied by each constituent. Fig. 2 is constructed for the



copper-zinc alloys from the data of Shepherd.\* The ordinate at the point  $x$  indicates that an alloy containing 61 per cent. Cu and 39 per cent. Zn will consist of 75 per cent.  $\alpha$  and 25 per cent.  $\beta$ .

The use of the planimeter in the microscopic examination of metals has already been applied to the estimation of carbon in steels† by measurement of the areas occupied by the eutectoid perlite, which contains 0.9 per cent. C, and to that of oxygen in cast copper by measurement of the cuprous oxide eutectic areas.‡

The application of the method may be illustrated by the following examples:—

Alloy.	Constituents Present.	Area of one Constituent.	Calculated from Area.	Found by Analysis.
Cu — Al	$\alpha + \beta$	72.5% $\alpha$	9.4	9.26% Al
Cu — Al	$\alpha + \beta$	49.0% $\alpha$	10.2	10.97% Al
Cu — Al	$\beta + \delta$	48.6% $\delta$	13.7	13.7% Al §
Cu — Zn — Sn	$\alpha + \beta$		42.8	42.95
"	$\alpha + \beta$		41.0	40.60
"	$\beta + \gamma$		49.4	49.50
"	$\alpha + \beta$		43.1	43.07
"	$\alpha + \beta$		42.2	42.10

We have tested the method most fully in the case of the copper-phosphorus alloys. Phosphor-copper, containing about 10 per cent. P, was taken as the starting-point, and alloys richer in copper were prepared by fusion with electrolytic copper, the cast alloys being annealed in a Heraeus electric furnace. The alloys take a high polish, and when etched with dilute nitric acid develop a well-marked structure. The nature of the micrographic constituents in alloys containing from 0 to 15 per cent. P is shown in Fig. 3, the structures actually observed being shown by the photo-micrographs, Figs. 4–10, these being selected as typical of a large number actually taken.

\* Shepherd, *Physical Chem.*, 1904, 8, 421

† Sauveur, *Metallographist*, 1898, 1, 27.

‡ Heyn, *Zeitsch. anorg. Chem.*, 1904, 30, 1.

§ Calculated with the aid of Guillet's diagram. *Rev. de Metall.*, 1905, 2, 565.

|| The calculations in the case of copper-zinc alloys containing tin has been made by means of Guillet's formula (*Rev. de Metall.*, 1906, 3, 243).

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Copper retains up to 0.175 per cent. P in solid solution, but an increase in the quantity of phosphorus causes the appearance of a eutectic containing the phosphide  $\text{Cu}_3\text{P}$ . With increasing phosphorus, the eutectic increases in quantity at the expense of the copper crystals, which appear dark in the photographs. At 8.27 per cent. P the whole alloy consists of eutectic, and on still further increasing the phosphorus, rounded white crystals of the phosphide make their appearance, until at 14.09 per cent. P, corresponding with the compound  $\text{Cu}_3\text{P}$ , they fill the whole area. From 14.09 to 15 per cent. P, the limit obtainable under ordinary pressure, the alloys consist of a homogeneous solid solution.

The results of the planimetric measurement are shown in Fig. 3, the observed points being indicated by crosses. As will be seen, they are far from coinciding with the theoretical values, which should fall on the diagonal straight lines. When this work was nearly completed, a paper on the copper-phosphorus alloys by Heyn and Bauer appeared,\* in which the series was

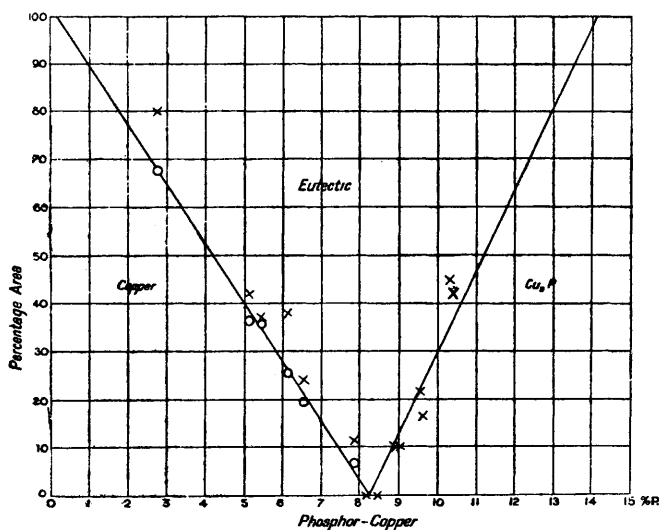


Fig. 3.

very thoroughly studied, and some planimetric measurements on the left-hand side of the eutectic in the diagram were made. These authors noted the same kind of deviation from the theoretical line, and constructed a curve to replace the diagonal for the purposes of practical measurement. They did not, however, attempt any explanation of the discrepancies. An examination of the photographs, Figs. 4-6, suggests the true explanation. As will be seen, the copper crystallites, which appear dark in the etched specimens, are surrounded by a belt of white copper phosphide, separating them from the copper-copper phosphide eutectic, easily recognised by its banded structure. The formation of this belt is due to segregation. It is well known that the large and small crystals of a salt are in contact with its saturated solution the large crystals tend to grow at the expense of the smaller. The same thing has been observed in the case of solid solutions. When steel containing the eutectoid pearlite is maintained for a sufficient time at a suitable temperature,

\* Heyn and Bauer, *Mitt. k. Materialprüfungsamt*, 1906, **24**, 93; *Zeitsch. anorg. Chem.*, 1907, **52**, 129.





FIG. 4.  
2.73 per cent. P.  $\times 300$ .

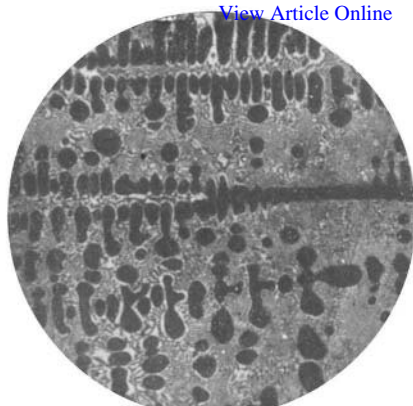


FIG. 5.  
6.11 per cent. P.  $\times 100$ .

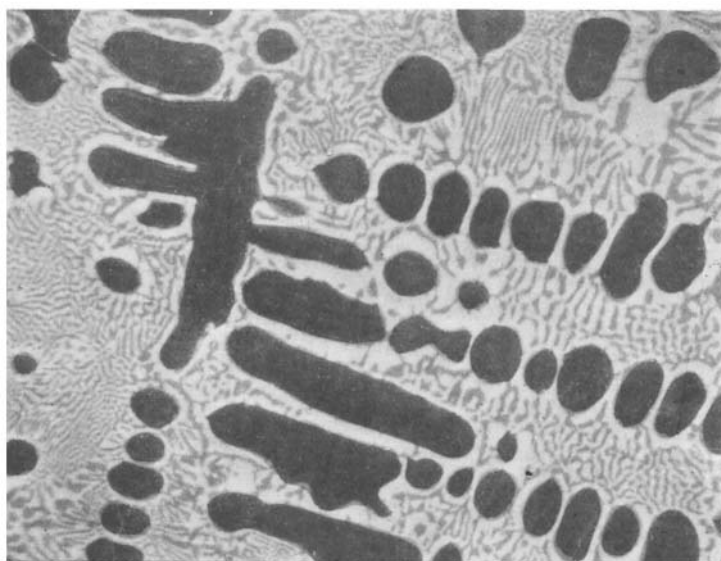


FIG. 6.  
6.11 per cent. P.  $\times 300$ .



FIG. 7.  
8.25 per cent. P.  $\times 300$ .



FIG. 8.  
8.93 per cent. P  $\times 100$ .

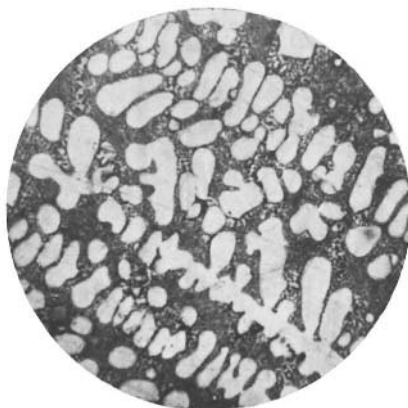


FIG. 9.  
10.30 per cent. P.  $\times 100$ .



FIG. 10.  
10.30 per cent P  $\times 300$ .



FIG. 11.  
Ag. Cu.  $\times 300$ .

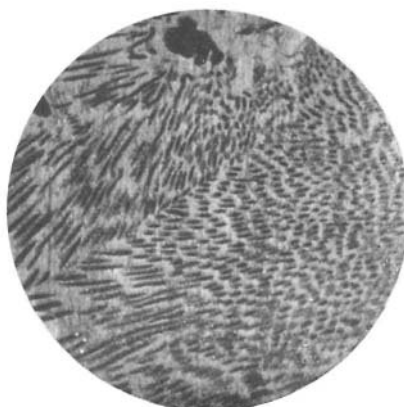


FIG. 12.  
Ag. Cu eutectic.  $\times 300$ .



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the pearlite becomes coarser, and in time the segregation becomes complete, the component structural elements of the pearlite, namely, ferrite and cementite, being entirely separated, so that masses of pure cementite occupy the positions originally occupied by perlite. The formation of a clear belt around crystals may be observed in certain igneous rocks, such as perlitites. The crystals at first formed in the process of devitrification of the glassy magma attract to themselves the minute dust-like crystallites in their immediate neighbourhood, leaving a clear space, called by petrologists the "Krystallisationshof," which is thus correspondingly poorer in the mineral which has first crystallised than the mass of the rock. In the case of phosphor-copper the result of the segregation is that the copper crystals occupy an area greater than that corresponding with the equilibrium. They have drawn to themselves a part of the copper of the surrounding eutectic.

It is possible to correct for this segregation in the following manner. The white belt of copper phosphide is a measure of the amount of segregation which has taken place, and it is therefore necessary to make planimetric measurements, not only of the copper areas, but also of the enveloping belt of phosphide.

The two components of the eutectic are copper phosphide,  $\text{Cu}_3\text{P}$ , containing 14.09 per cent. P, and a solid solution of phosphorus in copper, containing 0.175 per cent. P. As the eutectic contains 8.27 per cent. P, its composition by weight is given by the equation :

$$14.09x + 0.175(100 - x) = 100 \times 8.27,$$

or  $x = 57$  ; that is, the eutectic is made up of 57 parts by weight of  $\text{Cu}_3\text{P}$  and 43 parts of the solid solution of phosphorus in copper. The specific gravities of the solid solution and of copper phosphide being given by Heyn and Bauer (*loc. cit.*) as 8.86 and 7.18 respectively, the eutectic must contain 62 per cent.

Number.	Fig.	Structure.	Area of Crystals. Per Cent.	Corrected Area. Per Cent.	Per Cent. P by Planimetric Measurements.	Per Cent. P by Analysis.
225	4	Cu + eutectic	80.0	67.8	2.75	2.73
227	5 and 6	" "	42.0	36.4	5.30	5.08
226		" "	37.8	25.7	6.15	6.11
216		" "	37.0	36.0	5.38	5.45
205		" "	24.0	19.3	6.65	6.55
202		" "	11.2	6.8	7.60	7.88
224	7	All eutectic	—	—	8.27	8.25
204	8	" "	—	—	8.27	8.50
201		$\text{Cu}_3\text{P}$ + eutectic	10.0	—	8.85	8.93
203		" "	10.0	—	8.85	9.05
222		" "	16.6	—	9.28	9.64
241		" "	21.8	—	9.50	9.59
199	9 and 10	" "	45.0	—	10.9	10.30
271		" "	43.0	—	10.8	10.70

of  $\text{Cu}_3\text{P}$  and 38 per cent. of the solid solution by volume. This will also be the ratio of the superficial areas occupied by the two phases in a microscopic section. A belt of segregated phosphide, therefore, corresponds with  $\frac{38}{62} = 0.61$  of its own area of copper, and this amount has accordingly to be deducted from the measured area of the copper crystals (properly crystals of the solid solution, containing a small amount of phosphorus) in order to arrive at the true area. The results obtained are shown in the table above, in which

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the areas given are usually the mean of several concordant measurements. The corrected points are shown in Fig. 3 as circles. It will be noticed that the correction for segregation, in the case of alloys containing free copper, is large, but that when this is taken into account the percentages of phosphorus estimated planimetrically are in remarkably close agreement with those found by analysis. When the phosphorus content is low, as in the first alloy in the table, no eutectic structure is visible, the copper crystals being separated by clear areas of phosphide, from which all the intermixed copper has been withdrawn by segregation (Fig. 4).

In the case of the alloys containing free copper phosphide, segregation of the kind described above does not take place, and the crystals of  $\text{Cu}_3\text{P}$  are in immediate contact with the beautifully laminated eutectic. The area of the phosphide crystals found by the planimeter tends to be higher than that corresponding with the analysis when the percentage of phosphorus is high. This appears to be due to imperfect equilibrium in the process of solidification, the separation of crystals along the copper phosphide branch of the freezing-point curve being continued beyond the eutectic point, owing to the failure of the second constituent to crystallise. Such super-fusion is frequently observed, and its effect on structure has been recently discussed for the cases of organic mixtures and igneous rocks, by Prof. Miers & Miss Isaac.\*

The copper-phosphorus alloys are not the only examples of segregation giving rise to a band surrounding the crystals first formed. The phenomenon is well observed in the alloys of silver and copper, the constituents of which are two solid solutions, the one rich in copper, the other in silver (Figs. 11 and 12). The outer boundary of the segregated silver-rich band is, however, too indefinite to allow of satisfactory planimetric measurement.

In dealing with metals which have been slowly cooled from the fused state, so as to allow sufficient time for the attainment of equilibrium, the planimetric method may be found of considerable practical use, especially in routine work, in which the alloys dealt with are only liable to vary within comparatively narrow limits. When the proper conditions are fulfilled, the accuracy is sufficient for all practical purposes. The method may also find application in the investigation of new series of alloys, when it is necessary in any case to anneal the specimens so thoroughly as to ensure equilibrium, and the planimetric measurements of the proportions in which the micrographic constituents occur may be found to be a valuable check on the results of thermal analysis.

In conclusion, we wish to express our thanks to Mr. A. B. Licence for assistance in the planimetric measurements, and to Miss E. A. Macadam, A.I.C., who made the chemical analyses quoted in the paper.

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