38. MICROSTRUCTURE. — This genesis which we have been following, the freezing out first of the excess-substance and then later of the eutectic, is reflected in the microstructure. Thus in a microsection of a copper-silver alloy richer in copper than its eutectic ratio of 72 silver 28 copper, we find (Fig. 17) the excess of copper in small dark crystallites grouped together like a fernleaf or pine-tree. Thus in freezing this copper has arranged itself around definite crystalline axes, the trunk and branches of the

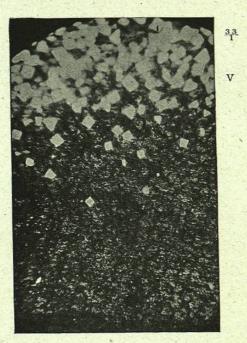


Fig. 16. Alloy of 90 per cent Tin, 10 per cent Antimony.

Showing how the Cubes of Tin Antimonide (Sn Sb) have risen by Gravity to the Top of the Ingot. Vertical Section of the Ingot.

Prepared by William Campbell in the Author's Laboratory.

pine-tree, and in doing so has displaced the still molten eutectic, which, on later reaching its own freezing-point, has solidified in these spaces into which it has thus been driven between the pine branches.

And here we have a first example of the kind of evidence that guides us in deducing from the microstructure the order of birth of the different constituents. It is a natural principle that the earlier born constituents should assume their own crystalline forms, since at the time when they are solidifying the remainder

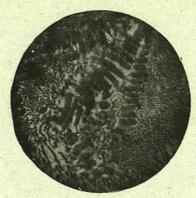


Fig. 17. Eutectiférous Copper-silver Alloy, Heat-tinted.

C. H. Eckerson and the Author.

The dark fern-leaf crystals are the excess-metal, argentiférous copper. The eutectic is shown both in plate and spheroidal shape.

EXCESS AS NETWORK, EUTECTIC AS MESHES.

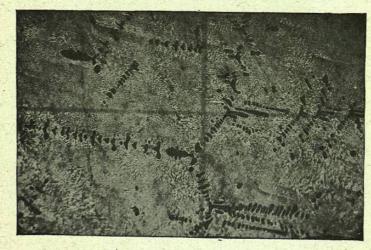


Fig. 18. Alloy of 80 per cent Copper, 20 per cent Silver.

The eutectic is Levol's alloy, copper 28.1, silver 71.9 per cent. The black arborescent network is the excess of copper over the eutectic ratio.

Prepared by E. J. Hall in the Author's Laboratory for this work.

of the mass is still a molten menstruum, in which they are free to grow; whereas the constituents which form later, through later freezing, find themselves at birth already displaced by their elder

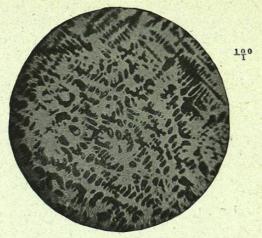


Fig. 19. White Cast Iron, Etched with Tincture of Lodine.

(F. Osmond, Private Communication; see also The Metallographist, III, 197.)

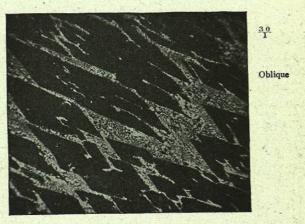


Fig. 20. Alloy of Copper 45 per cent, Aluminium 55 per cent. Made in the Author's Laboratory by William Campbell.

brothers, and occupying the spaces between them, the only space that is left. In short, the early freezing substances would naturally form "idiomorphic" crystals or crystalline groupings, while the later freezing ones would naturally be grouped pseudomorphically. (For definitions see § 39, p. 51.)

Now, a pine-tree or fern-leaf crystalline grouping, like that in Fig. 17, certainly appears to be idiomorphic. Even if we did not know the history from other data, we should say that this fern-leaf is an early-born substance, and the eutectic between is of later birth. This is shown even more clearly in Figs. 18 and 19, the dark rows of semi-arborescent crystals in which are evidently free growths in a menstruum at least mobile enough to enable the growing tree or bough to push it aside.

The interpretation of polygonal structure, like the dark network\* and light polygons of Figs. 1 and 2, pp. 3 and 4, needs more care, because each constituent might be at first sight reckoned either idiomorphic or pseudomorphic. But the fact that spines of the dark network protrude into the light meshwork,\* and that well-oriented stripes of the former occur in the latter, indicates that the former is the earlier formed; for if the network were formed after the polygons had already solidified, it is less likely that its nascent spines and stripes could thus have thrust themselves into the already relatively firm polygons. In case of Fig. 1, we know from Osmond's independent data, embodied in Roberts-Austen's diagram, Fig. 68, p. 194, that the dark network of ferrite is of earlier birth than the light polygons of pearlite. (See § 169, p. 198.)

Further examination of this type of structure as shown in Figs. 21 to 23, p. 50, goes farther to show that the network of the excess-substance ferrite (shown in these three figures as the lighter constituent) is older than the meshwork or matrix-substance, the quasi-eutectic or eutectoid pearlite, because of the way in which the fine spines of the former shoot out into the latter.

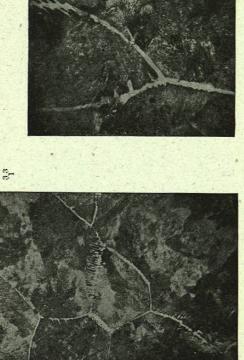
But in other cases it is the eutectic which forms the network and the excess-metal the meshwork or polygons, as in Fig. 20. Here, then, the polygons are the earlier and the network the

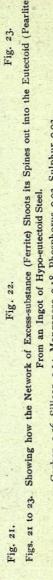
<sup>\*</sup>For the benefit of any to whom the distinction between the terms "network" and "meshwork" may not be perfectly clear, the following definitions from Webster's Dictionary are given:

Network — A fabric of threads, cords, or wires crossing each other at certain intervals, and knotted or secured at the crossings, thus leaving spaces or meshes between them.

Mesh—The opening or space enclosed by the threads of a net between knot and knot.

EXCESS AS NETWORK, EUTECTIC AS MESHES.





later born, in contrast with the condition of affairs in Figs. 1, 2 and 18.

This diversity of arrangement, this having the excess-substance form in some alloys the network and in others the meshes, is due to a corresponding diversity in the way in which the earlier formed, the excess-substance, crystallizes. With the great diversity in the forms which ice assumes under different conditions we are all familiar, the transcendently beautiful hexagonal stars which snow forms on some very cold days, the arborescent tracery on our window-panes and even at times on the sidewalks, the stout columnar structure of our artificial ice ingots. And like diversity is found in many minerals.

In general, where in any given alloy the excess-substance forms arborescent or hollow crystals, or crystals which enclose space, it tends to form the network, leaving the eutectic to occupy the meshwork thus left between the crystalline branches or plates. And where, instead of forming arborescent, hollow, or other crystalline forms enclosing space, the excess-substance forms solid crystals, each of which grows from a centre, growing as a solid cube for instance from some starting-point, then the excesssubstance tends to form the meshwork, expelling into the spaces between these crystals the mother-metal, which will eventually turn into the eutectic. At first these intercrystalline spaces occupy the greater part of the whole mass; but with the growth of the individual crystals, the intercrystalline spaces are progressively encroached upon, and are later reduced to a mere network. These generalizations are not intended dogmatically or as of universal application, but rather to suggest to the student the manner of growth, and to aid in deducing from the crystalline arrangement the seniority of the different components.

39. DEFINITION. — An idiomorphic or automorphic crystal is one with a shape due to the crystalline nature of the substance of which it is composed, as distinguished from a pseudomorph, *i.e.*, one with a shape due to other causes, such as the shape of the space in which the substance is confined, the shape of a previously existing substance which it replaces, *etc*.

Valuable evidence as to seniority can often be had by examining the different constituents with a view to deciding which of them on one hand exist in idiomorphic crystals, or in shapes indicating that they have formed freely in a liquid or plastic medium, and which simply occupy the spaces left by the earlier formed crystals of other constituents. This criterion must, however, be used with great caution. Thus in Fig. 20, p. 48, certain off-shoots of the eutectic into the dark ground mass might readily suggest that they were idiomorphic. But, on closer examination, we see that these spines really follow the orientation of the dark crystals, so that the eutectic, instead of having sent out early spines which have persisted, has simply occupied certain spaces left within the crystals of the earlier formed constituent.

## CHAPTER III. - FREEZING-POINT CURVES

40. Physical Properties of Series of Alloys, or The General System in which the Changes in any Given Critical Point or Critical Composition Occur as we Pass from One End of a Series to its Other End. — The importance and indeed the meaning of this class of studies can best be seen after we have examined an individual case, of which the "freezing-point curve" is probably the most important.

41. Freezing-point Curve. — In the cooling curves in Figs. 8, 9, 11, and 28 B, C, D and F, pp. 18 and 60, we may note two critical temperatures, B at which the freezing of the excess-substance begins, and CD at which it ends and the freezing of the eutectic occurs. For brevity we may call these the two freezing-points, e. g., for each alloy of lead with tin. Now, to bring together and compare the teaching of all these cooling curves and to see in what manner these freezing-points vary, as we pass from pure lead through the lead-tin alloys to pure tin, we may plot, as in Fig. 24, p. 54, with temperature as ordinate and percentage of tin as abscissa, the position of these two freezing-points, when we find that the upper freezing-points fall into a V-shaped curve, ABC, underscored by a horizontal line aBc, the freezing-point of the eutectic.\* Let us here

at once recognize this, the essential feature of this family of curves, the underscored V. The line AB is the locus of the temperature at which lead begins to freeze out from molten lead-tin alloys which contain an excess of lead over the eutectic ratio of 31 per cent, starting with 326° C., the melting-point of pure lead, and ending with 180°, the freezing-point of the eutectic. So, too, BC is the locus of the temperature at which the freezing of tin begins in case of all alloys of lead with tin containing less than 31 per cent of lead, or in other words containing an excess of tin over the eutectic ratio. The line aBc represents the temperature at which the eutectic freezes in each alloy.\*

42. Twofold Aspect of the V-Curves.—We saw in § 29, p. 33, that during selective freezing the mother-metal was at every

<sup>\*</sup>Let the reader clearly impress on his mind at the outset that each point in this and like diagrams represents both a specific temperature through its vertical distance from the horizontal axis, and a specific composition through its horizontal distance from the vertical axis. For instance, the point B represents the temperature of 180° through its height, and it also represents the composition lead 31 per cent, tin 69 per cent, through its distance to the right of the axis OA.

<sup>\*</sup>To make perfectly clear the relation between the freezing-point curve and the individual cooling curves, of the two freezing-points of which it gives the loci, let us follow the cooling of some one alloy, say that of 55 per cent of lead, and hence with 24 per cent excess of lead over the eutectic ratio. Let us assume that the molten alloy has been first superheated above its melting-point, say to 350°, G. Following the course of its cooling along the line GHJK, it cools past 326°, the freezing-point of lead, without undergoing any freezing; the lead remains molten at a temperature below its own freezing-point, because the new substance, the molten solution, which its integration with the tin forms, has a lower freezing-point; the tin dissolved in the lead lowers the freezing-point of the lead. Only when the temperature falls to about 225° C. does any lead begin to freeze. As the temperature further falls from H to J, crystals of lead continue freezing out within the molten metal, while the mothermetal, or part still remaining molten, thereby grows correspondingly and progressively richer in tin and leaner in lead. This continues until the temperature has reached 180°, when the molten mother-metal will have become so far impoverished in lead as only to contain 31 per cent of that metal; in short, it will have reached simultaneously the freezing-point of the eutectic and the composition of the eutectic. At this point further cooling is arrested by the heat liberated through the solidification of the eutectic; and only when the whole of the mother-metal shall have frozen, yielding the well-known interstratified plates of the eutectic, only then will the temperature again begin to fall. In this line then, GH corresponds to the part AB of the cooling curve in Fig. 28 D; HJ represents the excess-freezing period and corresponds to BC; the point J represents the jog CD, the eutectic-freezing period; and JK represents the part DE. The fact that the line aBc is horizontal represents the fact that the jog BD has the same ordinate, i. e., that the eutectic freezes at one and the same temperature, no matter what the initial percentage of lead and of tin in the molten alloy is.