

PHILOSOPHICAL TRANSACTIONS.

I. BAKERIAN LECTURE.—*On the Constitution of the Copper-Tin Series of Alloys.*

By C. T. HEYCOCK, *F.R.S.*, and F. H. NEVILLE, *F.R.S.*

Received February 26,—Read February 26, 1903.

[PLATES 1-11.]

CONTENTS.

SECTION I.—SUMMARY OF RESULTS.

	Page
The cooling curves	3
The temperature concentration diagram	4
The solidus	5
The substances occurring in the alloys	9
Classification of the alloys into groups	11

SECTION II.—ON THE SOLIDIFICATION OF A METAL.

The development of a pattern	17
Preparation of the ingots	18
The melting-point and the rigidity of the alloys at high temperatures	19

SECTION III.—THE MICROSCOPIC STUDY OF THE ALLOYS.

Identification of the substances as seen in the photographs	23
The evidence from the microscopic structure of the chilled alloys	26

SECTION I.

SUMMARY OF RESULTS.

THE immediate origin of the present paper lay in a suggestion of the late Sir G. G. STOKES, made early in 1900, that we should attempt the microscopic examination of a few bronzes as an aid to the interpretation of the singularities of the freezing-point curve. This curve was at the time fairly accurately known, largely through the researches of the late Sir W. ROBERTS-AUSTEN and Dr. STANSFIELD, published in 1895 and in 1897, and partly by our own work. Microscopic studies of the alloys had been also published by Dr. CHARPY and by Mr. STEAD, but, so far as we are aware, no attempt had been made to correlate the



two lines of research, and the exact nature of this group of alloys remained very obscure.

The ingots of alloy which we studied at first had been allowed to cool somewhat slowly and spontaneously in the furnace, so that there had been no sudden chill or alteration in the rate of cooling. Polished and etched sections of these ingots were found to contain very varied and complicated patterns that sometimes appeared to have no connection with the singularities of the freezing-point curve. For example, a tin-rich crystallisation which appeared to be primary, was found to *increase* to a maximum amount as we *descended* a branch of the curve, and in more than one region undeniable primary crystals which stood out in relief on the outside of the ingots were found, when polished half-through, to be full of smaller and quite different crystals. In fact, it became evident that the final patterns we were examining were of the nature of a palimpsest in which several different records were superposed, some of these being due to recrystallisations that had taken place after solidification. Two other considerations pointed to the same conclusion, the first was derived from the very valuable cooling curves, published by ROBERTS-AUSTEN and STANSFIELD in 1895, which revealed the fact that far below the temperature of solidification considerable evolutions of heat occurred in the alloys as they cooled. The second was derived from Professor ROOZEBOOM's paper on the "Solidification of Mixed Crystals of Two Substances," published in the 'Zeitschrift für Physikalische Chemie,' of December, 1899. These two researches have been respectively the experimental and the theoretical basis from which the present work has grown, and the possibilities of interpretation which they promised have induced us to make a much more serious study of the bronzes than we originally intended.

It soon became clear that in order to understand the nature of the alloys it was essential to examine their structure at all temperatures, from the freezing-point downwards. We therefore adopted the plan of chilling small ingots at selected temperatures. We hoped that, as in the case of steel, the structure existing at a particular temperature would be so far stereotyped by the sudden cooling of the chill as to be recognisable under the microscope. This hope has been to a very large extent justified, most of the doubtful points as to the nature of the bronzes having been cleared up by the evidence derived from the chilled ingots. In February, 1901, we published in the 'Proceedings of the Royal Society' a short paper describing the method, and gave some photomicrographs illustrating the extraordinary changes that a solid alloy can undergo as it cools, and in December, 1901, we read before the Royal Society another short paper on the same subject. The latter paper contained a diagram giving a complete view of the conclusions we had arrived at, concerning the nature of the copper-tin alloys. The paper was published in the 'Proceedings,' vol. 69. The photomicrographs, which formed an important part of the evidence for the truth of the diagram, were exhibited by one of us when the paper was read, but were not included in the paper. The present paper does not represent any great

advance beyond that of December, 1901, although the diagram (Plate 11) now given is in some minor points more accurate than the earlier one, and a change has been made in the notation. The main purpose of the present paper is to give the evidence for the correctness of our views, evidence which is largely drawn from the photographs of the chilled ingots.

The photographs are reproduced in Plates 1 to 9, containing figs. 1 to 101 arranged in order; opposite each plate is a table giving a brief description of the figures contained in it, the composition of the alloy, the method of etching the ingot, and the magnification employed in taking the photograph.

Before considering the photographs it will be necessary to discuss the cooling curves of Plate 10 and the equilibrium diagram of Plate 11. We shall thus be able to present an outline of our conclusions which will, we hope, render the bulk of the evidence, which is given further on, more intelligible. *We think that a reader wishing to understand the results of our work without desiring to weigh the evidence minutely would find Section I., and an examination of the plates and photographs referred to in Section I., almost sufficient for his purpose.*

The Cooling Curves.—(Plate 10.)

Although the pyrometric work of ROBERTS-AUSTEN and STANSFIELD gave us most valuable suggestions, we did not find it possible to use it quantitatively. This was partly due to the small size of their published curves, and partly to their being constructed on a thermometric scale different from the one employed by us. We therefore determined to repeat a good many of the cooling curves and to reconstruct the thermal diagram of the alloys. Plate 10 gives the more important of the cooling curves obtained by us, but we have in addition traced the cooling curves of alloys with more tin. Our curves are very similar to those of ROBERTS-AUSTEN and STANSFIELD, and we are not prepared to say that they contain any additional information, but they are in a form convenient for use with the present paper. They were traced by means of a platinum-resistance pyrometer and a Callendar recorder, in which a pen, controlled by the pyrometer, writes on a rotating drum.

In Plate 10 the horizontal ordinate is time, and it is reckoned from left to right, the vertical ordinate being temperature reckoned downwards. A scale of Centigrade degrees is placed at each end of the diagram, which will enable the temperature of an alloy at any point on its curve to be read off. It may be noticed that equal vertical distances do not quite correspond to equal ranges of temperature, but that the scale becomes more open as the temperature falls. This peculiarity arises from the curves having been traced automatically on the platinum scale. The curves are an exact copy half-size of those traced on the recorder. The number at the head of each curve indicates the atomic percentage of tin in the alloy. In tracing a curve a mass of about 300 grammes of alloy was melted in a double or treble crucible and allowed to cool spontaneously with the pyrometer immersed in it. The time of

tracing a curve was generally about two hours, and a little carbon was thrown on the surface of the ingot, to avoid oxidation, or, as an alternative, a little coal-gas was allowed to burn at the mouth of the crucible.

A detailed discussion of the various curves is not necessary here, as they will be referred to later on, but it may be worth while to say a few words about their general character. If a substance remained liquid throughout the whole range of cooling and underwent no chemical change we should expect its cooling curve to be a sloping line, probably somewhat steeper at high temperatures than at low ones, but free from abrupt changes of direction. The short upper branches of all the curves, near to where they are numbered, correspond to this cooling of a uniform liquid. But when solidification, or any other exothermic change, begins the rate of cooling will be abruptly decreased and the cooling curve will tend to become horizontal. This is well seen in the upper-most curve of Plate 10, the flat under the letters "Cu" being due to the isothermal solidification of the copper. The upper flat in the curve of Sn 4 is also due to the formation of solid, and in this case a slight surfusion must have occurred, the temperature of the liquid falling below the freezing-point, and then, by the evolution of the latent heat of solidification, being perceptibly raised. But the flat is shorter than with pure copper, and rapidly rounds off in consequence of the solidification not being an isothermal process. The solidification of Sn 4 is probably completed at 850° , and below that point there is no marked singularity in the cooling curve. But if we consider the curves of Sn 6, 8, 10, 12, or 14, we see that not only does the uppermost halt, the freezing-point, become lower and lower as the percentage of tin increases, but that some distance below this halt, at a temperature almost the same for all the curves, there is a second evolution of heat which becomes more and more marked with increasing content of tin. Moreover, in the curves of Sn 10 to Sn 15, there is a third evolution of heat at about 500° , and this, as we shall be able to prove, occurs in an absolutely solid alloy. Similarly Sn 17 is solid at 700° , but its cooling curve shows well marked heat evolution at a temperature below 500° . Valuable though cooling curves are for indicating critical points in the cooling, they have a defect; in order to make the whole period of tracing the curve a reasonable one, it is unavoidable that the cooling at the higher temperatures should be somewhat rapid, hence certain rather sluggish reactions do not complete themselves at the equilibrium temperature, and may indeed never become complete. One must, in consequence, exercise some caution in attempting to infer the magnitude of the heat evolution due to a particular change from the length of the flat it produces.

The Temperature Concentration Diagram.—(Plate 11.)

The information supplied by the cooling curves can be presented in another and for some purposes more convenient form by taking the composition of each alloy as the horizontal ordinate, and temperature as before for the vertical one. Our Plate 11 is constructed in this way. Here all the first halts of the cooling curves are used to

form the "freezing-point curve" ABLCDEFGHIK. This has been very carefully investigated by ROBERTS-AUSTEN and by us. It contains angles at C, D, G, H, and I, which divide it into six branches, each corresponding to the crystallisation of a different solid. ROBERTS-AUSTEN and STANSFIELD have also shown that it is possible to draw a continuous curve through corresponding lower halts in the cooling curves of the alloys from Sn 15.5 to Sn 27, and thus obtain the curve C'XD'E'f, to which we, on other grounds, have added the branch lC'. The whole of this "transformation" curve, as the discoverers called it, has recently been traced by us from our own experiments, so that, as given in Plate 11, it is a confirmation but not a copy of that of ROBERTS-AUSTEN and STANSFIELD. The transformation curve has some analogy with the freezing-point curve, inasmuch as when the temperature of an alloy falls to that of a point on either of the two curves crystallisation commences, but while at the upper curve the new solid crystallises out of a uniform liquid, at the lower curve the phenomenon is a recrystallisation out of a body already solid and crystalline.

At the top of Plate 11 there are two scales, the upper gives the percentage by weight of tin in the alloy, and the scale of equal divisions slightly lower down gives the atomic percentage of tin. Compositions expressed in atomic per cents. have the advantage of being at once convertible into formulæ. Thus 25 atomic per cents. of tin, or, as we write it, Sn 25, implies Cu 75, and, therefore, the formula Cu_3Sn , and so on.*

One way of looking at the diagram is expressed by the statement that a vertical line stands for an alloy of a particular composition, irrespective of its temperature, while if we follow such a vertical line from the top to the bottom of the diagram we are, *diagrammatically*, watching the alloy cool.

The freezing-point curve ABLCDEFGHIK divides the area into two parts such that above the curve every alloy is a homogeneous liquid, while, immediately below, it is a mixture of solid and liquid. We shall in future abandon the term "freezing-point curve" and employ the term "liquidus," suggested for such a curve by Professor ROOZEBOOM.

The Solidus.

Professor ROOZEBOOM, in the paper already referred to, has defined another curve, the "solidus," which is the complement of the liquidus. Suppose an alloy, or any other mixture, caused to cool so slowly that all parts are, at every temperature, in true equilibrium with each other. Then when the temperature falls to the liquidus a little solid will be formed, and as the temperature continues to fall, more and more solid will form, until finally a temperature is reached at which the last drop of liquid solidifies and the mass becomes wholly solid. This temperature is a point on the "solidus," and the curve passes through the *solidifying*, as distinguished from the *freezing*, points of all the alloys represented on the diagram. Just as (in the concentration-temperature diagram we are considering) all points immediately above

* In calculating the atomic percentage from the percentage by weight, the atomic weights employed were, Cu = 63.3, Sn = 118.1.

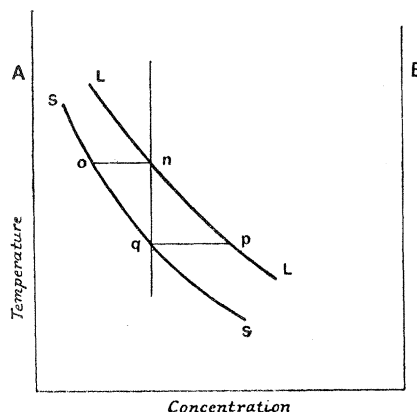
the liquidus represent liquid states, so all points immediately below the solidus represent wholly solid states of the system.* Points between the solidus and the liquidus stand for states of the system in which it is a mixture of solid and liquid.

The determination of the solidus by experiment is much more difficult than the determination of the liquidus. By stirring an alloy during solidification, and noting the temperature at which the stirrer becomes immovable, one gets a very rough approximation to a point on the solidus. A measurement from the cooling curve looks more promising, but is liable to prove very misleading. For example, in the cooling curve of Sn 12, solidification begins at the upper flat near 870° , but is far from complete at the end of that flat, continuing, of course with evolution of heat, to a little way below the end of the second flat at 790° . This temperature is a point on the solidus. Such cooling curves as those of Sn 4, Sn 17, or Sn 26 would leave the position of the solidus still more uncertain. It would seem that, assuming perfect equilibrium at all stages, the solidus must be identical with the "melting-point" curve, a point on the latter being defined as the temperature at which an alloy which is being very slowly heated begins to melt or form liquid. Here, again, on account of the impossibility of maintaining true equilibrium between the various crystals in a heterogeneous alloy, the experimental error would be large. We have attempted to determine points on the solidus by very slowly warming small rods of alloy and at the same time subjecting them to a slight strain, the temperature at which the rod breaks being taken as that of the solidus. These experiments have not given very consistent results, but they have been valuable in showing the high temperature up to which many of the alloys retain their rigidity.

We have found that by far the most satisfactory method of determining points on the solidus was through the study of polished and etched sections of chilled ingots of alloy. These show quite plainly how much of the ingot was liquid at the moment of chilling, and by chilling at successively lower and lower temperatures one can determine the temperature at which the whole ingot has become solid. In our Plate 11 the branches of the solidus were determined by such a study of the chilled alloys; for this purpose many chills were made in addition to those described in Section III.

Professor ROOZEBOOM defines the solidus differently, although the same curve is ultimately arrived at. As a clear understanding of Professor ROOZEBOOM's view is essential for the argument of the present paper, perhaps we may be excused for restating it here.

* It is more accurate to say that if we travel from A to I along the *solidus*, points on our right represent wholly solid states.



Let the figure be a portion of the concentration-temperature diagram of binary mixtures containing the two components A and B, the concentration being measured horizontally and the temperature vertically. The vertical line on the extreme left corresponds to pure A, and that on the extreme right to pure B, every other vertical line corresponding to a particular mixture. Now let the curve LL be a portion of the liquidus or freezing-point curve, and let us draw a vertical straight line, cutting LL in the point n . Let us consider the particular mixture represented by this vertical straight line, and think of it as cooling. When the temperature has fallen to the point n , the liquid mixture will be saturated, and if maintained slightly below this temperature it will, if surfusion be avoided, deposit a small quantity of a crystalline solid. This solid phase may be either the pure substance A, or a pure compound of A and B, or it may be, and this is the case we wish specially to consider, an isomorphous crystalline mixture of A and B or of compounds of the two.

(The German word for such a phase, "Mischkrystalle," naturally translates itself as "mixed crystals," but this phrase is liable to be misunderstood, in so far as it may be taken to stand for a complex of two or more different kinds of crystals instead of for crystals all alike and each a homogeneous mixture of two components, the latter being the real meaning. We have, therefore, reluctantly decided to abandon the term and use instead the term "solid solution." This term implies that the two components are capable of being as uniformly mixed as in a liquid solution, and also implies the possibility of continuous variation in the percentage composition of the mixture. It does not imply the necessity of crystalline structure, and therein the phrase has a wider scope than the otherwise identical term "isomorphous mixture" or isomorphous crystal. But, so far as we know, all the solid solutions met with in alloys are crystalline, and we shall, therefore, use the three terms as synonymous. The idea does not exclude the possibility that the same crystal may, as is often the case, be made up of layers of different composition but, contrary to the views of some writers, we are disposed to think that such a structure is not essential, but is the result of imperfect equilibrium adjustments during the formation of the crystal; this, we believe, is the view of Professor ROOZEBOOM.)

Whether the solid phase which crystallises from the saturated liquid n be pure component, compound, or solid solution, it must, if left long enough in contact with the liquid at the constant temperature n , become homogeneous and of quite definite composition, for the phase rule forbids the possibility of two different solid phases being both in equilibrium with the same liquid except at points where two branches of the liquidus meet. If, therefore, the crystals were extracted and analysed, their composition and temperature could be represented by a point o on the diagram, the line no being horizontal. We know, moreover, that the solid phase will be richer in the component A than the liquid with which it is in equilibrium; in other words, that o will lie to the left of n . It is evident that, conjugate to every point on the liquidus, there is one and only one point analogous to o . The curve through all these points is the solidus as defined by ROOZEBOOM. In other words, if a horizontal line be drawn cutting the liquidus and the solidus, then the two intersections give the compositions of the liquid and solid phases that can exist in equilibrium at the temperature of the

horizontal line. In all cases in which the two components form solid solutions the solidus is a sloping line.

The case where the solid phase is a pure component or a pure compound may be regarded as a limiting case in which the mutual solubility in the solid condition is indefinitely small. The solidus is then the vertical line through the fixed composition of the solid phase, while from another point of view it may be regarded as the horizontal line through a lower eutectic point or angle in the liquidus. This will become more evident if we follow ROOZEBOOM through his very important description of the complete solidification of a liquid which finally forms a uniform solid solution.

Returning again to the mixture represented by the vertical line through n , let us suppose that, after the formation of a very little of the solid phase defined by o , the system is allowed to cool very slowly. The separation of the o crystals will cause the residual liquid to be richer in B, that is, to be represented by a point on the liquidus a little to the right of n , and as more and more solid is formed, the point defining the residual liquid will travel more and more to the right. But such liquids will not be in equilibrium with the crystals first formed, and hence if sufficient time is allowed in the cooling, a continuous *re*-solution or transformation of the solid phase will go on, while at the same time it grows in amount. Finally, when the temperature q is reached, defined by the intersection of the vertical through n with the solidus, the system will, in the ideal case of perfect equilibrium adjustments, be a uniform crystalline solid solution, the crystals being surrounded by a vanishingly small amount of mother-liquid of the composition p , where p is defined as the intersection with the liquidus of the horizontal through q . Of course, in a real experiment, for which infinitely slow cooling is not possible, there will be a chance that the earlier crystals may never be wholly transformed, but may remain as cores richer in A than the solid outside them. In this case the temperature of complete solidification will be lower than the theoretical one given by the point q .

The fact, taught us by the phase-rule, that in a binary mixture in which only concentration and temperature are variable a particular liquid can in general only be in equilibrium with one solid phase makes it certain that the solidus as defined above is theoretically the same curve as the melting-point curve.

We can now proceed to consider the special form taken by the solidus in the copper-tin alloys. As determined by us through the study of chilled alloys, and drawn in Plate 11, the solidus consists of the broken line $AbcmdefE_2E_3H'H''K'$. The angular points on this broken line, with the exception of m , are pretty accurately determined, but the exact shape of the branch Ab has been rendered uncertain by the impossibility of obtaining true equilibrium transformations during the cooling of the corresponding alloys, and the branches lc and $mdef$ may, from the same cause, be a few degrees too low. Again, we have drawn E_2E_3 as a vertical straight line, while it is possible that it may be slightly sloping and curved. The point H' is fairly certain, while we have not yet enough evidence to fix H'' . But, on the whole, we have

considerable confidence that the solidus, as we have drawn it, is a good first approximation to the truth.

The Substances occurring in the Alloys.

The diagram of Plate 11 also contains a number of thick vertical and horizontal lines which divide up the area below the liquidus into closed compartments. Each of these compartments embraces all the temperatures and percentages for which the alloys are in a particular state of aggregation, and the phases making up the aggregates are indicated for each compartment.

The following phases may occur :—

Liquid, which is found in every compartment that lies between the liquidus and the solidus ;

Crystals of five different types, which we designate α , β , γ , δ , η , and H ;

The substance crystallising along the branch IK of the liquidus, which must be pure, or nearly pure, tin.

The liquid may, of course, have any percentage weight of tin in it from 0 per cent. to 100 per cent. The α crystals are solid solutions, apparently isomorphous with pure copper. They may contain any percentage of tin not greater than 9 per cent. The β crystals are also solid solutions, perhaps isomorphous with the α . They range in composition from 22.5 per cent. of tin to about 27 per cent. No uniform solid solutions are formed with percentages of tin between 9 per cent. and 22.5 per cent. of tin. The γ crystals are also solid solutions of copper and tin or of compounds of the two metals. They do not appear to be isomorphous with the preceding. They range in composition from about 28 per cent. to about 57 per cent. of tin. The δ material possesses a well-marked crystalline character and is very constant in appearance in all the alloys in which it is found. It may be a solid solution of varying composition like the preceding, but we are disposed to think that it is more probably the pure compound Cu_4Sn . The η forms large crystalline plates, often bounded by plane faces making definite angles with each other. It occurs in all alloys between E and H, and in many of these alloys we have proved by isolation and analysis that it is the pure compound Cu_3Sn ; it also occurs in the alloys between D and E, here it has the same crystalline form, but there is some reason to think that it may be a solid solution of varying composition.

The H substance does not differ much in composition from the compound CuSn ; it plays an important part in anti-friction alloys. We have made many analyses of H, and find it very constant in composition ; but it contains a few per cent. more copper than corresponds to the formula CuSn ; it is probably CuSn containing some Cu_3Sn in solid solution.

The substances α , β , γ , η and H are found as primary crystals and mixed with liquid in ingots chilled between the liquidus and solidus ; the δ substance never crystallises

from the liquid, but appears as a recrystallisation out of homogeneous solid β or γ . All these substances, except β and γ , are stable under certain circumstances at ordinary temperatures and are therefore found in slowly cooled unchilled ingots; on the other hand, the two latter are unstable at low temperatures, and are only found in certain chilled alloys.

The angle C of the liquidus indicates that the composition of the solid phase here changes abruptly,* for while the branch ABC corresponds to the solidus Ab , the branch CD corresponds to the solidus lc . The angle at C was a great difficulty to us so long as we only examined alloys that had not been chilled, but ROOZEBOOM'S theory explains in the most perfect manner all the phenomena connected with this angle. It tells us that just above the temperature C the cooling saturated liquid deposits, and is in equilibrium with the α solid solution whose composition is given by the point b , while just below the temperature C the liquid forms β solid solution, much richer in tin and given in composition by the point l . Thus as the saturated liquid cools through the temperature C an isothermal transformation $\alpha_b + \text{liq}_c = \beta_l$ takes place. The heat evolved by this reaction is well marked in the cooling curves. No uniform solid solution of percentages between b and l can exist.

The angle D indicates another break in the series of solid solutions, and we have indicated a corresponding break between c and m in the solidus. The study of the chills in this region affords, as will be seen later, some evidence for the break cm , but this evidence is not altogether conclusive. However, we propose to speak of the solid solutions of the branch $mdef$ as γ crystals, to distinguish them from the β crystals of the branch lc . Both the cooling curves and the microscope indicate that in alloys between Sn 17 and Sn 20 an isothermal exothermic reaction occurs when the temperature falls to that of the point D. This reaction must be either $\beta + \text{liq} = \gamma$, or $\beta = \gamma$. The first equation corresponds to our figure, in which c and m are separated, the second to the case of m and c being really coincident.

Thus the branch ABLC of the liquidus deposits α solid solutions, the branch CD deposits β solid solutions, and the branch DEFG deposits γ solid solutions.

The branch GH of the liquidus deposits crystalline plates of the substance η , which in this region consists of nearly or quite pure Cu_3Sn .

The branch HI deposits crystals of the substance H, which is certainly very near in composition to CuSn , although it has a slight excess of copper, probably due to a small amount of η in solid solution.

The liquid of the branch IK deposits crystals that must be very nearly pure tin.

* During the experiments for the determination of the liquidus, described in a previous paper ('Phil. Trans.,' A, vol. 189, p. 50), the cooling alloy was sometimes stirred by means of a hand stirrer during the freezing-point experiments. On such occasions we noticed a marked difference between the precipitates formed a little above and a little below C; above C the solid forming was soft, and we compared it to mud, but as soon as the temperature C was reached the precipitate became hard and gritty, and we compared it to a sharp sand.

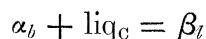
Below the lines $Ablcdef$, E_3H' and $H''K'$ the alloys are wholly solid, if they have been cooled with extreme slowness; we have succeeded in verifying this fact, but, unless great care is taken to ensure slow cooling before the chill, alloys chilled a little below these lines, which together make up the solidus, will be found to contain liquid at the moment of chilling.

Classification of the Alloys into Groups.

Vertical lines through the points B, L, C, D, E, f , G, H, I, divide the alloys into groups having special qualities. We will trace the complete cooling of an alloy from each group.

(1.) The AB alloys, containing less than 5 atomic per cents. of tin, that is less than 9 per cent. by weight. When these alloys begin to solidify they form, while above the line Ab , a mixture of α crystals and liquid (fig. 2). When the temperature of an alloy has fallen below the line Ab , it consists of uniform α crystals embedded in a very little of a tin-rich mother-substance, which owes its existence to imperfect adjustment of the equilibrium between solid and liquid during the last stages of solidification. This small residue of liquid is absorbed by the α crystals at temperatures a little below bC and modifies the margin of these crystals, but in spite of some deceptive appearances, these alloys, at all temperatures below Ab , consist substantially of one phase, namely, the uniform solid solution α (fig. 7).

(2.) The BL alloys, containing from 5 to 13.5 atomic per cents. of tin, that is from 9 to 22.5 per cent. by weight. These alloys, like the preceding group, commence their solidification by the formation of α crystals, but these never fill the whole volume, for when the temperature C (790°) is reached the reaction



commences and continues until all the C liquid is exhausted. (The sub-indices b , C, l , indicate the compositions of the particular kind of α , liquid and β respectively that take part in the reaction.)

Thus, when the temperature falls below C, assuming that the ingot has been kept long enough at the C temperature, the alloy is wholly solid and consists of α crystals of the percentage b embedded in β crystals of the percentage l . These β crystals are uniform, and at lower temperatures play the part of a mother substance to the α crystals, which grow at the expense of the β while the solid alloy cools through the range of temperature bb' . This growth in the solid is very remarkable in alloys near the composition l , and accounts for the fantastic angular shapes seen in the α combs of the slowly cooled and unchilled alloys. Fig. 27, Plate 3, an ingot of Sn 13.5, chilled at 558° , is a good example of this effect. The α combs are light and the uniform solid β out of which they have grown, is dark. When the temperature falls below 500° (the eutectic line of ROBERTS-AUSTEN and STANSFIELD), the residual β

decomposes into a very minute complex (fig. 19) of α and the tin-rich body δ , which we strongly suspect is the compound Cu_4Sn . Thus at all temperatures below $l'C'$ this group of alloys consists of the complex $\alpha + \delta$.

(3.) The LC alloys, containing from 13.5 to 15.5 atomic per cents., that is from 22.5 to 25.5 per cent. by weight of tin. These alloys commence their solidification by the formation of α crystals, but this process soon ceases, for at the C temperature the α is wholly changed into β of the l percentage, and then this β reacts along the lines lc and CD with the residual liquid in the manner described on p. 8. When the temperature has fallen to the solidus lc , the alloy is a uniform solid solution. It is a mass of β crystals, chemically identical, but forming crystalline grains differently oriented and therefore showing, after etching, differences of brightness on tilting or rotating. This uniform solid solution continues to exist until the temperature falls below the line $l'C'$, which is comparable to a freezing-point curve, inasmuch as on cooling to a point on this line, the uniform β becomes saturated with α , and below the line the α crystallises out in large copper-rich crystals. Finally, as before at 500° , the residual β breaks up into the C' complex. Below the $l'C'$ line these alloys, like the preceding, consist of the complex of $\alpha + \delta$. An examination of the photographs we give of Sn 14 (Plate 3) will be found to confirm these statements. The C' complex has often, of course, been previously observed in unchilled alloys, but, so far as we know, without its real nature being discovered.

(4.) The CD alloys, containing from 15.5 to 20 atomic per cents. of tin, that is from 25.5 to 31.8 per cent. by weight. These alloys begin to solidify by forming large, comparatively copper-rich combs of β immersed in a liquid considerably richer in tin, and, as far as Sn 16.5, the alloys when just solid, are a uniform mass of β crystals. Although the alloys from Sn 16.5 to Sn 20 form similar β crystals during the first stages of solidification, these crystals never entirely fill the ingots, and below the temperature D they are transformed into what appears to be uniform γ . The uniform character of the solidified alloys persists so long as the temperature is above the line $C'XD'$. These solid solutions are very homogeneous, and we have not been able to detect much, or any, difference between the appearance of the uniform β of Sn 16 at 700° and the uniform γ of Sn 18 at the same temperature, provided both alloys have been very slowly cooled.

In all the alloys of this group, when the temperature falls below $C'XD'$, the phase δ crystallises out in ribands at the borders of the crystal grains of the solid solution, as well as in the form of fern-leaf or rosette scattered through the grains. This crystallisation is well seen in the photographs of Sn 17, 18, and 19, that accompany the paper (see Plates 4 and 5). The δ , as seen in the photographs, is white; it contains a larger proportion of tin than the mother-solid round it, and the δ increases in amount as the percentage of tin in the whole alloy increases. The δ first appears in the ribands which border the grains, these ribands being produced at higher temperatures than the fern-leaf. We are disposed to think that this peculiarity is due to the fact

that, in spite of the approximate uniformity of the alloy above the line $C'XD'$, there must be round each β grain an envelope, somewhat richer in tin than the grain itself, produced by the collection between the grains of the last traces of mother-liquid. These intergranular spaces would, therefore, as the temperature fell, be the first parts to become saturated with tin, and the tin-rich δ , in consequence, began to crystallise in these spaces. The substance between the crystals of δ is uniform until the temperature X is reached, when the residual solid solution breaks up into the C' eutectic complex of α and δ . A careful examination of this complex with a high power proves it to be essentially the same in all alloys from Sn 6 to Sn 20. The photographs we give will, we think, justify this statement. The fact that the eutectic point C' of the LC alloys is a little higher than the eutectic point X of the CD alloys is evident in the pyrometric curves of ROBERTS-AUSTEN and STANSFIELD, and we have also verified it, as may be seen in our cooling curves. But Professor ROOZEBOOM suggests that the true eutectic angle for all alloys from l to D' is at C' , and that the apparent depression of X is a retardation due to the difficulty experienced by the α in crystallising without a nucleus of its own kind. Thus in the region XD_2D' the alloys are a complex of β (or γ) and δ , while below XD_2 they form a complex of α and δ .

The curves $lC'XD'$ record the equilibrium between the solids α and δ and the solid solution out of which they crystallise, and the method of examining chilled ingots has enabled us to follow the whole process in a very satisfactory manner. The α must be itself a solid solution, but we are strongly disposed to think that δ is the compound Cu_4Sn . The alloy Sn 20, although the cooling curve indicates that it undergoes a well-marked exothermic transformation at the D' temperature, remains substantially uniform after the transformation. The fact that it has recrystallised is, however, shown in the ingots chilled below D' , by minute traces of the C' eutectic visible between the large crystals of δ that almost entirely fill the ingot. It may be that the chemical compound Cu_4Sn does not exist above the temperature D' .

(5.) The DE alloys, containing from 20 to 25 atomic per cents. of tin, that is from 31.8 to 38.4 per cent. by weight. When chilled between the liquidus and the solidus, these alloys are found to contain primary combs of γ . On the solidus, these combs fill the alloy, and just below it they form a uniform solid solution, but it is very difficult in this region to prevent, by chilling, a commencement of the transformation proper to the $D'E'$ curve. However, our chilled ingots afford a considerable amount of evidence that the condition of the alloys at temperatures between de and $D'E'$ is that of a uniform solid solution. When the temperature falls below the curve $D'E'$, long, straight, very uniform bars separate out of the solid solution. These are richer in tin than the solid out of which they crystallise. They are dark in the photographs. Near D' these bars are usually very slender and scanty, but they increase as we approach E' , and at that point they fill the whole alloy. These bars appear, from what one occasionally sees in some ingots, to be really plates seen edgewise, and their

greater or less breadth is partly due to their varying inclination to the plane of the section. These plates, the first appearance of the η phase, must be either pure Cu_3Sn or solid solutions of Cu_4Sn and Cu_3Sn ; we are not at present able to decide this point. Thus immediately below D'E' the alloys are a complex of η and residual γ . But ROBERTS-AUSTEN and STANSFIELD have proved that when any of the DE alloys fall to the temperature D' they evolve heat (see cooling curves of 20, 21, and 22). This must be due to the conversion of the residual γ into δ , so that below D'E'' the alloys form the complex $\delta + \eta$ (Plate 5, fig. 56).

(6.) The EF alloys, containing from 25 to rather more than 27 atomic per cents. of tin, that is, from 38.4 per cent. to 41 per cent. by weight. These go through the same stages of $\gamma + \text{liquid}$, then homogeneous γ , then $\gamma + \eta$; but when the temperature of the line fG is reached, the residual γ breaks up into η and liquid of the composition G. Thus these alloys present the somewhat rare phenomenon of the partial melting of a solid brought about by cooling it. The transformation $\gamma_f = \eta_{E'} + \text{liq}_G$, or, as we may safely write it, $\gamma_f = \text{Cu}_3\text{Sn} + \text{liq}_G$, is the transformation which causes the angle at G in the liquidus. It is accompanied by a large evolution of heat, well seen in the cooling curve of Sn 27.

It may be noted here that the triangular area lXf forms a region of uniform solid solutions, which could only have been discovered by the examination of chilled alloys, inasmuch as these solid solutions break up into two phases when slowly cooled.

(7.) The FG alloys, containing from 27.5 to 42 atomic per cents. of tin, that is, from 41 per cent. to 57.5 per cent. by weight. These, like the preceding, begin to solidify by forming the complex $\gamma + \text{liq}$ (figs. 75 and 76), their state, when the G temperature is reached, being that of γ crystals of the f percentage and liquid of the G percentage. The isothermal transformation $\gamma = \eta + \text{liq}$ now commences, and completes itself abruptly with a heat evolution very well marked in the alloys near f . The alloys become perceptibly more liquid as the temperature falls,* and the microscope shows very well the change from the rounded, uniform γ combs to the complex of liquid between plates of η (figs. 73 and 74).

When an FG alloy has cooled below the G temperature the η continues to crystallise out of a liquid which is continually becoming richer in tin. This process goes on between the G temperature of about 630° and the H temperature of 400° . Below 400° the FG alloys follow the same course as the next group.

(8.) The GH alloys, containing from 42 to about 87.5 atomic per cents. of tin, that is, from 57.5 per cent. to 93 per cent. by weight. When these alloys begin to solidify they deposit plates of η , and this process continues until the liquid has the

* This peculiarity was noticed during the operation of chilling the ingots: a little ingot of, say, Sn 28, chilled just above the G temperature, was not distorted by the sudden immersion in water employed to chill it, but a similar ingot chilled a little below G was converted into a mass resembling granulated zinc; this difference was observed more than once.

composition H and the temperature is 400° . At this temperature the η becomes less stable than the body H, and the reaction $\eta + \text{liq} = \gamma$ commences.

The reaction is closely analogous to that characteristic of the C point in the copper-rich alloys, and like it is a very slow one. The H at this temperature has a composition very near Sn 45; the η is still almost identical with Cu_3Sn . This reaction should complete itself isothermally until, for alloys to the left of H' the liquid, and, for alloys to the right of H', the η is wholly transformed. But as soon as the plates of η have become completely coated with H, the reaction, which is now a process of diffusion through the solid H, becomes extremely slow, and, with ordinary rates of cooling, it never reaches anything like completion. The result of this imperfect reaction is that the diagram contains four compartments in the space E_3SUH , in each of which one of the phases that are found would be absent if the equilibrium transformations had been completed. Professor ROOZEBOOM has suggested the excellent plan of putting a bracket round the symbol of the phase that has no right to be present. We retain this notation because it indicates the ordinary condition of the alloys as most observers will find them; we have, however, succeeded, by maintaining the ingots for many days at a temperature a little below 400° , in completing the reactions and removing the third phase.

(9.) The HI alloys, containing from 87.5 to 98.3 atomic per cents. of tin, that is, from 93 per cent. to 99.1 per cent. by weight. In these alloys the solid first formed is H, and the diagram sufficiently explains itself.

(10.) The IK alloys, containing more than 98.3 atomic per cents. of tin. These alloys contain primary crystals of pure, or very nearly pure, tin in a eutectic made up of H and tin.

SECTION II.

ON THE SOLIDIFICATION OF A METAL.

Our experience, and we believe it to be identical with that of most who have studied the subject, points to the comparative rarity of the formation of large crystals with plane faces during the solidification of a metal or alloy. The first solid structure is generally a crystal skeleton, which in its simplest form consists of a stem with radial branches projecting from it. This may be compared to a fir tree, and in many cases the branches are at right angles to the stem and to each other. Such a structure, when cut by a plane, gives rise to the fern-leaf or dendritic forms so often seen on the surface of cast metal, or in the etched and polished surface of a section of an ingot.

Let us think of the case in which such a crystal skeleton has been produced in an otherwise liquid mass of metal. As the branches give off what we may call twigs, and these may develop other systems of twigs, and so on indefinitely, it follows that

from an original centre of crystallisation a uniformly oriented scaffolding may stretch out in three dimensions until it meets similar structures starting from other centres. The figures we give of an unchilled ingot of Sn 1, of the chill of Sn 6 at 966° , and of Sn 12 at 805° , all illustrate this process. If the centres of crystallisation were uniformly scattered through the liquid, and if the velocity of crystallisation were everywhere the same, we could predict the shape of the outer boundary of a crystal skeleton, but, as a rule, on account of unequal velocities of crystallisation, due to local temperature differences and other causes, the skeletons vary very much in size and shape. If the substance is a pure or nearly pure metal, or an alloy that solidifies to a uniform solid solution, the skeletons become solid by the thickening of the bars and the growth of new orders of twigs, and in the wholly solid ingot when cut and polished each skeleton is found to have given rise to a grain. The sections of the grains are irregular polygons, and, although the original skeleton can often no longer be detected in the polygon, yet a uniform orientation persists throughout a polygon and often causes it, when etched, to reflect light at a particular angle. Thus when parallel light falls on the surface, some polygons will appear dark and others bright, but each polygon will have a uniform degree of brightness throughout its area. The chill of Sn 2 at 957° (Plate 1, fig. 3A) shows skeletons which have grown until they almost fill the whole alloy. The same surface (fig. 3) when illuminated by oblique light, shows that there are several grains differently oriented.

If the substance contains an impurity, which is not isomorphous with the material first solidifying, this impurity will be principally found as an envelope round each grain, and in a section of an ingot it will appear as a slender network round the polygons. Some of this mother-substance must, however, from the peculiar skeletal manner of growth of the grains, exist in minute particles enclosed in the grains, though it may not always be possible to detect it. If there is very little impurity it may not form a complete network round the polygons, but only be found in isolated patches where three polygons meet. The chill of Sn 28 (fig. 73), and the unchilled Sn 6 (fig. 12), are good examples of this. If there is a good deal of impurity, so that the substance first crystallising ceases to form before the metal is solid, and if the remainder of the liquid produces an entirely different solid, then the original skeletons never fill up, and can be detected in the polished and etched sections. They then appear as fern-leaf markings, as gridirons, or as combs, distinguished by colour or by texture from the mother-substance that solidified at a later stage. The chill of Sn 9 at 777° (Plate 2, fig. 15) is a good example of the phenomenon, the pale skeletons being composed of a copper-rich substance which ceased to form some time before the whole mass was solid. It is surrounded by, and sharply divided from, the tin-rich matter, dark in the figure, which solidified later. The existence of such combs in an alloy often enables us to form a correct inference as to the material that solidified first, but we shall see in the course of this paper that it is not always safe to assume that the material of the fern-leaf or comb pattern was the first to solidify.

Most of what we have said above is a matter of very general knowledge to students of metals, but as the argument of the present paper depends largely on the interpretation of the patterns seen in the etched surfaces, we have thought it well to state the more obvious rules for interpreting such patterns. The uniformly oriented scaffolding or grain is by some writers called a "crystal." We, on the whole, prefer the term "grain," or the more descriptive term, "crystal skeleton." Crystals of considerable size, with plane faces, are sometimes found in alloys; one at least of the substances described in the present paper is found in such crystals; we have also seen them in alloys of aluminium with nickel or with platinum.*

The Development of Pattern.

When there is a difference between the chemical composition of the combs and the matter surrounding them the pattern can be developed in several ways. If there is a difference in hardness, one of the two materials will be etched out by polishing and a pattern formed in relief. The pattern thus obtained is often very well seen when the surface is examined with a lens, but in the CuSn alloys we have not found it suitable for microscopic examination or photography. A better method with all the bronzes ranging from pure copper to the alloy with 25 atomic per cents. of tin, is to heat the polished surface cautiously by laying it on an iron plate over a small flame. The copper-rich parts of the alloy then oxidise more rapidly than the tin-rich parts, the tints orange, red, blue, white, red and blue appearing in succession in such a way that the copper-rich parts are always a tint ahead of the tin-rich. Very splendid patterns are thus obtainable in the case of the ABC alloys, and the method is most valuable in determining the parts richest in copper. BEHRENS and STEAD have both drawn attention to the applicability of this method of heat oxidation in the study of the bronzes. The chilled alloys, however, are in an unstable condition, and we have sometimes found that the heat needed to bring out pattern by oxidation produced changes in the structure of a chilled alloy. It is, therefore, best to commence the examination of a chilled alloy by a chemical method of etching.

Many re-agents are available for etching, the most suitable for a particular alloy depending on the position of that alloy in the series. Ammonia readily attacks, dissolves and darkens the copper-rich α combs of the ABC alloys, leaving the remainder of the surface, as a rule, a dead ivory white, and where, as in unchilled alloys of the region CD, there is α , or a copper-rich phase resembling α , that also is attacked. A prolonged exposure to strong ammonia generally brings out a striation in the β ; ammonia does not touch alloys containing more than 20 atomic per cents. of tin. Strong hydrochloric acid is similar in its action to ammonia on the alloys from

* What has been said above as to the formation of crystal skeletons does not preclude the possibility of the phenomenon, observed by LEHMANN, QUINKE, and others, that the solid skeletons may be preceded by the separation of droplets of an unstable liquid phase; the highest chills of the DE alloys strongly suggest this (fig. 54). See also the note, p. 19.

A to D, attacking and dissolving the copper-rich parts. With more tin than 25 atomic per cents. the action of the acid is reversed, the tin-rich parts being dissolved and the η and H bodies not being touched until all the excess of tin has been removed. It is improved in its action by the addition of small quantities of an oxidising agent such as bromine or ferric chloride. But the latter re-agent often reverses the light and shade of the pattern by what appears to be an electrolytic deposit on the tin-rich material. Such complications are not, however, confusing if one examines the same alloy in succession in different ways.

In the case of the alloys discussed in the present paper the different ways of bringing out pattern confirm each other and leave not the slightest doubt as to which part of an alloy is tin-rich or copper-rich. We find that for photographic purposes an etch with a dilute solution of ferric chloride acidulated with hydrochloric acid has been most frequently successful. Its principal drawback is the conscientious way in which this solution develops every polishing scratch, however minute.

Preparation of the Ingots.

We prepared the little ingots containing from five to ten grammes of alloy in three ways. The simplest was to melt the weighed materials, or the previously made alloy, under charcoal and to allow the ingot to cool spontaneously in the crucible, which remained in the furnace until cold. Such a process of cooling is more rapid at high temperatures than at low, but there is no abrupt chill or change in the rate of cooling. We call these "unchilled ingots." In our experiments the ingots generally took from two to three hours in cooling. The alloys prepared thus may be said to be in the ordinary state in which previous workers have examined them. We soon found, however, that the patterns in these unchilled ingots were too complicated to admit of a satisfactory interpretation, inasmuch as the records of successive changes were superposed on each other in the same ingot. We therefore adopted the plan of allowing a small ingot to cool somewhat slowly to a selected temperature and then chilling it by withdrawal from the furnace and instantaneous immersion in water. We thus stereotyped the larger structures that had formed during the slow cooling previous to the chill, and although we did not always prevent the changes that were due at lower temperatures, yet the very short period of time available for them caused the corresponding detail to be, in most cases, very small and readily distinguishable from that formed before the chill. We call these "chilled ingots" or "chills," and speak, for example, of "the chill at 775° ," the temperature being that to which the alloy had fallen in the furnace before its extraction for chilling.

These chilled alloys gave us much valuable information, but we found that some of the transformations, especially those of the C, D and H temperatures, required a period of at least some hours to complete themselves, and that the cooling antecedent to most of our chills had not in general been slow enough to allow of complete

transformation. In fact, when the cooling is spontaneous, that is, brought about by extinguishing the gas and allowing the ingot to cool in the furnace, although the total time spent in cooling may be considerable, yet the rate of cooling at the higher temperatures will always be rapid. We therefore made a series of chills, preceded by a cooling which was very slow from the freezing-point of the alloy down to the moment of chilling. We took especial care to ensure that the time of cooling through a range of a few degrees above and below the critical point C or D should last several hours. In these chills, which we call "slow-cooled chills," and sometimes indicate by the letters "s.c.c.," the detail formed before the chill is naturally large and the transformations at the critical points are much more complete.* This slow and regular cooling was obtained by carefully regulating the gas pressure and at the same time slowly and automatically cutting off the supply. (The arrangements for the automatic reduction of the gas supply are described in a paper in the 'Journal of the Chemical Society,' 1898, p. 714.) Some of these slow coolings required watching for twenty-four hours, and we are much indebted to Mr. W. FEARNSIDES for carrying them out. They would have been impossible without a temperature recorder such as that of Professor CALLENDAR, which we employed.

On the Melting Point and the Rigidity of the Alloys at High Temperatures.

Although the photomicrographs of the successive chills of an alloy enable us to determine with considerable accuracy the temperature at which the crystalline phase fills the whole volume of the ingot, this method gives us no information as to the solidity or rigidity of the solid phase at high temperatures. For example, in Sn_2 , chilled at 1025° (fig. 2, Plate 1), large primary combs of oriented and therefore crystalline substance certainly existed at the temperature of 1025° , and the chill at 957° (fig. 3) shows that the crystals at this temperature occupy almost the entire volume; but the question whether at such high temperatures the crystals are rigid, like ordinary crystals, or plastic like the so-called liquid crystals, must be attacked by other methods.† Our attempts to determine the melting-point, as distinguished from the freezing-point, though unsuccessful in their primary object, which was to prove that the solidus was identical with the melting-point curve, have established the great rigidity of the crystals, even at very high temperatures.

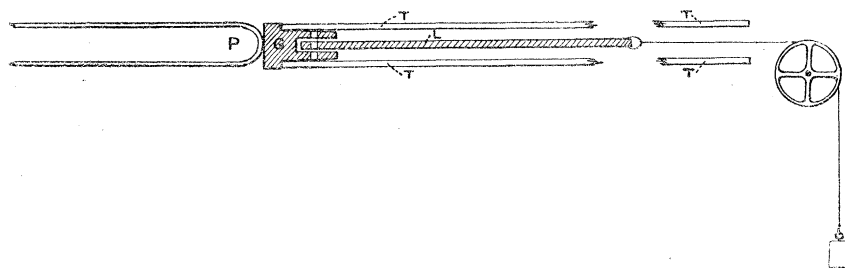
We attempted to find the melting-points by two different methods. The first method was to subject a little bar of alloy to transverse strain while it was gradually

* When the cooling, before the chill, was exceptionally slow, the abbreviation v.s.c.c., for very slow cooled chill, is used.

† The rounded form of the lobes of the primary skeletons in many of the upper chills suggests the action of surface tension and therefore of some plasticity in the crystals, but the continual transformation undergone by a crystal of solid solution as it grows may account for the rounding without the assumption that the crystals are plastic.

heated to higher and higher temperatures, until finally it broke. The temperature was called the *breaking-point*.

The arrangement was as follows:—A porcelain tube, open at both ends, was fitted at one end with a cork or plug of soft graphite. (We are much indebted to Messrs. ALLBRIGHT and WILSON for their kindness in giving us a suitable sample of graphite.) The porcelain tube had a diameter of rather less than a centimetre, being identical



with the tubes containing the pyrometers. In the figure, G is the plug of graphite closing one end of the tube T. A saw-cut, about 2 millims. wide and a centimetre deep, was made longitudinally in the plug, and at right angles to the plane of the saw-cut a circular hole of about a millimetre in diameter was also drilled through the plug. A lath of graphite just fitting into the saw-cut, and with a corresponding hole drilled in it, passed along the axis of the porcelain tube. A little rod of the metal or alloy to be examined was fitted through the holes in the lath and the plug, as it were riveting them together. The lath and plug with the alloy were then fitted into the tube, and the tube introduced into a tubular electric furnace, and secured in that position. The outer end of the lath was connected with a string passing over a pulley and stretched by a 50-gramme weight, a transverse stress of definite amount being thus maintained on the rod of metal. A pyrometer P was pushed into the other end of the furnace, so that the end containing the coil was in contact with the outer end of the graphite plug, the end of the pyrometer and the plug being as nearly as possible in the middle of the furnace tube. The heating current was then started, and very slowly and automatically increased. By this arrangement the temperature of the rod of alloy was known at each moment and could be raised with any desired degree of slowness. Finally, the rod broke quite suddenly, the weight fell and started an electric alarm so that the breaking temperature might be noted.

The time occupied in heating the alloy up to its breaking temperature was three or four hours, or even longer. The graphite appeared to protect the metal perfectly against oxidation, and yet it burnt away so slowly that the same plug and lath were serviceable for several experiments.

In order to test the method we began by determining the breaking-points of pure metals. The following table gives the results. Column I. states the freezing-point, as determined by our pyrometers, and Column II. gives the breaking-point, as determined by the above method.

	Freezing-point.	Breaking-point.	Pull-out.
	°	°	°
Copper	1082	1084	—
Silver	961	972	—
	—	970	—
	—	969	—
	—	967	—
Aluminium	655	640	654
	—	637	654
	—	630	—
Magnesium	633	644	—
	—	650	—
	—	655	—
Antimony	630	—	630
	—	—	625
Zinc	419	426	—
	—	426	—
Lead	327	—	332
Bismuth	266	—	272
Tin	232	—	235
	—	—	235

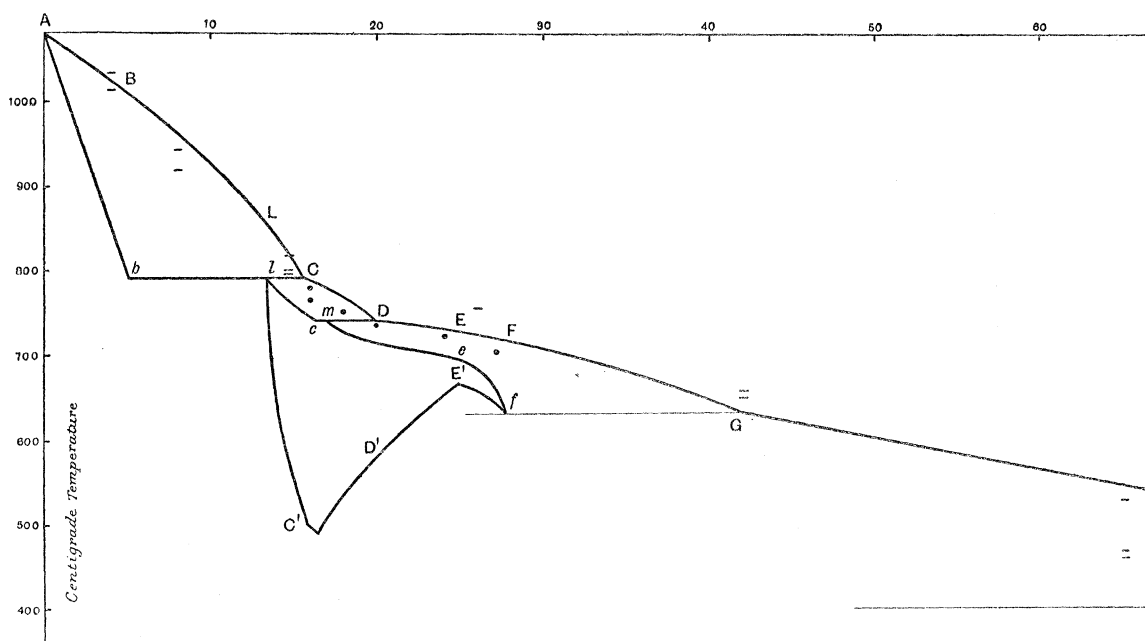
It will be seen from the table that, except in the case of aluminium, all the rods of metal broke at temperatures a little above the freezing-point. This peculiarity of aluminium is due to the fact that the metal has no constant temperature of solidification, but behaves more like a mixture than a pure substance.

The apparatus was withdrawn from the furnace as soon as the weight fell, and the residue of the rod was examined. As a rule the rod had completely melted into two or three round beads, but the rod of aluminium broke without melting.

The second method was a pull-out method similar to that employed by MEYER, RIDDLE and LAMB in the study of salts ('Ber.,' 1894, Jahrg. 27, p. 3129), and later by us ('Journ. Chem. Soc.,' 1895, p. 190). A Jena tube of about 5 millims. internal bore was sealed at one end and the end slightly enlarged into a bulb. A gramme or two of the metal or alloy was then melted in the tube so as to fill the little bulb, and, while the metal was still liquid, an iron wire was pushed into the metal so that the end was immersed. When the metal had solidified, the iron wire became firmly fixed in the metal, and on account of the bulbous shape of the end of the tube the ingot was also fixed in the tube. The tube was then placed vertically, so that the lower end containing the metal was immersed in a bath of molten tin. The upper end of the wire projecting out of the tube was connected with a string passing over a pulley and stretched as before by a 50-gramme weight. A pyrometer was placed in the bath of tin and the temperature slowly raised, until the wire was pulled out of the metal. We called this the "pull-out" temperature. In some cases the end of the iron wire was bent into a little hook before immersion in the metal, in other cases the end was straight; both gave the same results. The heating was not, as a rule, so slow as in the bar-breaking experiments, the time of heating not, as a rule, exceeding

an hour. But in the case of Sn 27 a slow heating of several hours was tried ; it gave exactly the same pull-out temperature as a much more rapid heating had given.

The results for pure metals are stated in the third column of the table. They are in very fair agreement with the freezing-points. It is rather curious that the result for aluminium should be practically the same as the freezing-point. We then applied both methods to a few alloys. The results are shown below, the breaks by short



horizontal lines, and the pull-outs by round dots. It is evident that the alloys remain practically rigid up to temperatures well above our solidus, indeed nearly up to the liquidus. We infer from these results that the alloy gives way, not when the eutectic, or other mother-substance, between the primary combs begins to melt, but at considerably higher temperatures, when a good deal of the primary has itself been dissolved. The skeleton crystals of the solid phase must form a sufficiently rigid framework to prevent the breaking of the bar, or even the pull-out, although they are surrounded by liquid. From the nature of the equilibrium in the region between the solidus and the liquidus it is quite conceivable that the rigid scaffolding might become more infusible by the draining away of the liquid from the bars. Thus the temperature we were measuring was necessarily indefinite, but depended more on the melting-point of the solid phase than on the commencement of liquefaction.

The experiments failed to throw any light on the position of the solidus, but they have proved that the skeletons of the solid phase are, even at the temperatures between the solidus and the liquidus, rigid structures and not plastic masses. This fact, together with the photographs which indicate when the solid phase fills the ingot, entitles us to say that *below the solidus Ablcmdef, as drawn by us, the alloys, though they may be at a bright red heat, are rigid solids. Hence any crystallisations taking place below the solidus occur in an already solid and crystalline body.*

SECTION III.

THE MICROSCOPIC STUDY OF THE ALLOYS.

Identification of the Substances as seen in the Photographs.

The α Material.—This is the only substance present in unchilled alloys of the AB group. It is best seen in chilled ingots, appearing in the form of isolated combs or skeletons in the chills taken above the solidus, for example, in figs. 2 and 3A, where it is the darker part, and in fig. 6, where it is the somewhat lighter part. The α also forms the primary crystallisation in the BL alloys, as in fig. 10, in which the α is dark, and fig. 11, in which it is the lighter part.

The rectangular network of raised crystals that covers the outside of the ingots of all the alloys from A to L is entirely composed of α . This network is evidently the substance that solidified first, from which the mother-liquid retired in consequence of contraction due either to cooling or solidification. Both in the raised network, and in such sections as that of figs. 10 and 28, one sees the very rectangular character of the skeletons; where the angle of intersection of two branches is not a right angle it is very frequently an angle of 60° , though for obvious reasons this cannot always be the case. It will be observed that in all ingots chilled above bC , or even a little lower, especially in the slowly cooled chills, the individual lobes are rounded; this is well seen in fig. 6. On the other hand, in the lower chills this roundness is absent, having been succeeded by an almost flamboyant angularity, well seen in fig. 22.

The α is much richer in copper than any other material found in the alloys; it is, consequently, softer than the tin-rich material surrounding it, and polishing alone develops the pattern. In the pattern thus obtained, the copper-rich α is red or yellow, and the tin-rich material is pure white. Prolonged polishing accentuates the pattern by oxidising the α to a deep red or purple, and in the method of developing the pattern by heat-oxidation, the α is always oxidised more rapidly than the surrounding material. Ammonia or hydrochloric acid attack, dissolve, and generally darken the α , leaving the tin-rich matter surrounding it a pure silvery white, as for example, in fig. 3A. The acid solution of ferric chloride that we have used in etching the surfaces for the photographs we reproduce has a similar action on the alloys chilled well above bC , but when, as in the case of alloys chilled below this line the α is in contact with β , the α is paler than the β , this substance being often left very dark, as in figs. 15 and 16.

The α combs, at all events in ingots chilled below the solidus, often have another peculiarity; they are cored, that is to say, they contain an inner skeleton differing somewhat from the outer portions of the crystal. These cores oxidise more rapidly than the material outside them, and they are more rapidly attacked and darkened by

such re-agents as ammonia. Hence they are evidently richer in copper than the outer parts of the crystals. The most striking and certain way of developing cores is to take a polished surface of an ingot of Sn 5 that has not been chilled nor very slowly cooled, and to heat-oxidise it. Oxidation through orange, red, blue to the white stage may not develop much pattern, the α combs, which up to Sn 6 almost entirely fill the field, remaining of a flat tint; but when the white stage is reached, the outlines of the combs may be here and there marked by a trace of mother-substance which has remained an indigo blue. If, however, we proceed to heat further, a pattern of deep red or blue cores will develop itself, while the surrounding α , probably three-fourths of the area, remains white. This colour combination does not photograph well, but we sometimes get the core pattern with the first orange, in which case it can be photographed. We show the effect in the photograph of the unchilled Sn 1 (fig. 1).

As visible in unchilled alloys, these cores have been described by STEAD and by CHARPY. The cores are not divided from the substance outside them by a sharp line, but by a blurred or graded zone, so that under a high power there seems to be no boundary at all. Herein the cores differ from the α combs, the margin of which, whenever visible, is a sharp line even under the highest powers. The v.s.c. chill of Sn 4 at 775° , fig. 8, shows the character of the cores. They are only seen in the ABL alloys, and in the AB group they can, by slow cooling, be made very faint, or by rapid cooling very well marked. A decidedly slowly cooled ingot of Sn 4, chilled at 800° and etched with HCl, fig. 5A, shows the complete α combs with sharp margins, but the darker cores, due to the earlier α , are also evident. These developed in the interval of time between etching and photographing, and are due to the more rapid air-oxidation of the copper-rich parts. This ingot was not cooled with the extreme slowness of that of fig. 7, hence a few dark spaces can be found that may have been due to a trace of mother-substance liquid at the moment of chilling.

When the cores have been developed by etching, their intensity depends very much on the nature of the etch and on the time that has elapsed between the etch and the examination; for example, the s.c. chill of Sn 6 at 805° can be so treated as to show well-marked cores or none. We must conclude, therefore, that though the presence of cores indicates some difference of composition, yet the intensity of the visible core cannot be taken as a measure of the difference in composition existing between it and the matter outside it.

The β Material.—This is always considerably richer in tin than the α , hence when both substances are present it is easy to distinguish them. This can be done by heat-oxidation when the α oxidises first, by etching with strong ammonia when the α is darkened and dissolved and the β left a pure ivory white, or by etching with acid ferric chloride. Ferric chloride, the re-agent we almost invariably employ in preparing the surfaces for photography, acts on a mixture of α and β in such a way as to darken the β and to leave the α bright; this effect is well seen in figs. 15, 16,

and 31 (Plates 2 and 3). But there are cases, especially where β and α occur together, in which the β has undergone, during and after the chill, a change into an apparently fibrous condition which gives it a structure like that of asbestos, except that in the β there are several intersecting systems of fibres. This is well seen in fig. 21. When this change has become very pronounced in the β , ferric chloride does not produce so marked a contrast between the shade of the two materials, though, as the α is never striated, we have in this peculiarity another distinction between the two. In the chills of Sn 16 and Sn 17, chilled between the liquidus and the solidus, in which case α is absent and the β combs are embedded in a tin-rich mother-substance, the β is darkened by etching or ignition, and is rarely striated, while the tin-rich mother-substance remains a pure white.

The γ Mixed Crystals.—These occur as the primary crystallisation in all the DEFG alloys, provided they are chilled above the line *cdefG*. The γ combs are distinguished from the preceding by a well marked obliquity; instead of gridirons, they resemble sprays of foliage with rounded leaves. Heat-oxidation fails in this region, but HCl, with or without an oxidising agent, darkens the ground and leaves the γ combs pure ivory white (see Sn 38, fig. 79). The γ material is never found in unchilled alloys, for in cooling below the G temperature it breaks up into η and liquid.

The δ Material.—This substance, which we are strongly disposed to regard as the compound Cu_4Sn , occurs as the white tin-rich ingredient of the eutectic in all the BLCD alloys, provided they are unchilled or chilled below 500° (fig. 19). It also occurs in larger masses as a rosette or fern-leaf and in bars in the CD alloys, provided they were not chilled above the line C'D' (fig. 49A). In all these alloys heat-oxidation leaves the substance δ white when the copper-rich α present has turned to a deep brown, but a better contrast is obtained by etching with HCl, when the α is blackened and eaten away and the δ left untouched in the purest white. Ammonia has no action on this substance.

The η Material.—This occurs mixed with δ in the DE alloys when they have been chilled below the line D'E'. We believe it to be in general the compound Cu_3Sn . When in presence of δ the η can be distinguished by heat-oxidation, under which treatment the invariable rule holds good that the copper-rich δ oxidises and darkens faster than the tin-rich η , we thus get a pattern in which the η is white and the δ dark brown. But for photography a sharper result is obtained by etching with a mixture of HCl and FeCl_3 , when the η is blackened and the δ remains white (fig. 56).

In alloys containing more than 25 atomic per cents. of tin, at all events those chilled above 400° , the η is unattacked by etching re-agents, while the more tin-rich matter surrounding the η is eaten away and darkened. The η rarely forms crystal skeletons, but occurs in plates which are crystals bounded by plane faces; this is particularly well seen in the GH alloys, as in these the η has crystallised out of a liquid. If, however, these alloys are unchilled, or chilled below 400° , the η crystals are coated with H, as a result of the imperfectly accomplished transformation

$\eta + \text{liquid} = \text{H}$. Etching with HCl leaves such an alloy at first with the η and H both pure white and the mother-substance dark, but in time the η darkens through oxidation, while the border of H remains of the purest white. There is thus no difficulty in distinguishing the two substances (fig. 92).

The H Material.—This substance appears to resist completely the action of even the strongest HCl, or of mixtures of the acid with ferric chloride. It also resists the slow oxidising action of the air much better than η , remaining a very pure white for days or months. We find it bordering the η , as in the lower chills of Sn 29, in round or oval spots, as in the prolonged mercury-boiled ingots of Sn 50, and in definite crystalline shape in chills of Sn 90 (fig. 89).

The Evidence from the Microscopic Structure of the Chilled Alloys.

The AB Alloys.—As will be seen in the cooling curve of Sn 4, these alloys present but one halt in their cooling curves, so that, as far as such evidence can be trusted, they appear to solidify in one continuous process; we hope that the micro-photographs will be found to confirm this view. It is evident that if Sn 2 and Sn 4 both solidify in this manner, then the solid in these alloys cannot be a pure body, but must be a solid solution.

Sn 1. 1.85 per cent. by weight of tin (Plate 1, fig 1).

In unchilled and moderately slowly cooled ingots polishing, even without etching or ignition, brings out a pattern of long slender combs well seen with a power of 10 diameters. This pattern is probably due to the more rapid oxidation of the first formed α , which was very rich in copper. Heat-oxidation develops the same combs, which do not fill more than three-quarters of the area. The lobes of a comb are not isolated, but form a continuous skeleton. In every case a higher magnification makes it evident that these combs are not sharply divided from the material round them, but fade softly into it. In fact, the margin of a comb does not mark an abrupt change in the process of crystallisation. This important point became very evident in a section etched electrolytically by being made the anode in a cell containing dilute sulphuric acid. This method of etching revealed the margins of the real skeleton crystals. They have sharp edges, and occupy at least 99 per cent. of the area. It is thus evident that the combs brought out by polishing or ignition, as seen in fig. 1, are cores to the real skeletons of α , these latter being so closely packed that it is only here and there that we can detect their boundaries. Thus, in spite of the fact that the cores are somewhat richer in copper than the outside layers, we feel justified in stating that the alloy solidified in one continuous process. Moreover, the cavities between the real margins of the combs show that these combs, which so nearly fill the field, are primary, that is to say, were formed *during* the process of solidification, the small cavities being caused by the presence of gas or by the

retirement of the mother-liquid during the contraction accompanying solidification. The coreing is evidently due to imperfect adjustment of the α to the liquid, a result likely to occur during the solidification of a solid solution, and is a strong confirmation of the view that the α crystals vary in composition.

The chills of Sn 2. 3.67 per cent. by weight of tin.

Chills were taken at the following temperatures:—1025°, 982°, 957°, 932°, 907°, 882°, 800°, 770°; all but the first of these were very slowly cooled before the chill.

The upper chill was not cooled with any precautions to ensure slow cooling, being allowed to cool in the furnace after the gas had been extinguished, but the others were very slowly cooled from the freezing-point down to the moment of chilling. The total time required for an ingot to cool from the freezing-point down to 770° was eight or ten hours, and for the upper chills the times were proportionately less.

Sn 2. *Chilled at 1025° (Plate 1, fig. 2).*

The ingot was compact, but showed some signs of granulation, on account of its semi-liquid state at the moment of chilling. It was cut in two, polished and etched with ferric chloride, but the pattern was well seen after the polish. It consists of copper-rich α combs, dark in the figure. These sometimes stretch half across the face of the ingot and are well seen under a magnification of 5 diameters. They fill about one-third of the area, and their margins are sharply divided from the mother-substance round them. They are primary crystals, the matter which was already solid at the time of chilling. The material of these combs appears to be uniform throughout, it being impossible to develop cores in them. The magnification of the photograph is too high to show the great symmetry and length of the combs, but it makes it just possible to distinguish the network of much smaller combs in the ground. These are rectangular, and in all respects except size resemble the large combs. They are evidently chill primary, that is, α which crystallised *during* the rapid cooling of the chill. In the interstices between both sets of combs there is a small amount of a quite different material. This is the true mother-substance, a white tin-rich body that solidified last of all.

Sn 2. *Chill at 982° (not reproduced).*

This was cooled very slowly down to the moment of chilling. Like all which follow, it was a compact ingot completely covered externally with a rectangular network of α combs in relief. It was cut and polished. Prolonged polishing develops an oxidation pattern of large plump copper-rich α combs, filling at least nine-tenths of the area. These show no cores. They are surrounded by a network of a white tin-rich mother-substance, containing minute copper-rich chill primary.

The growth of the large combs, which now so nearly fill the field, shows that the process of solidification has made great progress since the previous chill, but the minute combs of chill primary are an evidence that the crystallisation of the α was not quite complete.

Sn 2. *Chilled at 957° (fig. 3A and fig. 3).*

The surface, when examined under the usual normal illumination, was full of uniformly dark α combs in a slender network of pure white. It is evident that before the moment of chilling the solid α had grown until it almost filled the ingot. No cores can be detected (fig. 3A). The photograph we reproduce, in fig. 3, was taken with oblique illumination in order to show the differences in orientation that exist in the different grains, or filled-out skeletons, that make up the ingot. A change in the direction of the incident light would have completely altered the disposition of light and shade. By this method of illumination the mother-substance, which does not scatter much light, is less evident. The three figures, 2, 3, and 3A, taken together, illustrate excellently the growth of a granular solid from skeletons. Figs. 3 and 3A are photographs of the same portion of the surface of the ingot.

Sn 2. *Chilled at 932° (not reproduced).*

As usual in this group of alloys, the white substance between the combs becomes visible by polishing alone. HCl turns the combs a rich copper colour and leaves the mother-substance white. It is now present in smaller amount, not in a continuous network, but as rows of isolated dots and short lines, and in the three-branched patches to be found where three lobes of α meet. The amount of mother-substance was estimated by counting the squares of a ruled grating. Several independent determinations gave values between 2 and 3 per cent. for the fraction of the whole area occupied by this white mother-substance. A higher power still shows the merest trace of chill primary. The α combs must be very uniform, for a prolonged polish leaves them a uniform purple, and by no method of etching can cores be developed in them. It may be mentioned here that a slowly cooled chill at 940° was heat-oxidised to the second series of tints, but at no tint did any trace of cores appear. This is the most severe test of homogeneity in the α that we know of.

Sn 2. *Chill at 907° (not reproduced).*

The whole section of the ingot is similarly oriented, and it evidently consists of one crystal. We can now see cores in the α .

Sn 2. *Chill at 882° (fig. 4).*

In this ingot the specks of tin-rich mother-substance are reduced to much less than half a per cent. of the whole area. Our photograph shows a very uniform surface

almost free from cores, but some weeks after etching, large faint cores were found to have developed, so that the α is not absolutely uniform.

However, it appears evident that, with a very little allowance for lag in the transformations due to too rapid a cooling, we are entitled to say that from a chemical point of view the alloy Sn 2 solidifies to a completely uniform solid at a temperature near 900° . The resulting solid must therefore be a solid solution, or, what is the same thing, an isomorphous crystalline mixture of copper and tin, or of copper and some compound of the two metals. The process of solidification revealed by these chills, in which the solid phase differs considerably in tin content from the liquid phase, but gradually absorbs it, is an exact verification of ROOZEBOOM'S theory; we must infer that the α combs seen at the various stages of the solidification are all solid solutions.

The absence of cores in the higher chills must be interpreted as indicating that the adjustment between the successive solid and liquid phases was, at these high temperatures, a fairly perfect one, but it is not improbable that, with still slower cooling, the mother-substance would have disappeared at a somewhat higher temperature. It is obvious that while each α crystal is bathed on all sides by mother-substance, it will be favourably situated for maintaining its uniformity by diffusion from the margin to the centre; but when the solidification has so far progressed that the crystals touch each other over a great part of their surface, the remaining drops of mother-liquid will be very liable to react with the margins only of the large combs, and to leave the cores of the crystals unduly rich in copper. This retardation will also have as a result that the complete solidification of the alloy will occur at an unduly low temperature. We shall find examples of this later on in spite of all our efforts to attain perfect equilibrium by slow cooling.

Sn 2. *V.s.c. chill at 800° (not reproduced).*

This is a beautifully uniform alloy. There is no mother-substance. The polished and etched surface contains two patches belonging to two crystals, distinguished by reflecting light differently. These two touch along a continuous line without a trace of mother-substance between them. We have here a very good proof of the solid solution theory, for otherwise, what has become of the tin-rich matter? However, when freshly etched with HCl, a lens shows large cores differing very little from the rest of the matter round them, so that the process referred to above has occurred. These cores are lost under the microscope.

Sn 2. *V.s.c. chill at 770° (fig. 5).*

This consists of two or three homogeneous grains of α , fitting closely together without mother-substance. There is a trace of vague coreing.* We do not reproduce

* The striations visible in the lighter grains of α in fig. 5 are due to scratches, which are almost inevitable in polishing this very soft material.

the chills at 800° and those below 770° , as the characters of a uniform solid solution are more conclusively exhibited by Sn 4.

The unchilled very slowly cooled ingot (not reproduced).

This ingot was examined to ascertain if Sn 2 underwent any changes in the solid when cooled below the bC line. The polished surface, after etching, consists of several irregular rounded polygons, dovetailing into each other without a trace of mother-substance. These show the rotation effect. There is little or no indication of cores.

Sn 4. *7.2 per cent. of tin by weight.*

This alloy, containing about 7 per cent. of tin, affords a more striking example of solid solution than the preceding.

Sn 4. *Chilled at 990° (not reproduced).*

The ingot was granulated by the operation of chilling, but it was possible to polish a good face on it. It contained the same pattern as the highest chill of Sn 2, that is, large primary combs of α , filling perhaps a quarter of the area, a good deal of chill primary, and a small amount of white mother-substance. It is clear that the large α combs were the only parts solid before the chill. As this closely resembles the upper chill of Sn 2, we do not reproduce it.

Very slow-cooled chills were made at the following temperatures:— 900° , 835° , 775° , 700° , and one ingot was slowly cooled down to the melting-point of tin. All these proved to be compact ingots, and were completely covered with a raised network of rectangular α combs. Besides these, other ingots were chilled after a somewhat more rapid, but still a slow cooling.

Sn. 4. *The chill at 900° (fig. 6).*

This contained large almost coreless α combs, filling about 90 per cent. of the area; in the interstices between the large combs there is a very beautiful crop of chill primary embedded in a little of a tin-rich mother-substance, but a higher magnification is needed to show the chill primary. At the time the photograph was taken the α , though much more oxidised than the ground, was blue and hence actinically active. Consequently the contrast between the two materials is weak and reversed in the photograph.

Sn. 4. *Chill at 835° (not reproduced).*

This contains very little, not more than 1 per cent., of mother-substance, and the α combs are so fused together that their margins cannot in general be distinguished,

except by the different grains reflecting light differently. The α is not, however, homogeneous, for after a time a pattern develops on the etched surface consisting of dark copper-rich combs. These are similarly oriented throughout a grain and are not separated from the α outside them by a sharp margin. They are evidently cores produced by the imperfect assimilation of the last drops of liquid. The appearance of this chill leads us to think that Sn 4 is completely solid at all temperatures below 830° . Thus the microscopic examination of chills of Sn 2 and 4 gives us, at all events approximately, two points on the solidus Ab.

V.s.c. chill at 800° (fig. 7).

This contains no tin-rich mother-substance (an estimate made the amount less than one-tenth per cent.), but no ingot was obtained free from cores, although in the most perfectly slowly cooled ingot, which we reproduce in fig. 7, these cores can barely be detected. In order to show the character of the coreing in the α combs, we give in fig. 5A a photograph of an ingot, also chilled at 800° , after a cooling that was slow, but not quite so slow as that of fig. 7. The combs have grown so as to form three grains reflecting light differently, but in two of the grains there are well-marked copper-rich cores. The difference between the soft indefinite boundaries of the cores and the sharp margins of the combs is characteristic. The very dark angular spaces between the combs were cavities from which the mother-substance had receded during the cooling.

Sn 4. *Chill at 775° (fig. 8).*

In the best slowly cooled chills there is no mother-substance, the patches that represent separate α crystals dovetailing into each other with no interstitial matter. But even in the most slowly cooled ingots there are cores in the α , and in ingots rather more rapidly cooled there is a complete pattern of such cores. Even in the presence of cores, if the cooling before the chill has been at all slow, there is extremely little of the tin-rich mother-substance. The photograph we give closely corresponds to the above description.

Sn. 4. *Unchilled (fig. 9).*

The ingot fig. 9, cooled slowly down to the melting-point of tin, is important, as it is quite free from the brilliant white tin-rich patches of the C' complex that form such a well marked feature in the Sn 6 similarly treated. This slow-cooled Sn 4 shows no cores, and consists of several patches fitting closely together and only distinguishable by the different angles at which they reflect light. The small black spots, a millimetre or two across, seen in the photograph are holes in the alloy. This photograph closely resembles photographs of pure platinum and pure gold that have been

published by Mr. ANDREWS and others. We thus see that the whole of the 7 per cent. of tin has been absorbed into the α .

We think that we have demonstrated that the condition of this solid alloy, provided that it has been cooled so slowly that the solid and liquid phases have always remained in equilibrium, is finally that of a uniform solid solution. This uniformity is no doubt rarely attained in practice, a not specially slow-cooled chill at 740° (not reproduced) more nearly representing the usual state of an ingot soon after solidification. In this there is a complete pattern of cores forming combs about the size of those on the outside of the ingot, and evidently coincident with them. These merge into another material, which is later formed, α . Finally, sharply divided from all the α , there is a very perceptible amount of mother-substance, which, however, was solid at the moment of chilling. Owing to the action of the ferric chloride etch this mother-substance, which is β , has become black. It has, strictly speaking, no right to be present in an alloy of the AB group, but is the result of imperfect transformations. Thus we see that the soft bronzes of the AB group, unless very slowly cooled, are likely to be non-homogeneous in two complementary ways—the α grains may be cored with a material richer in copper than the mean of the alloy, and between the grains there may be a little of a hard, brittle tin-rich substance.

Repeated rolling and annealing at a sufficiently high temperature ought to bring about a re-action between the cores and the tin-rich substance, and so promote a real chemical homogeneity which would be impossible in the alloys with more tin. The indication of the cooling curve that these alloys solidify by one continuous process is, as we have shown, confirmed by the microscope.

The BL Alloys.—These alloys show at least two halts in their cooling curves, the first at the freezing-point, the second at 790° , the temperature of the line $b1C$, a halt common to all the group.

We now observe a different final structure, however slow the cooling may have been. In the slowly cooled and unchilled alloys the α combs no longer fill the whole area, but are surrounded by a new type of mother-substance, the complex C' . This is well seen in the photograph of the slow-cooled Sn 6 (fig. 12), where the angular patches of pure white are derived from a tin-rich material that was left liquid at the termination of the α crystallisation.

Ingots of Sn 6, chilled above the C temperature, that is, above 790° , resemble the corresponding chills of Sn 4 in containing large primary combs of α surrounded by chill primary, the whole being imbedded in a tin-rich matrix. The chill at 966° , fig. 10, is a fine example of this structure. Here the large α combs are remarkable for a great rectangular symmetry, and are quite free from cores. The ingot was not specially slow-cooled.

Sn 6. *V.s.c. chill at 805° (fig. 11).*

This has large combs of primary α and at least 10 per cent. of mother-substance

containing chill primary, the whole of this 10 per cent. having been liquid at the moment of the chill. This should be compared with the chill of Sn 4 at 800° , in which there is practically no mother-substance. The α in the chill of Sn 6 is remarkable for the deep cores that appear in the combs some time after etching, although in the figure we reproduce, which was put for a moment on the polishing wheel after etching for the purpose of simplifying the pattern, no cores are visible, and the combs are, on the whole, lighter than the mother-substance.

Sn 6. *S.c. chill at 775° (not reproduced).*

This shows about as much mother-substance as the preceding, but this mother-substance is now β , which had solidified at the C temperature and is consequently darkened by the FeCl_3 etch.

Sn 6. *Unchilled, v.s.c. (fig. 12).*

This ingot affords the most striking evidence that Sn 6, when solid, is a complex. Here, in the slow cooling through the C' temperature of 500° , the small amount of β between the α crystals has broken up into the C' complex of $\alpha + \delta$. As the white δ is predominant in these patches, they appear after the ferric chloride etch as a very brilliant white, while the α is darkened. The plate shows two large crystals of α differently oriented, and, therefore, reflecting light differently. Inclosed in them, in the form of the usual very angular patches of a scanty matrix, are several per cent. of the white body. (The striations in the lighter grain of α are due to imperfect polishing.)

In order to show the character of the C' complex, we give a more highly magnified patch of this mother-substance taken from the same ingot (fig. 13). Here it is evident that the patch is margined by a homogeneous band of the white δ , but that inside this border the δ is mixed with lines and spots of a darker substance, which proves on examination with an immersion lens to be identical with the α surrounding the patch. *As the slow-cooled Sn 4 contains only α , while Sn 6 has several per cent. of this complex, we have placed the boundary between the two groups at Sn 5.*

Sn 6 may be regarded as the first of the BL group of alloys, the harder gun-metals, which when solid are a complex of two phases; but with increasing content of tin, as in Sn 9, the characteristic features of the group show themselves more plainly, the α decreasing in amount, and there being a corresponding growth of β or, in the lower chills, of the C' complex, and therefore of δ .

Sn 9. *15.6 per cent. of tin. Chill at 880° (fig. 14).*

This was a very much granulated ingot, the result of throwing the semi-liquid alloy into water being to blow away the still liquid part and to leave the skeleton crystals of α as a mass of little fir trees. A portion solid enough to grind down and

polish was found with difficulty. A section etched with FeCl_3 is reproduced. The magnification is too high to show the large α combs well, but individual lobes are seen lighter than the ground. The section contains rounded α combs filling rather less than half the area, and immersed in the mother-substance are the minute combs, also of α , that were formed during the chill. On heat-oxidation the large combs turn red more rapidly than the minute ones, presumably because the large ones are richer in copper. It can be seen that the minute combs sometimes grow out from the margin of the large ones. We have here a very good example of the result of chilling a semi-liquid alloy.

Sn 9. *Slow-cooled chill at 805°* (not reproduced).

This chill shows very large and symmetrical primary combs of α , but their area is much less than in the corresponding chill of Sn 6. A ferric chloride etch leaves the α combs bright and darkens the mother-substance, but in the heart of each patch of mother-substance there is often an irregular line of pure white, which a high power shows to be a final tin-rich residue, the last matter to solidify. The alloy gives one the impression of having been chilled rather below the intended temperature. The rounded character of the lobes or teeth of the combs is noticeable.

Sn 9. *Slow-cooled chill at 775°* (not reproduced).

In the interval of several hours that elapsed between this chill and the preceding the re-action $\alpha + \text{liquid} = \beta$ has been going on, the original α combs have been much modified and somewhat diminished in amount, and the surrounding β shows the characteristic striation pattern. We do not give photographs of these two ingots, because the important change produced in the alloys by the C re-action is better seen in such an alloy as Sn 12.

We give, however, in fig. 15, a ferric chloride etch of an alloy not quite so slowly cooled and chilled at 777°. This is a typical example of a ferric chloride etch of an α and β complex, the α combs being light and the β dark. In the heart of the β one can see threads of a white tin-rich material that must have been liquid at the moment of chilling. The presence even of this minute amount of liquid at 777° is a result of a somewhat too rapid passage through the C temperature. Polishing this and similar alloys without etching leaves the α a bright copper colour and the β a pure tin white, and a strong ammonia etch has the same effect, but for photographic purposes we prefer the effect of ferric chloride. The β in this ingot does not show striation, it is apparently uniform.

Sn 9. *V.s.c. chill at 546°* (figs. 16 and 18).

All the chills down to above 500°, for example that at 546° (fig. 16), are like the above, and if there is any growth of α in the solid alloys, it is not enough to be

detected, except, perhaps, by an increasing angularity in the margins of the combs. Moreover, the action of ferric chloride on all these alloys is the same, the α remains bright and the β is turned dark, but seems to remain homogeneous. But at 500° the β breaks up into the C' complex of $\alpha + \delta$, and the action of the ferric chloride is reversed, as it now darkens the α and leaves the δ a pure white.

Sn 9. *V.s.c. chill at 470° (figs. 17 and 19).*

We here see the transformation, the α has become dark and the β has broken up into a pearlite or solid eutectic. As this transformation is common to all alloys containing β when they cool slowly through the C' temperature of 500° , we give in fig. 18 a more highly magnified patch of β from an ingot of Sn 9, very slowly cooled to 546° and then chilled. It will be seen that although there is a narrow line of white, probably δ , separating the α and the enclosed patch of β , yet the latter is patternless and, as usual with a ferric chloride etch, darker than the α surrounding it. This should be contrasted with the patch of the C' complex taken from the alloy chilled at 470° and also etched with ferric chloride, fig. 19. Here we see that the border of δ has become very wide and that the interior of what was the patch of β has broken up into a complex of δ and a copper-rich body which so closely resembles α that we give it the same name. These two photographs were both taken at a magnification of 280 diameters.

This transformation $\beta = \alpha + \delta$ is an exothermic one, and gives rise to the halt in the cooling curve that we first see in our cooling curve of Sn 10 at 500° , though, as we have shown (fig. 13), the same transformation can be detected by the microscope even in Sn 6. In fact, this change of solid β into a complex occurs at or a little below 500° in all alloys from Sn 6 to Sn 20. It is marked in our diagram (Plate 11) by the broken line $b'C'XD_2$. It must be borne in mind that at this temperature the alloys are rigid solids.

Sn 12. *20.3 per cent. by weight of tin.*

The solidification of this alloy begins, as in the cases already discussed, by the crystallisation of α combs, but when these cease to form, on account of the residual liquid having reached the C composition, there is much more of the liquid than in the case of Sn 9, and hence the *re-solution* of the α during the transformation at the C temperature is more marked. This is well seen in the cooling curve of Sn 12, in which the C halt is a prolonged one, but it is made evident in another way by an examination of the ferric chloride etch of the v.s.c. chills at 805° and 775° (figs. 20 and 21). The first of these shows us the maximum possible amount for this alloy, of primary α , and also a minute dark chill primary which is probably β . The lower chill, made after a very slow cooling of several hours through the intervening 30° , shows much less α , and what is left has a disjointed look, as if the combs had been

subjected to the action of a solvent (fig. 21). Moreover, the ground has entirely changed, being now full of the striation characteristic of β . We may regard the s.c. chill at 775° as giving the minimum proportion of α to be found in this alloy, for as the temperature falls from C to C', that is, from 790° to 500° , the α grows in amount at the expense of the solid β . The alloy chilled at 550° and etched with ferric chloride, fig. 22, illustrates this growth of the α out of a solid solution. This particular ingot was not cooled before the chill so slowly as were the preceding, and therefore the detail is somewhat smaller, but the ratio of the white α to the darker β has evidently increased enormously, being greater than in the chill at 805° . The peculiarly pointed and flamboyant character of the α which has grown out of the solid β should be compared with the rounded lobes of the α combs in the chill at 805° . The general character of the pattern in the chill at 550° resembles that in an unchilled alloy, except that the unchilled alloy, or one chilled below 500° , would, with the same etch, have the α dark and the ground a brilliant white. The ground, moreover, in the chill at 550° is uniform β , but in the unchilled alloy it would be the C' complex.

Sn 13.5. 22.5 per cent. by weight.

This alloy is important, because it fixes the point l at which the amount of α formed above the C temperature is just enough to re-act with the whole of the residual C liquid in order to form β ; in fact, the re-action $\alpha_l + \text{liquid}_C = \beta_l$ can complete itself in this alloy.

Sn 13.5. S.c. chill at 805° .

This has less α than the chill at the same temperature of Sn 12, but otherwise it closely resembles it; hence we do not give a photograph.

Sn 13.5. Chills at 775° .

If an ingot of Sn 13.5 be cooled very slowly through the C temperature, so as to be maintained for several hours at or very near 790° , the α is entirely dissolved and we obtain an ingot composed wholly of β . In the photograph (fig. 23) one can see a single minute spot of α that has survived, and is paler than the β . But this β , after chilling and etching with ferric chloride, has the well marked striation pattern. Considerable light is thrown on the transformation of the α into β by the examination of some ingots which were cooled somewhat too rapidly through the transformation point to allow of a complete solution of the α . A chill at 765° , etched with ferric chloride (fig. 24), shows the effect well—there is still a little α in slender combs and crosses, and these, though isolated from each other, are so symmetrically arranged as

to make it evident that they once belonged to larger skeletons. Round these, and enveloping them symmetrically, is a complete system of fat rounded combs of β , which sometimes stretch right across the surface. Outside this β there is matter that we must suppose was not solid at the moment of chilling. The photograph does not show striation in the β , but a somewhat deeper etch and a higher power brings out the striation perfectly. A photograph (fig. 25) at 45 diameters shows the striated β round the lobes of α , as well as the tin-rich material outside the β , material that was liquid at the moment of chilling. One can also see in one corner something which looks very like chill primary of β . The enormous growth of the α out of the solid β at lower temperatures can be best illustrated by the two following photographs, both at the same magnification. The first is a chill at 740° (fig. 26), that was not slowly cooled enough to dissolve quite all the α , a very little of which can still be seen in slender lines and rows of dots. It must be remembered that even this could have been dissolved by a slower passage through the C temperature. Contrast this with the other, a chill at 558° . In this (fig. 27) the enormous increase in the α and the jagged appearance of the crystals are well marked. There is no doubt that this growth of α took place in a rigid solid.

It will be noticed that in the chill at 558° there is no residue of the striation effect so marked in the very slow-cooled chill at 775° . This is one reason why we think that the striation does not exist in the β until it has cooled below 500° . We think that as the chilling alloy cools rapidly through 500° a partial breaking up of the β sometimes occurs and shows itself in the striation pattern. The two phases into which the β breaks up through the imperfection of the chill may not, however, differ so much in composition from each other as do the α and δ of the slowly cooled C' complex, for ignition which readily distinguishes between α and δ does not readily bring out the striation even when we know it to be on a large scale. Another point is that the striation does not show itself in the chilled β of Sn 16 or 17, which has never been in contact with a nucleus of α . Under such circumstances we suppose that the state of supersaturation is more easily maintained. This view that the striation does not appear in the β until it has cooled down to 500° is of some importance, as otherwise we are hardly entitled to speak of β as a uniform solid solution. Another argument is that now and then we find a chill containing unstriated β , for example the patch of β of Sn 9 chilled at 546° and shown magnified 280 diameters. This is quite free from striation, as are all the other patches in the section (fig. 18).

The very symmetrical way in which the β grows round the α (see fig. 24) during the $\alpha + \text{liquid} = \beta$ reaction, suggests the view that the two bodies may be isomorphous. Moreover, the primary combs of β seen in the chills of Sn 16 and Sn 17, taken between the solidus and liquidus, are indistinguishable in form from α combs, although they have never been in contact with that body. The facts already known with regard to solid solutions of saline mixtures would not have led us to expect such

a case of isomorphism in what may be called two conjugate solid solutions, but the great frequency of the regular system in the crystallisation of metals renders it more probable than it would otherwise be.

The LC Alloys.—This small group, covering the atomic percentages from Sn 13·5 to Sn 15·5, consists of alloys which polish to a yellowish-white. The unchilled alloys are compact, hard, and tough.

We detect three well marked halts in the cooling curves of this group, one due to the latent heat of crystallisation at the freezing-point, the second to the heat evolved at the C temperature by the reaction $\alpha + \text{liquid} = \beta$, the third at the C' temperature, due to the breaking up of solid β into the C' complex, a reaction which we think is represented by the equation $\beta = \alpha + \delta$.

There must also, both in these and in the preceding group, be heat evolved when the temperature of the cooling alloy crosses the lC' line and the crystallisation of new α in large crystals out of the solid β commences; but this is a gradual process, and the heat evolved at any one temperature is apparently not enough to produce a perceptible effect on the line of the cooling curve.

Like the preceding group, these alloys commence their solidification by the formation of α combs, but when the temperature has fallen to that of the point C and the α combs cease to form, there is more than enough liquid to transform all the α into β ; hence, with sufficiently slow cooling, ingots chilled between lC and the solidus lc will be found to consist of β combs immersed in a tin-rich mother-substance, while, when the temperature has fallen to a point on the solidus, the ingot will be a uniform mass of β . The ingot will then remain uniform until the line lC' is reached, when the solid β will have cooled to a point at which it is saturated with α , and that body will separate out in large crystals; the amount of these increases until the C' temperature is reached, at which temperature the β becomes also saturated with δ , and the eutectic separation commences. The two bodies, α and δ , will now crystallise simultaneously and form the pearlite eutectic, similar to that in fig. 19. The chills of Sn 14 afford good illustrations of these changes.

Sn 14. *Chilled at 800°. V.s.c. (fig. 28).*

These ingots are much distorted by granulation, but are compact enough for polishing. The simplest pattern is that developed by strong ammonia. This re-agent dissolves and darkens the α combs, and leaves the ground a very uniform dead white. One sees about 10 per cent. of α , arranged in very rectangular combs. The lobes are very rounded and often separated from each other, forming rows of rounded dots. A ferric chloride etch, fig. 28, shows the same combs light on a dark ground, and the ground is now seen to contain a good deal of dark chill primary, which is probably β . In essentials, the pattern resembles that of Sn 12 chilled at 805°, with the exception that in the chill of Sn 14 there is less α .

Sn 14. *Chills at 780° and 772°* (not reproduced).

These were not very slowly cooled chills, consequently the alloy cooled too rapidly through the C temperature to allow of the complete absorption of the α . As a result, the ammonia etch shows a few very isolated dots of α on a white ground, and the FeCl_3 etch shows large combs of β symmetrically including the dots of α , the β being surrounded by a bluish-white tin-rich mother substance that was liquid at the moment of chilling. In the 772° ingot the imperfect transformation had the effect of depressing the temperature of complete solidification, for a v.s.c. chill at 775° shows the alloy completely solid at that temperature. The effect of the survival of α , through too rapid cooling, is so well shown in the photograph of Sn 13.5 at 765° (fig. 24), that we do not reproduce the Sn 14.

Sn 14. *V.s.c. chill at 775°* (not reproduced).

This, like all the chills of Sn 14, except granulated ones, is coated externally with a raised rectangular network of α or β combs, but the etched surface of the interior of the ingot shows no trace of combs. It is a compact mass of β , probably one crystal, containing no α . The striation in the β did not come at all readily, several etchings and polishings having been made before it was noticed. This is quite free from α , and closely resembles fig. 23.

Sn 14. *S.c. chill at 766°, FeCl_3 etch* (not reproduced).

A compact surface of striated β . No combs visible and no α . The chill at 740° is exactly similar.

Sn 14. *Chills at 715° and 705°.*

Consist of β striated as before, with polygonal boundaries beginning to show, though they are not a marked feature and have to be searched for. The direction of striation changes abruptly at a boundary.

Sn 14. *Chills at 675°* (fig. 29).

We have two; one a very slow cool (fig. 29). This contains only β , striated, but otherwise uniform, without polygonal boundaries or a trace of α . The other ingot is similar, except that there are a few specks of α , which is probably a commencement of the new crystallisation out of the solid that is so well marked in the next chill.

Sn 14. *Chill at 647°. NH_3 etch* (not reproduced).

This, at one end of the ingot, contains a few per cent. of the new α , but most of the surface is quite blank. No doubt, if etched with FeCl_3 , this ingot would have

shown striation in the β . The ingot appears to have been chilled almost exactly on the curve lC' .

Sn 14. *Chill at 600°. V.s.c. chill (fig. 30).*

We give a photograph of this ingot (fig. 30). The new α is seen as a pure white crystallisation, larger than the striation pattern and quite different in character from it. In this ingot we are evidently below the lC' line, but not far below it, as one end of the ingot, the larger half, is quite free from α . This portion is not shown in the photograph. The photograph brings out a very important point, namely, that in the immediate neighbourhood of an α crystal the β is dark and unstriated. We shall return to this point.

The chills at 675° and 600°, together with the chill of Sn 15 at 600°, determine a point on the lC' line with considerable accuracy, for this line separates the region in which the β is free from α from that containing the new α which has crystallised out of the solid β .

Sn 14. *The chill at 530°, v.s.c. chill (fig. 31).*

Here we have, as might have been expected, a much more abundant and large α crystallisation. Moreover, the β , except in one spot far removed from α , has not broken up into the striation. This phenomenon, seen also in the preceding chill, is one reason, perhaps the most conclusive, for the truth of our view that the striation did not exist in the β at temperatures above 500°, but is a change produced during and sometimes after the chill, and due to the fact that the β of Sn 14 is so rich in copper that at low temperatures it is in a very unstable state and readily breaks up into a copper-rich and a tin-rich phase, thereby producing the striation. It is clear that β slowly cooled below the lC' line, out of which α has already crystallised, will be less supersaturated and therefore more likely to bear a low temperature unchanged than the β chilled above the lC' line. For the same reason Sn 9 chilled at 546° contains a mother-substance of β unstriated. We shall see that the β of Sn 16 and 17, necessarily poorer in copper, is much more stable and rarely striates. We are not disposed to think that the two phases forming the striated β are identical with the α and δ of an unchilled alloy.

Sn 14. *The chill at 470°, v.s.c. chill (fig. 32).*

Here, as usual, the residual β has broken up into the C' complex of α and δ ; there is no β left in the ingot, consequently the α is darkened and the δ remains a pure white; a good example of the complete reversal in the etching that occurs when we pass below 500°. A close inspection of this eutectic shows that it differs very much from striated β , and could hardly have arisen out of it. This is another argument for the view that striation did not exist in the β at temperatures above 500°.

Sn 15.

The higher chills resemble those of Sn 14.

Sn 15. *Chill at 775°*, s.c. (not reproduced).

The ingot contained no α , but consisted of large β combs in a white tin-rich mother-substance. A glance at the diagram shows that this is what we should expect. The β was at first not striated, but an ignition to a temperature of about 300° developed striation when the surface was again etched.

Sn 15. *Chill at 600°*, v.s.c. *chill* (fig. 33).

This is important. It consists of several large polygons differing, on account of orientation, very much in brightness. There are also fainter polygonal boundaries, but these which do not separate regions of different brightness, may be cracks. There is no α , and the β is not striated. The ingot is undeniably a uniform solid solution. We have no other chills of Sn 15.

The fact that in this group of alloys all the primary α is absorbed at 790°, and that only at lower temperatures does α again crystallise, accounts for the singularly disjointed appearance of the combs seen in the unchilled alloys. The photograph of Sn 12, published in our paper in the 'Proceedings,' vol. 68, shows this peculiarity, but in slowly cooled ingots of Sn 14 it is much more marked. For in Sn 12 a little of the primary α has persisted, and so decided the orientation of the new α , while in Sn 14 there were no such nuclei, and the character of the primary α combs is not in the least reproduced in the later crystallisation. The chills of Sn 14 at 530° and 470° illustrate this when compared with the chill at 800° (fig. 28).

Sn 15.5. 25.5 *per cent. by weight.*

The alloy is important, because at this composition occurs the angle C in the liquidus, and also, apparently, the eutectic angle C' of the curve lC'XD'E', which is to the solid solutions β and γ what the liquidus is to a liquid. The cooling curves of Sn 15 and Sn 16 enable us to see what the cooling curve of Sn 15.5 would be like. The short upper flat of 15 would be absent and also the long flat at C, because there is neither crystallisation of α at the freezing-point nor an isothermal transformation of α into β . Instead, the commencement of solidification is marked, as in Sn 16, by a very gradual slope due to the heat evolved in the continuous reaction between the solid β and the remaining liquid, a reaction determined by the solidus *lc* and the liquidus CD, the process of solidification being quite similar to that of the AB group. The solidification having completed itself at about 740°, the cooling curve becomes steeper and corresponds to the cooling of a solid with no evolution of latent heat ;

but at 500° , or thereabouts, the cooling curve has a flat corresponding to the formation of the solid eutectic C' . Thus the cooling curve has only two singularities.

Sn 15.5 *chilled at* 767° , 760° , 759° (not reproduced; see fig. 34).

These, when etched with FeCl_3 , show a pattern of β combs on a lighter tin-rich ground, the pattern resembling that of Sn 17 chilled at 731° , though not quite so regular. The β combs in shape and arrangement closely resemble α combs, indeed, we think the two bodies are isomorphous. But these combs of β are distinguished from α in two ways, they etch out in polishing much more readily and deeply than do α combs, and in Sn 15.5 they can be made to show the striation pattern, though when originally examined they did not show it. After the first examination they were ignited, a process which brings out the combs dark brown on a white ground. A repolish and an etch with FeCl_3 now shows that many of the lobes have developed a large striation pattern identical with that in the β previously discussed. We give a photograph (fig. 34) of this effect at 750° , because it links up the β previously described to the unstriated β combs we shall find in the succeeding alloys. The photograph also shows chill primary of β immersed in the white tin-rich mother-substance. In the chill at 750° , which was not specially slowly cooled, the combs fill about three-fourths of the area. Had the cooling been slower, we think the alloy would have been entirely solid at this temperature.

Sn 15.5. *Chill at* 705° (not reproduced).

This, unlike the previous chills, does not develop a pattern by polishing, for the large primaries have disappeared from the interior, though they are still visible on the outside. Ignition to orange brings out a few large softly rounded patches, differing a little in tint, but nothing that could be called a pattern. Chemical etching also fails to develop anything except a few large polygons. The alloy is a very uniform body with no striation or other pattern. We infer that, before the chilling, the primaries had grown, assimilating the mother-substance as they grew, until their margins met. Thus at the moment of complete solidification the alloy consisted of crystal grains of the solid solution β , each grain having its own orientation no doubt, but being, from a chemical point of view, approximately uniform and identical with the other grains around it.

Sn 15.5. *Chills at* 600° and at 552° (fig. 35).

These resemble the preceding. They show a few polygonal divisions, but otherwise are uniform; they show no striation and no pearlite effect. We give a photograph of the chill at 552° (fig. 35), taken with oblique illumination, for comparison with the next alloy.

Sn 15.5. *The chill at 452° (figs. 36 and 37).*

Polish alone leaves this a perfect mirror with no pattern, but ignition or a slight etch with either ammonia or very dilute FeCl_3 brings out a fine mother-of-pearl effect, the surface being now full of iridescent reflections, especially under oblique illumination (fig. 36). These are in patches oriented in many different directions, so that the effect varies with tilt and rotation. It requires a power of 500 to resolve these striations, when we see that the material consists of two substances, one darkened by the etch, the other a pure white (fig. 37). These sometimes lie side by side in groups of very narrow lines, an arrangement which accounts for the iridescent effect. In other places the darker copper-rich α (as we think it) is in dots surrounded by the white δ . This is the solid eutectic of all the alloys up to Sn 20, but in Sn 15.5 *alone* it occurs free from large crystals either of α or of the white δ ; in Sn 16 we shall find such large crystals.

The CD Alloys.—All these, when chilled between the liquidus and solidus, or more exactly when chilled above $lcmD$, contain large copper-rich combs of β . These combs invariably etch out deeply in the process of polishing, and are then visible as a pale copper colour, while the mother-substance surrounding them is pure white. They etch with either ammonia or ferric chloride to a dark copper or black, and do not show any tendency to break up into the striation pattern. At the cmD transition temperature there is some difference between Sn 16 and the alloys containing more tin, but below the solidus all the alloys of the group, if they have been slowly cooled down to the moment of chilling, appear to be uniform solid solutions, a condition which persists with little or no change until the line $C'XD'$ is reached, when a crystallisation of δ out of the solid solution commences.

Sn 16.

The upper chills of this alloy throw a very clear light on the process of solidification. The ingots are all coated externally with a raised pattern of rectangular combs.

Sn 16. *Chill at 773°.*

When the ingot is cut and polished one finds that the polishing has etched out large combs exactly similar to those on the outside. A gentle ignition oxidises these combs more rapidly than the mother-substance, but on further heating the lobes of the combs develop margins, and changes evidently take place in them; the combs are β , very rich in copper, and therefore somewhat unstable.

Sn 16. *Chill at 752°, v.s.c. chill (fig. 38).*

The β combs are large and rounded, filling by far the larger part of the area, but

there is still a considerable amount of the tin-rich mother-substance, thus the ingot was not altogether solid at the moment of chilling. The β has a fine uniform grain, with no trace of striation or other change, and the margins of the combs are quite sharp. There was evidently a considerable difference between the composition of the solid and the liquid at the moment of chilling.

Sn 16. *V.s.c. chill at 738° (fig. 39).*

The ingot was allowed an hour and a-half to cool from 752° to 738°, in addition to the time given to the slow cooling of the preceding alloy. The ingot was quite solid, showing no trace of granulation. The bold regular gridiron of the more rapidly cooled alloys has disappeared from the outside. A polished and etched section makes it evident that the primary combs have now grown so as to touch each other nearly everywhere, but there are two small interspaces, covering together less than 1 per cent. of the area, and full of the white tin-rich mother-substance; here we can detect the rounded form of the lobes of primary. One also begins to see polygonal boundaries, meeting three together in angles of 120°. There are not many examples of this, and the boundaries are rather geometrical lines than ribands of perceptible width, but these lines run out of the two or three little pools of white, and it is clear that the boundaries are where the primaries met.

Here we observe a process of solidification that can only be explained by the theory of solid solution; the copper-rich solid grows and at the same time assimilates the tin-rich liquid, while the unabsorbed liquid down to the last drop remains quite different from the solid phase; the process we observe is exactly predicted by ROOZEBOOM'S theory. It is clear that the alloy does not solidify by the same steps as those that a pure or nearly pure body would follow, for in the case of such a substance the solid first forming would differ very little from the remaining liquid, while we find that in the case of Sn 16, however little solid has formed, it is considerably richer in copper than the mother-substance. If a pure body differing from the liquid in composition crystallised, it could never grow so as to absorb the whole of the liquid, and the resulting solid would be a complex of two kinds of crystals, a condition which does not exist in Sn 16 immediately below the solidus. The alloy is very uniform, showing no iridescence or striation.

These two chills would lead us to fix the temperature of complete solidification of Sn 16 at a point not higher than 740°, but we had some reason for suspecting that the pyrometer had altered a little between its last standardisation and the moment when these two chills were taken. We therefore made two independent chills at 750°. These were cooled very slowly before the chill, and on each occasion the pyrometer was carefully standardised before the experiment. Each of these ingots shows the alloy as completely solid, no mother-substance being visible, and the combs of β having disappeared and been replaced by the characteristic polygons bounded by

very slender white lines. The grain of the material of the polygons is very uniform; it is presumably the solid solution β . We therefore place the solidus at 750° . We do not give photographs of these, as, beyond fixing the position of the solidus more exactly, they do not add to the information supplied by the preceding photographs.

Sn. 16. *Chill at 725° . S.c.c. (not reproduced).*

This had all the slow cool of the alloy chilled at 738° , and, in addition, was allowed an hour and a-half to cool from 738° to 725° . There is now on the outside only a trace of a very coarse, rounded network. The cut and polished section is very uniform, with no polygonal boundaries—probably because the ingot has become all one crystal—no striation, indeed no pattern of any kind. The slow-cooled chill at 650° is similar, there is no sign of the solid solution breaking up. The chills at 546° and 500° were not slow-cooled, and therefore the number of polygonal divisions is larger, but the dividing lines are very fine, and the ground of the polygons is uniform. The sections do not show the pearlite effect when the polished and etched surface is obliquely illuminated.

Sn. 16. *Chill at 477° .*

This chill, which must be very close to, if not below, the curve $lC'X$, does not yet show the typical pattern of an unchilled alloy. There is no iridescence, the ground not having broken up into the C' eutectic. But there are some broad irregular bands of a tin-rich substance having an asbestos-like growth. There are also stars of true δ in the copper-rich ground. Ingots chilled a little lower, or unchilled alloys, are very different. In these, after polishing and etching the surface, the pearlite effect is very well shown; indeed, with oblique illumination, a lens, or even the unaided eye, shows the surface as made up of iridescent patches. The whole alloy has broken up into the C' eutectic, exactly like the photographs we give of the same phenomenon in the Sn 15.5; but, in addition, there is in Sn 16 a new feature; this consists in sprays of δ , which began to crystallise as soon as the temperature fell to a point on the curve $C'XD'$. We give a photograph (fig. 40) of an unchilled ingot showing this, because it proves that Sn 16 lies to the right of the solid-eutectic point C' , and consequently when the solid solution begins to break up, it is a tin-rich and not, as with Sn 14, a copper-rich phase which crystallises.

The Transformation at the Point D.

Sn 16, as we have seen, appears to solidify homogeneously to a uniform mass of β combs, but the alloys of the group with a larger percentage of tin do not do so. Although they all contain β combs when partially solid and chilled in the area $lcDC$, yet at the temperature of the cD line (740°) the β becomes unstable, and at this and

lower temperatures suffers a change into what we must suppose is γ . We give (fig. 41) a photograph of a v.s.c. chill of Sn 17, chilled at 745° , which, as it contains no chill primaries, may be taken to indicate the maximum amount of β that can exist in this alloy. The chills of Sn 18, Sn 19, and even Sn 19.5, at this temperature are exactly similar to that given of Sn 17, except that they contain less β . We also give a photograph (fig. 42) of Sn 17, chilled at 731° , as it emphasises the symmetry of the β combs and their great resemblance to α in form. The ingot was not especially slowly cooled before the chill, so that the detail is small. The ingot must have cooled too rapidly through the D temperature for the β combs to suffer much change, though a higher power makes it evident that their margins are softened by a commencement of solution. Other experiments show that if the ingot had not been chilled, the β combs would have disappeared at lower temperatures. The transformation at the D temperature is a slow one, though it probably goes on more rapidly a few degrees below that point, so that it is possible to find β combs, more or less recognisable, in alloys somewhat slowly cooled and chilled a little below D. Sn 18 chilled at 735° shows the partial solution of the β , which is recognisable in darker irregular patches. These retain, in a distorted form, some semblance of the shape of the β combs. This ingot was slowly cooled through the D temperature, but enough time was not allowed for the completion of the change. We do not give a photograph of this ingot. The same process of solution of the β is seen in the photograph (fig. 43) of Sn 18 chilled at 734° . Here the β combs must have been originally very symmetrical, but as the ingot was not slowly cooled before the chill, they are easily recognisable in spite of the lower chilling temperature. We have ingots of Sn 17 and Sn 19 which show the same partial solution of the β . One of these, a chill of Sn 19 at 733° , is reproduced in fig. 44.

When a patch of β undergoing this change is examined with a higher power, one sees that the grain of the material, originally fine and uniform, becomes coarser and develops into a flaky pattern of grey and white, and sometimes spherulitic crystals of a tin-rich material develop in the heart of what were uniform β crystals. All these obscure changes, however, result in the complete disappearance of the β , and the formation of a very uniform material, provided the alloy is cooled slowly to the solidus cd and then chilled. We give a photograph (fig. 45) of Sn 18 very slowly cooled to 728° and then chilled, in which the disappearance of the β is practically complete. The fine straight polygonal boundaries are present, but they have little or nothing to do with the original β .

This apparent uniformity in the CD alloys, when chilled below the solidus, has been confirmed in instances too numerous to mention in detail. For example, a very slow-cooled chill of Sn 18 at 728° was uniform, also one at 650° , and that at 550° , of which we give a photograph (fig. 48), is very nearly so. Again, very slow-cooled chills of Sn 19 at 719° and 710° are uniform except for polygonal boundaries; and the chills at 680° and 629° show, even after repeated ignitions to orange, no pattern except a

faint mottle and the polygons of slightly different tint, so common in the region of chemically uniform solid solutions. This observation, and others like it, do not, perhaps, exclude the possibility that some of the alloys below the solidus may be a *minute* complex of two materials. In accordance with the information supplied jointly by the microscope and the pyrometer as to the temperature of complete solidification, we have, therefore, ventured to draw the solidus *lcmd* with a flat between *c* and *m*. The position of *c* is, we think, correct, but that of *m* is very uncertain. The break is, however, useful as a reminder that *lc* and *md* are the solidi of two different substances. If the gap *cm* really exists, the solid alloys below it ought to be complexes of two bodies.

Although we have not been able to detect the fact, it is quite possible, from the way in which the β disintegrates, that there may be such finely grained complexes. For, unlike the C transformation, which is an obvious solution of α in a liquid followed by the crystallisation of the very different β , the D change is one of disintegration throughout each β crystal, a change that might conceivably be a separation into two phases. An alternative supposition is that the points *c* and *m* are coincident, and that the change at D is a case of dimorphism, the β and γ having, at their transformation temperature, the same composition. But the evidence we have for the position of the solidus makes it difficult to bring *m* up to *c*. We fear we must leave the question undecided. *It is certain, however, that there is a transformation at the D temperature, that the cooling curves of the Sn 18 and Sn 19 show heat evolution there, and that during this transformation the β combs disappear without having filled the alloy.*

The Transformation of the Curve C'XD'.

Whether the solid alloys below *lcmd* are all uniform or not, it is certain that they undergo a profound change after crossing the line C'XD', this change being accompanied, as the cooling curves show, by an evolution of heat. In the case of the alloys to the left of CC', the change consists in the crystallisation of copper-rich α crystals out of the solid, as we have already proved. In the case of the alloys to the right of C', it consists in the crystallisation of white tin-rich δ , which appears in the form of rosettes, bars and fern-leaf. The unchilled Sn 16, of which we give a photograph (fig. 40), shows these new crystals, but with more tin the new material grows in amount until at Sn 20 it practically fills the whole alloy. The changes are well shown in Sn 17. Chills at 668° and 616° were uniform. The chill at 547° is uniform so far as much more than 99 per cent. of the surface is concerned, but dilute FeCl₃ brings out a few large polygons bounded by extremely thin lines of δ , and in one place the lines have thickened a little by a moss-like growth of a similar white tin-rich body. There are also a few short lines of minute rosettes of white δ . This is the beginning of the pattern that develops at a slightly lower temperature, but the

traces of separation are as yet so slight that they have to be very carefully searched for. We do not reproduce this, because there is so little to see, and because what pattern there is closely resembles that of Sn 18 chilled at 550° (fig. 48), with this difference only, that the white is much more abundant in the Sn 18.

The chill of Sn 17 chilled at 495° , when etched as usual with dilute FeCl_3 , is still largely blank (fig. 46), but the white bands bordering the polygons are now much broader, and near some of the borders and angles there is a delicate but perfect growth of the white δ in sprays that we are in the habit of calling the "fern-leaf crystallisation." The central and much the larger part of each polygon is, however, blank, so that we have in this ingot a transition from the uniform solid solution to the two-phase state proper to the region below the curve XD' . According to the diagram, this ingot was chilled a little below the line. It is important to notice that the dark ground is uniform even to a high power, and that when examined by oblique light it shows no iridescence; the ground has not yet broken up into the C' eutectic. But the chill at 450° (fig. 47) shows the ground broken up into a minute complex,* and also the fern-leaf scattered uniformly over the whole surface. This ingot etches with very weak FeCl_3 and has the patchy iridescent effect of the low chill of Sn 15.5 due to the formation of the C' eutectic. These lower chills of Sn 17 were not slowly cooled before the chill, and hence the detail is small, but two ingots of Sn 18 (fig. 48) and Sn 19 (figs. 49 and 49A), both chilled at 550° after a very slow cooling, show the nature of the change of the XD' curve even better, and fix a point on it accurately. In the chill of Sn 18 at 550° (fig. 48), prolonged etching with FeCl_3 brings out very little pattern. There are, as the photograph shows, only a few small specks and threads of δ . This ingot was evidently chilled when in the triangle IXE' of uniform solid solutions. On the other hand, the chill of Sn 19 at the same temperature, even when lightly etched with FeCl_3 , develops a splendid pattern of white tin-rich δ in the form of bands, fern-leaf, and bars. Hence the ingot must have been chilled below the transformation curve. We also give a chill of Sn 18 at 501° (fig. 50), in which the D' crystallisation has taken place. It must be remembered that the curve $\text{XD'E}'$ has been determined from the halts in the cooling curves and not from the chilled alloys, but we see that the latter confirm its position.

The copper-rich ground in the chill of Sn 19 at 550° is uniform, but unchilled ingots, or those chilled below X' , show the ground to be the C' complex, fig. 53. It must also be remembered that in the chill of Sn 19 at 550° the crystallisation of the δ was arrested by the chilling before it was complete, hence this ingot does not show the δ fern-leaf so closely packed together as would be the case in an unchilled ingot.

Sn 20. 31.8 *per cent.* by weight of tin.

This alloy, the "speculum metal" of Lord Rosse, has the formula Cu_4Sn , and the

* This feature requires a higher magnification than that of fig. 47.

slowly cooled unchilled alloy may at ordinary temperatures consist of this compound. Occurring as it does at a singularity both in the liquidus and in the solid transformation curve, the alloy is a border-line one, separating two groups. Its cooling curve shows two well marked evolutions of heat, the first due to the latent heat of solidification, the second to the re-crystallisation that takes place in the solid at temperatures below the point D' .

As the diagram indicates, solidification is complete at a temperature not more than 30° below the freezing-point. Ingots chilled in the region of temperature between the liquidus and solidus contain copper-rich primary combs embedded in tin-rich mother-substance. These are well seen in a chill at a little below 740° , in which they are comparatively scanty, and in a chill at 726° , in which they fill more than half the ingot (fig. 51). These combs of primary are evidently β which has begun to disintegrate. The important point to notice is that this alloy, although it has a formula, does not solidify after the fashion of a pure body, but by the formation of crystals considerably richer in copper than the liquid. A little above 710° , however, these combs have disappeared, and from here down to 650° no pattern can by any means be developed in the chilled ingots, except sometimes the pattern of large polygons, or counties, so common in pure metals and solid solutions. The chill at 605° , only just above the point D' , requires very prolonged exposure to strong ferric chloride to bring out anything except the polygons, but by this means one sees that the polygons are bordered by broad but vague white bands. A high power makes it evident that these bands are of the angular patchiness seen in some previous ingots. This is evidently a growth of tin-rich material in places where broad ribands of compact δ would be seen in an unchilled ingot. It is quite doubtful whether these markings have any right to appear in this ingot, or whether they are not a result of imperfect chilling or a change that has taken place subsequently to the chill.

The chill at 558° , about 25° below D' , is full of a splendid pattern of the δ bands and rosettes. The only difference between this pattern and that of an unchilled alloy is that in the former there is rather more mother-substance, and that this is uniform, instead of being, as in the unchilled ingots, a complex. The photograph of an unchilled ingot that we give (fig. 52) shows how very little of this mother-substance (dark in the photograph) is to be found in the alloy. Moreover, this mother-substance is itself mainly composed of the same material as that of the bands and rosettes, its dark colour after etching or ignition being due to a small admixture of spots and lines of a copper-rich material, which we think is α . We give a higher-power photograph (fig. 53A) of a patch of this eutectic, taken from an unchilled and somewhat slowly cooled ingot of Sn 20; the darker straggling patch in fig. 53A corresponds to one of the minute specks of black in the preceding figure. We also give in fig. 53 a high-power photograph of the eutectic in unchilled Sn 19. The resemblance to the eutectic, also formed at the same temperature, of Sn 14 is very great, and we have little doubt that this eutectic complex, formed in the solid alloys at a temperature of,

or a little below, 500° , contains the same two phases, α and δ , in all the alloys from Sn 6 to Sn 20. Beyond Sn 20, *even with a mere trace more tin*, the eutectic vanishes, and there is so little of it in Sn 20 that we are disposed to regard it as an accident in that alloy, or as due to the fact that the alloys that we call Sn 20 may have a slight deficit of tin in them. If so, there is considerable reason to regard the δ substance of Sn 20 and of all the previous C' eutectics as being the compound Cu_4Sn . In this case the compound is not present, at all events in crystalline form, above the transformation curve, and is finally produced by crystallisation out of a solid solution. On this view the transition from the condition of the alloy just above the point D' to that just below it must be compared to the conversion of a pure substance from the liquid to the solid state, only that in the case of the alloy we are considering both states are solid. The change, like that from a liquid to a solid, is an exothermic one.

It is, of course, possible that the δ material found in all the alloys from Sn 6 to Sn 20 may be a series of solid solutions varying in composition throughout this range of alloys, but the great similarity in the appearance of the δ , from its first appearance in the scanty eutectic of Sn 6 to the moment when it fills the whole alloy in Sn 20, makes us think it far more probable that it is a pure compound of constant composition. Up to the present we have not been successful, by means of a chemical solvent, in removing the α from such an alloy as Sn 16 in order to analyse the δ .

The character of the pattern of riband, bar and rosette, or fern-leaf, seen in the CD alloys when cold and unchilled, is partly, we think, dependent on the greater or less perfection of the transformations that take place *during solidification*. Too rapid cooling during solidification will leave the grains somewhat copper-rich with some tin-rich mother-substance round them; in fact, the D transformation will not be complete. This will lead, when the δ crystallises, to its doing so in broad ribands, enclosing areas in which it is more sparingly distributed as rosette or fern-leaf. In the chill at 558° , and the same is seen in the unchilled alloy of fig. 52, the δ forms many straight pointed bars. This peculiarity, which is first seen in Sn 20, suggests the bars of Sn 21 and succeeding alloys.

The DE Alloys.—All slowly cooled ingots of the DE alloys, but especially the higher chills, are more or less covered, particularly on the top, with a raised primary crystallisation. This suggests bunches of grapes packed closely together, but sometimes, as in the upper chills of Sn 24 and Sn 25, there are suggestions of combs in the form of long bars with rounded serrations. In the lower chills the grape pattern alternates with patches of linear ruling, showing iridescence.

We have examined an unchilled ingot of Sn 20.5. This alloy seems to consist of masses of δ in close juxtaposition, the trace of the C' eutectic visible in the Sn 20 having disappeared. The bar pattern noticeable in some of the ingots of Sn 20 is now more marked, the bars having pointed ends, so that they resemble elongated willow leaves. But the bars now seem to differ a little in composition from the rest

of the alloy; they oxidise more slowly than the ground, so that they probably contain more tin. They are also blackened by FeCl_3 , a feature that becomes very marked in the succeeding alloys.

Sn 21. *S.c. chill at 725°* (fig. 54).

This ingot was very much distorted by granulation in the chill, a proof that it was far from solid at that moment. Polishing etches out the surface into a pattern of primaries, leaving these faintly copper-coloured on a dead white ground, and heat-oxidation darkens the primaries more rapidly than the ground, a proof that they are richer in copper. FeCl_3 is rather variable in its action on them, but, on the whole, it darkens them as compared with the ground. These primaries (fig. 54) consist of rounded blobs, often isolated, but sometimes grouped in oblique sprays, unlike the rectangular β . The lobes of primary, when examined with a higher power, are uniform, not showing any tendency to break up into the bar pattern of the lower chills, but in the chill primary, or in the mother-substance, one can see the beginning of the bar pattern.*

Sn 21. *S.c. chill at 710°* (not reproduced).

This is a smooth solid-looking lump, but cutting and polishing develop large cracks; polishing reveals no pattern. FeCl_3 acts very slowly, but finally brings out polygonal patches and some rotation effect, but no bars or other pattern. The ingot is a good example of a uniform solid solution, and shows that the solidus lies above 710°. The chill at 700° was uniform. That at 650° was a pattern of large patches (fig. 55), but each of these patches had a uniform surface, with no bars or other pattern. There is, therefore, a region of temperature in which the alloy is a uniform solid solution. Probably on account of fragments breaking off from the edges of the cracks, we found it impossible to avoid scratches in polishing this ingot.

Sn 21. *S.c. chill at 590°* (fig. 56).

Here we are a little below the transformation curve $D'E'$, and several per cent. of the new η body has crystallised out of the solid solution in curved bands which coincide with the previous polygonal boundaries, and in groups of parallel bars which generally start from a boundary. In the photograph (fig. 56), which is taken from a FeCl_3 etch, these are black, but they are richer in tin than the ground, for if the surface is heated, these η bars oxidise more slowly than the ground, remaining white while the ground turns a rich brown. The photograph tends to give a false impression as to the amount of the new material, as it was taken from a patch of the surface where it was abundant; really, there is less than 10 per cent. of it.

As the chill was made a little above the D' temperature of 580°, we should not have

* The striation visible in fig. 54 on the lobes of primary is due to imperfect polishing.

expected to find evidence of the ground having been transformed into δ , but this has occurred, and here and there are copper-rich gaps in the massive δ of the ground, in which the δ fern-leaf is seen growing out from the edge of the more massive δ . One of these gaps is visible in the figure. This ingot of Sn 21 would therefore appear to show the real nature of the ground as δ . In addition to the quite black bands of η , there are, in places, paler bands. These may owe their paleness either to a different orientation or to a somewhat smaller content of tin.

Sn 21. *Chill at 588°, not specially slowly cooled* (not reproduced).

This shows, perhaps, a little less of the bars, but it has some paler patches in addition to the black bars, also one or two small spots of δ granulation or fern-leaf. The bars are well seen to have the orientation of the grain of solid solution from which they were formed. There are also places where white δ bars crystallised on a darker ground.

Sn 21. *Chill at 580°* (fig. 57).

This ingot, chilled on the D' line, was not a slow-cooled ingot before chilling. When etched with FeCl_3 , it has a larger fraction of the surface covered with bands than fig. 56, but these vary in tint from black to the palest grey. The bars can, in some cases, be made to alter a little in shade by tilting and rotation, but not enough to make it possible to explain their very varied appearance as due to differences in orientation of a pure material such as SnCu_3 . Moreover, considering the percentage of tin in the alloy, the bars are far too abundant for such a hypothesis. It seems more probable that when the temperature of the transformation curve was reached at 600°, the solid alloy began to separate into two, or, through imperfect equilibrium, into several phases with different percentages of tin, all the more tin-rich phases re-crystallising in a form isomorphous with η , and therefore all to be classified as η . An analogy for this may, perhaps, be found in the breaking-up of a liquid into conjugates during rapid cooling. In such a case a whole series of liquid phases must through imperfect transformation exist together, and if a process analogous to chilling could be effected they would be stereotyped as we see them here. In the whitest parts, which in the FeCl_3 etch are the most copper-rich, the δ crystallisation has taken place. The bars, which are really sections of plates, have definite crystalline shape, and present many good examples of twinning. As Mr. FEARNSIDES has pointed out to us, it resembles the twinning seen in soda feldspars, but the fact that the bars darken at different rates when heat-oxidised, is some indication that they are not merely twins in a homogeneous substance.

Sn 21. *Slow-cooled chill at 570°* (not reproduced).

This has a decidedly smaller area of the new crystals than the chill at 590°, and the

same is true of all lower chills; for example, those at 556° and 380° , that is to say, of all ingots chilled below the D' temperature. But these ingots contain a new feature in the form of lace bars. The bars do not present the same variety of shade, and many of them are merely outlined and not completely filled in with the black, but their interior consists either of a fine ruling of black and white, or of a lace-work of the two. We are disposed to think that the lace bars are not bars imperfectly formed, but bars that have suffered a partial disintegration into two phases, which may be the final phases of δ and η . On this view we may presume that the broader uniform bands of the chill at 580° would have turned into lace bands if slowly cooled to a lower temperature before the chill. We do not reproduce the lace-bar effect in Sn 21, as it is even better shown in Sn 22.*

Sn 22. 34.45 per cent. of tin.

At this percentage there is a slight singularity in ROBERTS-AUSTEN and STANSFIELD'S transformation curve, and although our pyrometric determinations did not justify us in reproducing this singularity in our diagram (Plate 11), the microscopic study of the chills to some extent confirms their curve. The chill patterns resemble those of the preceding alloy, but there are certain differences.

Sn 22. Chilled at 733° (fig. 58).

This shows very well the characteristic clumsy γ combs, generally dark on a lighter ground. One also sees bars of η , as a rule, in the mother-substance.

Sn 22. Chilled at 710° (not reproduced).

The solidus appears to lie at 700° , for the alloy at 710° has abundant primary combs in it of the true γ type, with nothing rectangular about them. There is also a little chill primary. The combs are copper-rich, but the heat oxidation employed to prove this point has, in places, modified the somewhat unstable material and caused the growth of bars of η . The γ crystals will be found to be still more unstable when they contain a little more tin.

Sn 22. Chilled at 690° (fig. 59).

The ingot must have been quite solid at the moment of chilling, for the primaries have entirely gone and are replaced by large patches of uniform solid solution, but

* [At a later date the ingot of fig. 57 was re-heated to a temperature between 500° and 600° , cooled without chilling, polished and etched with FeCl_3 . The re-heating has entirely altered the pattern; the broad twinned bands of η have disappeared, by far the greater portion of the surface consists of white δ with some scanty lace bars of black η . Unfortunately, this experiment was made too late for the reproduction of the photograph.—June 29, 1903.]

the chill did not prevent the formation of a few long slender bars of η , dark in the photograph.

Sn 22. *S.c. chill at 680°, and chills at 650°* (not reproduced).

This is a remarkable example of the polygonal pattern produced by cutting the grains of solid solution composing the ingots at different angles, and so causing them to etch differently, though they are probably the same chemically. Tilting, or rotation under oblique illumination, does not much alter the relative shade of these patches, and they show no iridescent effect. The bars of η are much scantier than in the preceding ingot, but they can be found. The chill at 650° is very similar to the preceding, and as far as we can see it is free from bars. Another chill at 650°, very slowly cooled before the chill, has many more bars, but they are small and thin, and may, we think, be attributed to the chill not being sharp enough to arrest all further change. In fact, the bar pattern is so slight in all the above-mentioned ingots, that we think it almost certain that the alloy passes through a region of temperature in which it is really a uniform solid, as in the case of Sn 21.

Sn 22. *S.c. chill at 600°* (not reproduced).

We should have expected the bar pattern to become a real feature when the transformation curve was passed, as in the present chill, but it is, on the contrary, a very good example of a uniform solid solution consisting only of a few large patches, which turn from dark to light when tilted. There is hardly a trace of the bars. Even the chill at 588° is very similar, though here some of the polygons are bounded by straight lines and may be massive bars.

Hence, although the cooling curve of the alloy shows a considerable evolution of heat at 627° where the transformation curve is reached, yet the chills fail to show the corresponding change.

Sn 22. *Chill at 570°* (not reproduced).

The polygons, still very varied in tint, are now crossed and sometimes margined by massive bars of η , but there is no lace either in the bars or the ground.

Sn 22. *Chilled at 565°, a slow-cooled chill* (fig. 60).

This is certainly below the last, or D', halt on the cooling curve, a point marked in the cooling curve of this alloy by a somewhat sloping flat. A lens now shows massive bars and curved bands of η dark on a light ground. A slightly higher power brings out the fact that this ground is full of paler bars and of lace bars, the effect being even better seen in fig. 61. Thus the crystallisation has taken place in at least two stages: at first the massive η bars formed, and, secondly, the mother-substance broke up into

a copper-rich and a tin-rich phase. The lace bars are probably, as we said in discussing Sn 21, due to the similar breaking up of η bars that were too rich in copper for the final equilibrium. As in the ingot of Sn 21, chilled at 580° , the paler bars were probably intermediate phases.

A chill at 560° is very similar to that at 565° , but shows better the separate crystalline bars of the copper-rich phase.

Chills at lower temperatures show no further change, as can be seen from a not specially slowly cooled chill at 495° (fig. 61), so that the unchilled alloy must be a complex of two phases, which may be Cu_4Sn and Cu_3Sn , but are more probably conjugate solid solutions composed of these two bodies, and best described as δ and η .

An ingot that took several days to cool to ordinary temperature without a chill shows all detail on a very large scale. There is not the lace ground-work, though there are some traces of lace in the bars. Instead of the lace, the very slow cooling has allowed the white δ phase to crystallise in definite needles round the margins of the dark η bars, and sometimes in the heart of these bars.*

Sn 23. 35.8 per cent. of tin, and Sn 24, 37.1 per cent. of tin.

These alloys form copper-rich primaries of γ when chilled in the narrow region between the liquidus and the solidus, and at temperatures between the solidus and the transformation curve we believe that they form uniform solid solutions of γ , but we have never been able by chilling to obtain perfectly uniform ingots of the solid solution in this region.

Below the transformation curve a large scale crystallisation of η in bars and ribands take place. No change can be detected at the D' temperature, so that unchilled alloys at ordinary temperatures must be regarded as consisting of two phases, a copper-rich one of the δ type and a tin-rich one of the η type, the two being, as in Sn 22, either the two compounds themselves, or solid solutions of them.

Sn 23. *S.c. chill at 710° (not reproduced).*

The ingot was very liquid at the moment of chilling, and, consequently, was badly granulated and blown into holes, but one can very well see a few broken sprays of γ primary on a darker ground. The γ is sometimes twinned, part of a spray being light and the rest dark, and it is evidently very unstable, dark η bars being visible, running across the lobes of primary. There is a great deal of chill primary, indeed the true mother-substance is shown by a high power to be a thin network of grey.

* The flatness of the liquidus between D and E caused us to suspect at one time that the alloy, while wholly liquid, might have separated into two liquid phases; the above-mentioned extremely slow cooling was arranged in order that by difference of density two layers might be produced; there was no trace of such a separation, even the plates of η were uniformly distributed throughout the whole depth of the ingot.

Sn 23. *Slow-cooled chills at 690°, 685°, 680°, 650° (not reproduced).*

These are all very much alike; when ignited they are uniform, at all events to the eye or a lens, but FeCl_3 brings out a number of rather small angular and interlacing patches, which show the effect of varying brightness on tilting or rotation. A moderate magnification makes it evident that each patch is broken up into narrow bands with still narrower lines of a mother-substance between them. In fact, the separations proper to the region below the transformation curve have taken place although on a very small scale. This detail is not perceptibly larger in the chill at 650° than in that at 690°, although a long period of slow cooling was allowed between the two chills; hence we suspect that it occurred at lower temperatures during the chilling. Fig. 63, a chill at 685° of Sn 24, gives a fair idea of these ingots.

Sn 23. *S.c. chill at 620° (fig. 62).*

We are now below the transformation curve; the iridescence has increased and the patches are much larger, but, in addition, there has grown a large scale pattern of broad η bands and sprays of what may be likened to foliage. This is the true breaking-up of the solid solution into two phases, and we see that the η phase has very much increased as compared with Sn 22 and Sn 21. The chills at 590° and 570°, and indeed all lower chills, have the same pattern, so that the D' transformation has now vanished or become unimportant. Oblique illumination shows, by the position of the shadows, that the darker ingredient has been etched out below the level of the lighter ground. Thus the darkening of the tin-rich phase is due to a real attack by the etching reagent. The pattern seen in these lower chills reminds one of the alloys from C to D when chilled below the transformation curve. In both cases there are ribands of a tin-rich material, often enclosing polygonal areas, and, branching from these ribands, a fantastic crystallisation of the tin-rich phase partly fills the enclosed areas. But in the CD alloys the ribands and fern-leaf crystallisation is left white and not attacked by the etching, while in the DE alloys it is attacked and darkened; in the CD alloys it is δ , in Sn 23 and Sn 24 it is η .

Sn 24 is similar throughout to the above, with the exception that in the chills in which the η phase appears it is more abundant; in fact, nearly filling the alloy. Primaries and chill primaries are obtained by chilling above 700°, and between the solidus and the transformation curve the chills are uniform when ignited; but when strongly etched show the iridescence and patchiness due to minute separations, while as soon as the chilling temperature falls below the transformation curve, the solid solution breaks up and the bars, or really plates of η , nearly fill the field. We give two photographs of Sn 24. The first (fig. 63) was a slow-cooled chill at 685°, that is, a little below the solidus. It shows no primary, but is full of iridescence due to minute linear separations; there are also some long slender bars of η . It may seem

bold to assert that this ingot was, immediately before the chill, a uniform solid, but we are convinced that such was the case.

The other chill (fig. 64) of Sn 24 was also a slow-cooled chill at 635° , a little way below the transformation curve. It is at the same magnification as the preceding chill. We now see that the true crystallisation of η has taken place, and that the η nearly fills the ingot. Perhaps we may remind the reader that, on account of the ferric chloride etch, the tin-rich η is dark and the copper-rich mother-substance is white. Had the pattern been brought out by heat oxidation, it would have been reversed.

Sn 25. 38.4 *per cent. of tin.*

This alloy is especially interesting because it has the formula Cu_3Sn , and because of the many physical properties which reach their maximum intensity in the unchilled alloy of this composition. There has on such grounds been a consensus of opinion that it is a chemical compound. So far as the slowly cooled and unchilled alloy is concerned, this view is almost certainly correct. But we find that when a liquid of this composition begins to solidify, the crystals first formed are considerably richer in copper than the mother-substance, so that the crystals cannot be Cu_3Sn . At a lower temperature, however, the compound itself crystallises out of a solid solution. This occurs at E' , the summit of the transformation curve, a point where the cooling curve shows a large evolution of heat and a phenomenon analogous to surfusion.

Sn 25. *V.s.c. chill at 720° (fig. 65).*

The ingot was not granulated by the process of chilling, though the figure makes it evident that there was a considerable amount of matter liquid at the moment of chilling. Polishing alone shows the combs in a more brilliantly white network of mother-substance. The usual etching reagents do not give a contrast between the γ combs and the mother-substance sufficiently well marked for photography, we therefore adopted the method of heat-oxidation, the ingot being heated over a Bunsen until the first tint of orange appeared. Under this treatment the γ combs oxidised more rapidly than the mother-substance, becoming a dark orange while the latter remained almost white. This selective oxidation of the γ , which is reproduced in the photograph, proves that the γ combs are richer in copper than the liquid out of which they are crystallising, and therefore that they cannot be the compound Cu_3Sn . The heating has, however, to some extent decomposed the γ , leaving a rim of whiter material round each lobe of the combs. This and other features are better seen in fig. 65A, which is a more highly magnified photograph of the same ingot. Here we can see that not only the borders of the combs but also the whole of some of the smaller masses of γ are paler than the rest; this probably indicates that they are

richer in tin than the earlier formed γ . The central parts of the γ combs have also broken up into a complex, which reminds one a good deal of Sn 23 and Sn 24. This again is evidence that the γ is not a pure chemical compound. A little of this separation could be detected in the surface when etched with ferric chloride before the alloy was repolished for the heat-oxidation. A slowly chilled ingot, very sharply chilled at 715° , was almost untouched by the strongest mixture of hydrochloric acid and ferric chloride, but heat-oxidation still reveals a little mother-substance.

The lower chills were etched in the usual manner with ferric chloride. Many of these show polygonal divisions, but very little difference in the tint of the polygons, and no pattern in them. Even the strongly exothermic change at E' does not show itself by any pattern in the pure Sn 25, for the obvious reason that both before and after the change there are no two substances for the etching reagent to distinguish between. In quite the lowest chills, and in the unchilled ingots, the patches sometimes assume a bar-like form, especially if the polished and etched surface is exposed to the air for some days before examination. This appears to be due to the fact that the plates of η , of which the ingot is composed when the temperature is below E' , oxidise at different rates according to their position with reference to the plane of the section. This effect is seen in fig. 66, an unchilled ingot. A similar selective darkening of the η by atmospheric action was observed in a chill of Sn 28 at 725° .

The EF Alloys. Sn 26 and 27.—This region is not marked by a singularity in the liquidus, and in harmony with this fact the first steps in the solidification are very similar to those of the preceding alloys. But there is a greater difference between the composition of the first solid and that of the liquid, and consequently the γ combs of the upper chills are revealed by polishing alone through the more brilliant network of mother-substance around them. This effect is common to the upper chills of all the alloys as far as the point G of the diagram. This network is rapidly eaten out by etching re-agents, leaving the unchanged γ combs pale in a black network. Examples of the appearance are given in the photographs of the succeeding alloys. Below our solidus this network of mother-substance vanishes, and the only pattern is that typical of a chemically uniform solid made up of grains. The chills of Sn 26 at 677° and 656° are both of this character. A chill at 640° , that is, below the transformation curve, is extremely uniform, and most of the surface defies all the efforts to etch it, but a high power enables one to discover some places where a new network has grown, due, we presume, to the breaking-up of the solid solution into two phases, η and a little of a tin-rich phase. It is pretty certain that we may venture to be more precise, and say that the change is the crystallisation of the compound Cu_3Sn out of a solid solution containing rather more tin. This change is not complete at 640° , and there is very little of the new tin-rich phase. The chill at 612° shows the whole surface broken up into the characteristic bars of Cu_3Sn , and the dark lines between, where the tin-rich phase has been eaten out by the etch. We

give two photographs of Sn 26, one at 656° showing the characteristic light and dark patches of the grains of a chemically uniform body, fig. 67 (this is just above the transformation line), and also a chill at 612° (fig. 68), which shows the complete crystallisation of the Cu_3Sn .

An ingot of Sn 26 was slowly cooled to 380° , and maintained at that temperature for four hours, then chilled. The lines dividing up the η into bars are visible in places, though very narrow. They contain a little of the H body, and practically none of the I eutectic.

The cooling curve of Sn 26 has a peculiarity which at first looks like an accidental defect, but which we have verified. The first long halt gradually rounding to steepness is due to the almost isothermal solidification, the latent heat of solidification ceasing to be evolved when the temperature has fallen to 700° ; this gives us very roughly the position of the solidus. The singularity of the curve lies in the second halt. Here there is a sudden rise due to causes analogous to surfusion, the heat evolved being the latent heat of transformation of the solid γ into plates of Cu_3Sn . The short flat which follows the surfusion is unlike anything else in the cooling curves. It is due, we think, to a third evolution of heat rapidly following the second. We can only attribute this to the transformation of the residual γ into a mixture of Cu_3Sn and liquid, a reaction that becomes much more marked in the succeeding alloys. If this be the right explanation of the singularity, then the reaction occurs at a slightly higher temperature than in the case of alloys with more tin. This, again, may be due to the fact that when the change, $\gamma = \text{Cu}_3\text{Sn} + \text{liquid}$, takes place in Sn 26, there are already crystals of Cu_3Sn in the alloy which may serve as nuclei and precipitate the reaction. In order to verify this cooling curve we repeated it with a different pyrometer and a fresh sample of alloy, and found the same phenomenon.

Sn 27. *40.8 per cent. of tin.*

In the cooling curve of this alloy the second and third halts are completely merged into one. In fact, the solidus and the liquidus meet very near here at the temperature of the G point, and the possibility of a uniform solid solution ceases. The meeting of these two curves at the G temperature is, as Professor ROOZEBOOM has pointed out to us, a theoretical necessity.

Sn 27. *S.c. chill at 700° (not reproduced).*

This ingot is still covered externally with large rounded rosettes of γ in relief. When cut and polished, about half the surface of the section consists of similar rounded combs, the rest consisting of chill primary immersed in a slender, bright network of the tin-rich residue of mother-substance. The FeCl_3 etch blackens this network. The surface of the large γ combs is quite uniform and free from inclusions

of the tin-rich material; but the chill primary, when examined with a higher power, is a mass of rounded bars, and has these inclusions in it. We thus see that this chill primary was formed at lower temperatures than the large combs, and did not altogether escape the transformation of the G temperature.

Sn 27. *S.c. chill at 675°* (not reproduced).

This is similar to the preceding except that the large combs occupy a greater area and there is less of the chill primary. We do not give photographs of these upper chills, as the γ is sufficiently well seen in succeeding alloys.

Sn 27. *S.c. chill at 647°* (fig. 69).

In this the combs of large primary have almost entirely filled the ingot before the moment of chilling. It is quite possible, however, to detect here and there the gaps where three lobes of primary meet, and to see in such places a trace of chill primary which is now completely bar-shaped. The surface, when strongly etched, assumes the patchy appearance of a chemically uniform mass of grains, but in the photograph which we give this effect is barely visible.

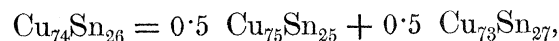
Sn 27. *S.c. chill at 635°* (fig. 70).

This ingot proves that Sn 27 is capable of existing as a uniform solid solution of γ without mother liquid. The G transformation has not yet taken place, the state of the alloy at the moment of chilling being represented by a point, very near f , in the angle between the lines ef and $E'f$. A few dark spots represent droplets of tin-rich mother-substance still liquid at the moment of chilling, and these contain chill primary consisting of η bars; this liquid is not sufficient in amount to invalidate the above statement that the ingot is a uniform solid solution.

Sn 27. *Chill at 625°* (fig. 71).

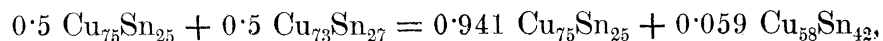
Here we see the same alloy as that of the preceding figure but chilled ten degrees lower, *after, instead of before, the G transformation*. The uniform γ has broken up into bars (really plates seen edgewise) of η , and at the same time liquid, represented in the figure by dark lines and rows of spots, has been formed.

As Professor ROOZEBOOM has pointed out to us, we can calculate approximately the amount of the G liquid formed in any alloy by the reaction $\gamma_f = \text{Cu}_3\text{Sn} + \text{liq}_G$. For, assuming that f is at Sn 27 and G at Sn 42, let us consider the changes in Sn 26. As the temperature falls through the short interval between the transformation curve ef and the fG line, the following gradual change occurs:—



or, more concisely, $\gamma_{26} = 0.5 \text{ Cu}_3\text{Sn} + 0.5 \gamma_{27}$, where the subindices give the atomic percentage of tin in the particular kind of γ .

The change that occurs abruptly in passing through the fG temperature is represented by the equation :—



or, more concisely, the final state is $0.941 \text{ Cu}_3\text{Sn} + 0.059 \text{ liq}_G$.

Thus, assuming that the unit of volume of each substance contains 100 atomic per cents. of copper and tin jointly, we may say that in this alloy the G reaction produces about 6 per cent. of liquid. Considering Sn 27 in the same way, we find for the final state, just below the fG line, about 12 per cent. of liquid. This liquid is represented in the photographs of Sn 26 and Sn 27 by the lines of dark and the rows of black dots in the bars of η . The regression of the solidus from f to E_2 records this partial liquefaction; although not unprecedented, it is not a very common phenomenon. The chills at 600° show the effect even better than that at 625° , and a chill at 565° , which was not cooled with extreme slowness before the chill, shows the rows of dots along the axis of each plate still better. We give a photograph of this (fig. 72).

The FG Alloys. -Sn 28. 42 per cent. of tin. S.c. chills at 650° and 625° (figs. 73 and 74).

In the upper of these (fig. 73), the rounded γ combs are quite uniform and free from inclusions, but the chill primary, of which there is a considerable amount, consists of bars of Cu_3Sn . In the lower chill (fig. 74), the rounded outlines of the γ combs are still visible, as they by no means fill the field, but are frequently separated by patches of chill primary. The G transformation has, however, taken place, for the combs are broken up into a delicate pattern of bars, and these have the rows of inclusions in them. It is clear that the γ combs do not, at this percentage, ever quite fill the alloy, so that the transition point f must lie to the left of Sn 28.

Sn 33. 47.9 per cent. of tin.

The highest chill we have of this alloy is at 676° , not more than 20° below the liquidus; it affords a good example of primary combs of characteristic γ (fig. 75), surrounded by a large excess of matter that was liquid at the moment of chilling; most of this is shown by a higher power to be chill primary, not unlike the large combs.

The chills of Sn 33 at 644° and 628° (figs. 76, 77, and 78) illustrate admirably the transformation at the G temperature. The combs of γ in the upper chill are rounded, quite smooth and free from the inclusions of liquid, while in the lower chill we see

instead an angular material, ruled with lines and containing, in what were the lobes of γ , many black dots due to the liquid liberated in the reaction.

The only other example we need give of this is in the case of Sn 38. Here, in the chill at 644° (fig. 79), the rounded combs of γ , though large, are scanty, and they contrast well with the abundant chill primary which approximates to the bar type. At 628° the γ has been transformed, though the parts that were γ combs can still be distinguished from the rest of the alloy, in spite of their now angular character and the bars that run through them (fig. 80). This ingot, however, was evidently chilled before the transformation had completed itself, and the orientation of the bars is very irregular. If we allow the change to complete itself during the slow cooling, we get the beautifully regular pattern of the chill at 606° , in which the large and small crystals are of the same type (fig. 81).

As far as Sn 42 (the G point), similar features are seen in the chilled alloys, but this point marks the extreme limit of the γ type of primary. We shall refer to the lower chills of the EG alloys in discussing the succeeding groups.

Before leaving the region of chills in which γ is found, we wish to draw attention to the resemblance between the combs of γ , from their first appearance in Sn 21 to the latest we reproduce in Sn 38. It is very difficult to get good γ combs in the upper chills of the DE alloys, because the material is so unstable that it is more or less transformed and turned into η during the chill. But with normal combs of γ , such as those of Sn 33 for comparison, it is easy to trace the γ character in the primaries of Sn 21 (fig. 54), Sn 22 (fig. 58), and Sn 25 (fig. 65). Sn 27 forms normal γ combs like those of Sn 33. The maximum amount of γ found in each of the FG alloys occurs in the chill slightly above the G temperature, and this maximum decreases from the whole volume of the ingot in Sn 27 to a vanishingly small fraction in Sn 42.

The GH Alloys.—These alloys, ranging in composition from Sn 42 to Sn 87, deposit, when they begin to solidify, crystalline plates of the η type. We have been able to isolate these and analyse them. They appear to be the body Cu_3Sn in an almost or quite pure state. We have, therefore, drawn the solidus as a vertical line, E_2E_3 at the atomic percentage Sn 25. For a particular percentage of tin the large primary plates of η (generally seen in the figure as bars) increase in amount the lower the chilling temperature, so long as this does not fall below 400° . The chill primary is a network of slender bars or plates, that in the polished section may be described as needles. Polish alone shows the η , both primary and chill primary, as a purplish-white surrounded by a pure white tin-rich substance. If the section is kept for some days the contrast becomes greater through the gradual oxidation of the η , the mother-substance remaining a very pure white. For photography a slight ferric chloride etch is preferable, as it leaves the η unchanged and dissolves and blackens the ground. The chills of Sn 42 at 600° , and of Sn 45 at the same temperature, are of this type, but in the former (fig. 82) the large bars of η have curved lines of the

tin-rich material (black in the figure) crossing them; these suggest that the very first solid may have been γ . In Sn 45 this feature is not so well marked. This peculiarity perhaps indicates that the curve FG might have been traced for some distance below GH, in a region of unstable equilibrium.

If we compare chills, taken at, or a little below, 400° , of all the alloys from Sn 27 to Sn 87, that is almost from E to H, we find the η decreasing in amount from a quantity that almost fills the alloy at Sn 27 to a vanishingly small quantity, and with the larger percentages of tin the ingots are very liquid at the moment of chilling. Figs. 83 and 84 of ingots of Sn 38 and Sn 50 that had been kept in the vapour of boiling sulphur (at 445°) for 70 hours and then sharply chilled, show the decrease in the η with increasing percentage of tin, and fig. 85 of Sn 80 chilled without a very slow cool at 433° illustrates this decrease in a more marked way.

In the sulphur-boiled ingots in which the η has been in contact with the liquid for a long time, no doubt at a slightly varying temperature, the bars are rounded, and in fig. 83 one sees a tendency for them to group themselves into families. This rounded appearance is not seen in the η except in the sulphur-boiled ingots; the more usual appearance is of great angularity in the outline of the crystals, as in fig. 86, of a slow-cooled chill of Sn 50 that was maintained at 420° for some hours and then chilled. In this ingot the plane of section coincided with the plane of the plates; an inspection of the outside of the ingot shows that a section at right angles would have cut the plates at right angles and given a pattern of bars.

If one of the FGH alloys is cooled below 400° before chilling the amount of η is not increased but the bars are margined by a new substance, and the same new body is present as chill primary between the bars. This new substance H is the primary crystallisation of the branch HI of the liquidus. H and η are both very little acted on by hydrochloric acid, especially if excess of tin is present, and etching consequently leaves them both white on a dark ground. But the η gradually oxidises in the air and darkens so that it is readily distinguished from the H. Fig. 87 of Sn 73, chilled at 373° , illustrates the effect. It will be noticed that the bars of η are true crystals bounded by plane faces. They remind one of the twinned bars of η seen in fig. 57. If we chill below 400° a little H can be detected even in Sn 26, but it is well seen in the ingot of Sn 29 that was chilled at 380° , after having been kept at this temperature for four hours (fig. 88). In this ingot, except a few holes which may have been full of tin-rich mother-substance before the etch, the η and H fill the ingot. The conversion of the η into H by reaction with liquid at the temperature of 400° requires more detailed study, but we will reserve this point until the survey of the remaining groups is complete.

The HI Group.—The singularity H occurs in the liquidus at Sn 87. The curve does not change its direction perceptibly here, but ROBERTS-AUSTEN and STANSFIELD found a row of second halts in the cooling at this temperature in all alloys from about Sn 27 to Sn 87. We have not verified their results pyrometrically, but the

microscope amply confirms them. The evolution of heat is due to the reaction $\eta + \text{liquid} = \text{H}$. With perfect equilibrium transformations the whole of the η in all alloys between the percentages given by the points H' and H ought to disappear at temperatures below 400° in consequence of this transformation, but in the alloys as usually prepared the H only forms a thin coating over the crystals of η , much of the η remaining even in ingots that have not been chilled. We have however succeeded, by maintaining the ingots for a very long time at temperatures a little below 400° , in removing all η from alloys between the points H' and H. We shall return to this point.

With more tin than that contained in Sn 87, that is, in the HI alloys, the primary crystallisation should consist of H, and, in fact, as an unchilled ingot of Sn 90 shows (fig. 89), the alloy consists of primary crystals of H in a eutectic of H and tin. The crystals of H are often hollow, as if they had grown round something that had afterwards disappeared; this again suggests the possibility that, through a surfusion of the H, the η may have formed first and been decomposed when the H began to crystallise. We are not quite confident that the above is the true explanation of the peculiar and well-known form of the H. It will be noticed that the exterior of the crystals of H is rectilinear and angular, and that in the neighbourhood of a large crystal of H the mother-liquid has been so much exhausted of that body that there are no particles of H in the eutectic, while in places remote from a large crystal of H the eutectic is full of minute specks of that body. The same feature can be detected in the long slender crystals of H in an unchilled ingot of Sn 95 (fig. 90).

The IK Alloys.—With more tin than corresponds to the point I, it is no longer a copper-rich body which crystallises first, but a tin-rich body which must be very nearly pure tin. A chill of Sn 99, when well polished, showed primaries of a new type in a eutectic, but etching reagents destroy the pattern of primaries and only leave the patchy appearance of a solid solution. This end of the series deserves more attention than we have as yet been able to devote to it.

The Transformation $\eta + \text{liquid} = \text{H}$.

This reaction, which commences when any alloy of a composition between Sn 25 and Sn 87 sinks below the temperature of 400° , is necessarily a slow one, for as soon as the plates of η have become covered with a coating of H, the process can only proceed by a diffusion through the thickening layer of H. The diffusion is far from rapid at temperatures near 400° , and at much lower temperatures it practically ceases. Consequently, with ordinary rates of cooling, these alloys contain when cold three phases instead of two. This is recorded in the diagram by placing a bracket round the symbol of the third phase whose presence is due to an incomplete reaction. But, although this incomplete equilibrium is the usual condition of the alloys, it can be avoided. We have succeeded in transforming all the alloys from

Sn 45 to Sn 87 into complexes of H and Sn, free from η , and although it will not be quite so evident from the photographs, we think we have also eliminated all the eutectic from the alloys between Sn 25 and Sn 45. This result was attained by maintaining the temperature of the ingots for hours, and, in some cases, for many days and nights, at a temperature near 350° . By varying the length of this period of incubation one can watch the gradual disappearance of the phase to be eliminated. The constant temperature was that of a bath of boiling mercury, the little ingots being sealed in glass tubes and suspended in the vapour. The first alloy systematically examined in this way was Sn 50, and the series of photographs we publish illustrate the changes very well (figs. 84, 91, 92, 93, 94).

The Sn 50 maintained for some hours at 420° and then chilled (fig. 86), has been already described; it contained no H. Fig. 91 is that of an ingot that was not cooled very slowly, but was not chilled at all. This section cuts the plates of η so that they appear as bars. The η has oxidised a good deal before the photograph was taken, and it is seen to be margined and traversed by narrow threads of pure white H. This small amount of H is what one usually finds when no special pains have been taken to complete the reaction by slow cooling.

The next ingot (fig. 92) had been maintained for 10 hours at 380° before chilling. The η is now seen to be surrounded by a thick margin of H, and although the photograph does not perhaps make it evident, the proportion of tin-rich mother-substance has decreased considerably. The next ingot was maintained for 60 hours in the mercury bath at about 350° . It will be seen from the photograph (fig. 93), that the η is now reduced to a few spots and lines enveloped in the massive H.

In order to ascertain whether the reaction could be made complete, an ingot was boiled for 21 days and nights in the mercury bath. This operation, as fig. 94 shows, has removed every trace of η , and very much changed the character of the masses of H. The shape of the H had been hitherto dependent on that of the original η , but now the grains of H are independent of each other, and though still rounded they are beginning to change into polyhedra with plane faces. It would be interesting to study the effect of a still longer incubation on the shape of the H. We have isolated these little pellets of H and examined them under a low power; they are then seen to be crystalline.

The ingot of Sn 50 (fig. 94) contains around the masses of H a considerable amount of tin-rich eutectic, in other words the H does not fill the alloy; consequently, this H cannot be exactly CuSn. We therefore examined ingots of Sn 40, 42, 45, as well as ingots of Sn 55, 60 and 85, that had all been heated for 21 days in the mercury bath. The result showed that all the η , except mere traces, could be removed from Sn 45, but that, although large portions of the section were compact H, yet there were large gaps in the H (fig. 95). These gaps appear, however, to be cavities in the ingot, and not spaces full of the eutectic. These gaps are numerous in all the alloys, such as Sn 45 to Sn 40, when they have been boiled for a long time in mercury; we think it

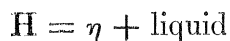
probable that they are due to a contraction accompanying the reaction in which the H is formed from the mixture of η and liquid.

The chill of Sn 42 (fig. 96), and in a still more marked degree the chill of Sn 40 (fig. 97), contains η uniformly scattered through the massive H. This study of the H transformation seems to point to the conclusion that the H body has at 350° a composition not far from that of Sn 45. This conclusion is confirmed by the results of analyses of the H extracted from ingots of Sn 90, which give the value of Sn 45.5. Thus neither the microscope nor the analyses allow us to regard H as pure CuSn, but it is very probably this body with a few per cent. of Cu_3Sn in solid solution.

Fig. 98 is a photograph of an ingot of Sn 60 after 21 days in mercury at 350° . Like most of the ingots boiled in mercury it was not chilled, although it was cooled rapidly at the end of the period of boiling. When compared with Sn 50 we see less of the H and more of the eutectic. The progress of the masses of H towards the condition of polyhedra is well marked.

Fig. 99 is an ingot of Sn 85 after 21 days in mercury. Some of the masses of H have the rounded form that indicates their origin from η , but there are other crystals of H which are probably idiomorphic.

Fig. 101 illustrates the facility with which the reverse change



takes place. It is an ingot of Sn 50 that had been heated for 10 days in mercury vapour, the η having been thus almost entirely removed; it was then heated for a few minutes to a temperature a little above 400° , with the result that all the masses of H have broken up into η and liquid. The pattern, resembling that of 93, produced by the mercury boiling, can still, however, be traced.

Fig. 100 records an early attempt to study the reaction of the H temperature. A considerable mass of the alloy Sn 90 was maintained for several hours at a temperature slightly below 400° , and it was automatically stirred by means of a massive copper stirrer made of coils of thick wire. The reaction, which produced nothing but H, was continued until the stirring was brought to an end by the large quantity of solid H that had formed. The ingot was then cut and polished as usual. A comparison with fig. 89 makes the great increase in the amount of H very evident.

The Isolation and Analysis of the Bodies η and H.—The fact observed during the etching of the alloys, that hydrochloric acid has no perceptible action on the crystals of η or H, can be utilised for the separation of these bodies from an alloy in which one of them is present together with tin. If we wish to get pure η , the alloy must be sharply chilled at a temperature above 400° ; to obtain pure H, the alloy must have been maintained at a temperature a little below 400° for a period long enough to transform all the η . It is in the observance of these two precautions that our method of isolating the substances constitutes an advance on previous work. We find that the ingots of alloy are rapidly disintegrated by the action of strong

hydrochloric acid at 30° C., and that if air is excluded there is no solution of copper until all the excess of tin has been dissolved. The alloys disintegrate to a grey or black mud, which can be elutriated, leaving as a residue well-formed plates of η or brilliant slender spearlike filaments of H. The washed H can be left for days in contact with strong cold hydrochloric acid without perceptible solution of either copper or tin. The η is more attacked when the excess of tin has been removed, but the attack is slight.

The following are the results of some analyses, the composition being expressed in percentage weights of tin. In a few cases the copper was independently determined.

COMPOSITION of η .

Alloy.	Chilled at	Percentage of tin in η .	Percentage of copper in η .
Sn 35	550	39·09	—
Sn 35	550	38·53	61·20
Sn 35	450	39·15	—
Sn 50	450	39·10	60·89
Sn 50	450	38·5	—
Sn 50	450	38·77	—
Sn 65	450	41·71	57·88
Sn 65	450	42·20	—

The above were early experiments, and no very great care was taken to maintain the temperature constant for a considerable time before chilling. Three ingots were however, treated after three days and nights in boiling sulphur vapour and then chilling. This preparation may be expected to ensure equilibrium between the solid and the liquid phases at 450°. The results are given below.

 η SULPHUR Boils 454°.

Alloy.	Sn 38.	Sn 38.	Sn 50.	Sn 70.
Per cent. of tin in the η	38·73	38·53	39·73	38·97

In theory, whatever the percentage of the alloy, the composition of the solid phase at a particular temperature should be the same, and depend on the temperature only. But the character of the ingot at the moment of chilling seriously affects the possibility of extracting the desired body free from excess of tin, as, unless each plate of η is separated from its neighbours, inclusions of tin may be unavoidable. Most of the discrepancies in the result are probably due to this cause. In view of the value

obtained from Sn 70 in the sulphur-boiled series, we do not think that the earlier very high values from Sn 65 are to be trusted; if we neglect these we get an average content of slightly under 39 per cent. of tin in the η , with practically no difference between the η at 550° and 450° . It must be remembered that no method of chilling will prevent the presence of a trace of H on the plates of η .

The percentage required by the formula Cu_3Sn is 38.35, so that the analyses are consistent with the view that the η is this compound with a little of a more tin-rich body in solid solution; but the excess of tin is so small and so easily accounted for that we have drawn the solidus from E_2 to E_3 as a vertical straight line.

The samples of H were prepared in various ways and isolated from excess of tin in the manner above described. The H prepared by the use of the copper stirrer, that is the H of fig. 100, contained 61.2 and 61.4 per cent. of tin; after re-crystallisation in tin in a vacuum tube and separation from excess of tin, it contained 61.5 and 61.85 per cent. Sn 45, after 21 days in mercury vapour, gave 60.42 per cent. Sn 60, similarly treated, gave 61.15, and Sn 90, after the same treatment, gave 60.8 and 61.2 per cent. All these, with the exception of the re-crystallised H, had been maintained for a long time at 350° . The mean value, neglecting that of the re-crystallisation H, is 61.1 per cent. A sample of Sn 90 was incubated for three days and nights at 250° , after a previous period at 350° : the H extracted from it contained 61.91 and 61.73 per cent. of tin. These two values suggest, though they can hardly be said to prove, an increase in the tin content of the H at lower temperatures. The percentage of 61.1 at 350° gives to the H an atomic percentage of 45.5, and agrees extremely well with the results of the microscopic examination of the alloys boiled in mercury. We have fixed the point H' in the diagram in accordance with these results.

There is a reasonable certainty that the H is not pure CuSn , though it may very well be that body containing a little of the higher compound in solid solution. There is very little justification from these results for the slope we have given to the branch H'H'' of the solidus, and we have therefore drawn it as a dotted line to indicate the uncertainty. We think a further examination of such alloys as Sn 47 after a prolonged heating at 250° may settle the position of H''. At present, the only argument for placing H'' at Sn 50 is to be found in the numerical value of the depression of the freezing-point of tin by small additions of copper, that is, from the slope of the branch IK of the liquidus. This appears to prove that, whatever the molecule in solution in the liquid tin, it can contain only one atom of copper.*

We hope that the experimental evidence given in the preceding pages will be considered to justify the general conclusions of Section I.

We are much indebted to Miss D. MARSHALL, B.Sc., Lecturer at Girton, and to Mr. W. FEARNSIDES, B.A., of Sidney College, for the help they have given us in the

* 'British Association,' 1900—"Report on Alloys," by F. H. NEVILLE.

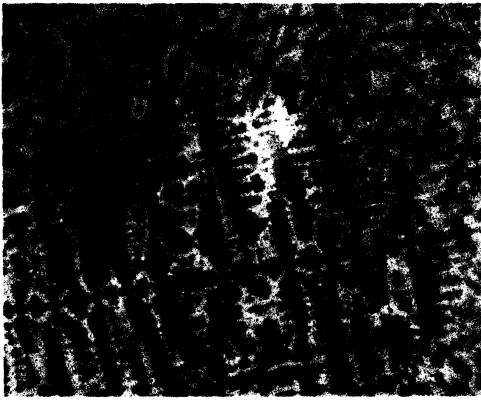
experiments. Mr. FEARNSIDES took many of the more difficult photographs, and carried out many of the tedious experiments on the slow cooling and chilling of the alloys.

During the course of the research Professor BAKHUIS ROOZEBOOM was kind enough to write to us several encouraging and instructive letters on the theory of the subject, and we wish here to express our gratitude to him.

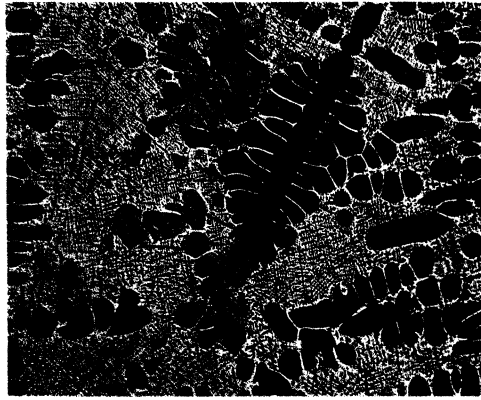
We have also had help and encouragement from the late Sir GEORGE STOKES.

PLATE 1.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
1	Sn 1	1·85	× 18	Unchilled	Ignited	Dark cores in the α .
2	Sn 2	3·7	× 45	C. 1025°	HCl + FeCl ₃	Dark α primaries.
3	"	3·7	× 10	S.c.c. 957°	"	Grains of α possessing different orientation. Oblique illumination.
3A	"	3·7	× 10	S.c.c. 957°	"	Dark α in white liquid. Vertical illumination.
4	"	3·7	× 18	S.c.c. 882°	HCl	Homogeneous α .
5	"	3·7	× 18	V.s.c.c. 770°	NH ₃	"
5A	Sn 4	7·2	× 18	S.c.c. 800°	HCl	Cores in the α combs.
6	"	7·2	× 18	V.s.c.c. 900°	HCl + Br	α combs and liquid.
7	"	7·2	× 45	V.s.c.c. 800°	HCl	Homogeneous α .
8	"	7·2	× 18	V.s.c.c. 775°	HCl + Br	Cores in α . No matrix.
9	"	7·2	× 18	V.s.c. not chilled	HCl + FeCl ₃	Grains of uniform α .
10	Sn 6	10·15	× 45	C. at 966°	"	Dark α in white liquid.
11	"	10·15	× 18	S.c.c. 805°	HCl and repolish	Light α and liquid.



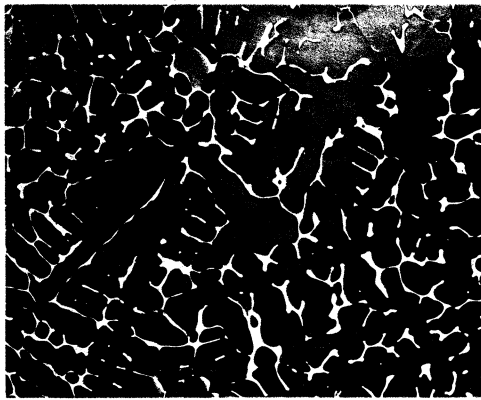
1



2



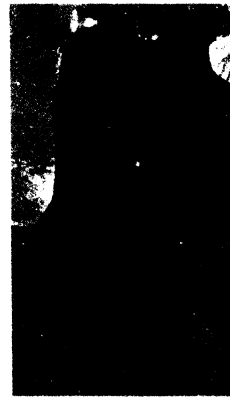
3



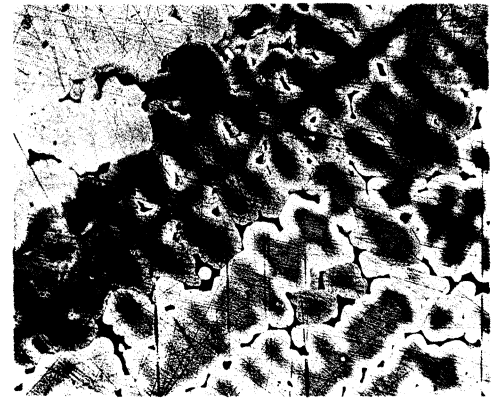
3A



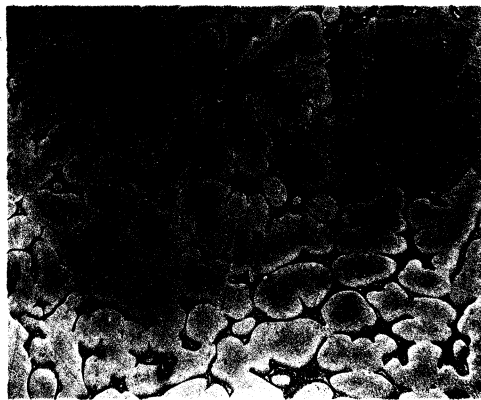
4



5



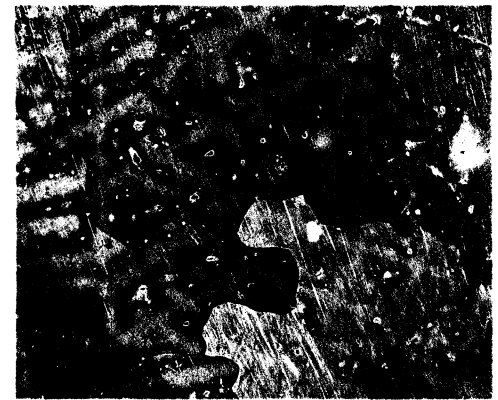
5A



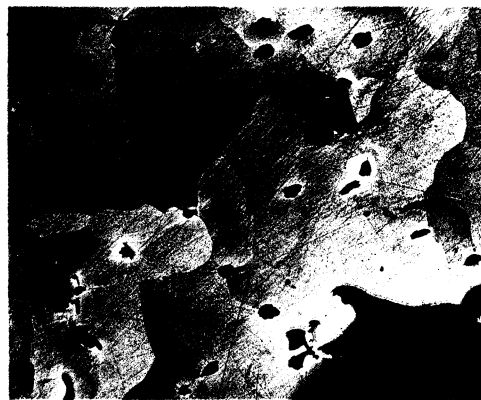
6



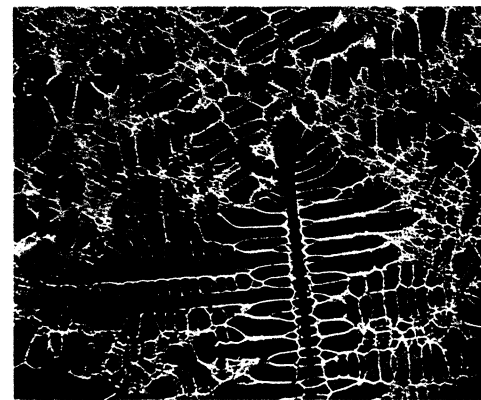
7



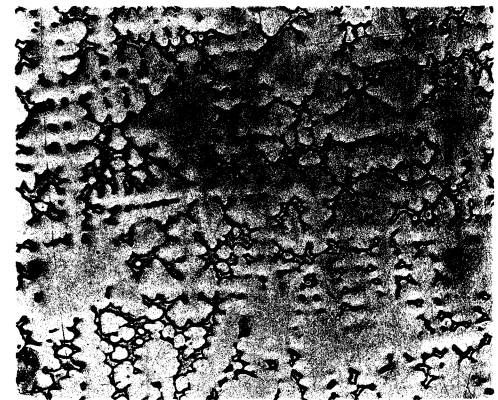
8



9



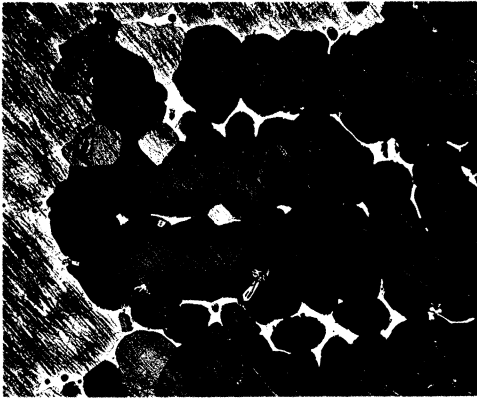
10



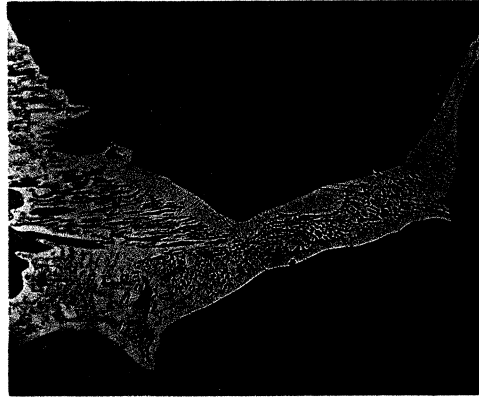
11

PLATE 2.

Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
12	Sn 6	10·15	× 18	V.s.c. not chilled	HCl + FeCl ₃	α , dark. C' complex, light.
13	„	10·15	× 280	„ „	„	Patch of C' complex ($\alpha + \delta$).
14	Sn 9	15·6	× 120	C. 880°	„	Primary and chill primary of α (light), in matrix that was liquid at chilling temperature.
15	„	15·6	× 18	C. 777°	„	α , light. β , dark.
16	„	15·6	× 18	V.s.c.c. 546°	„	„ „
17	„	15·6	× 18	V.s.c.c. 470°	„	α , dark. C' complex, light.
18	„	15·6	× 280	V.s.c.c. 546°	„	Uniform dark β , margin of white δ . α outside.
19	„	15·6	× 280	V.s.c.c. 470°	„	Patch of C' complex ($\alpha + \delta$), bordered by δ . α outside.
20	Sn 12	20·3	× 18	S.c.c. 805°	„	Primary α , light. Liquid darker. Chill primary of β , darkest.
21	„	20·3	× 18	V.s.c.c. 775°	„	Partly dissolved α , light. Ground of solid striated β .
22	„	20·3	× 18	C. 550°	„	Light α that has crystallised out of the solid uniform β . Dark β .
23	Sn 13·5	22·5	× 18	V.s.c.c. 775°	„	Striated β free from α .



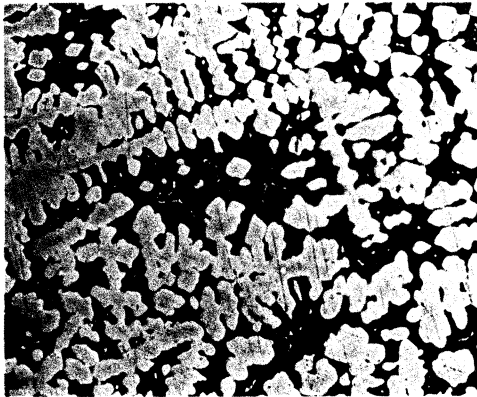
12



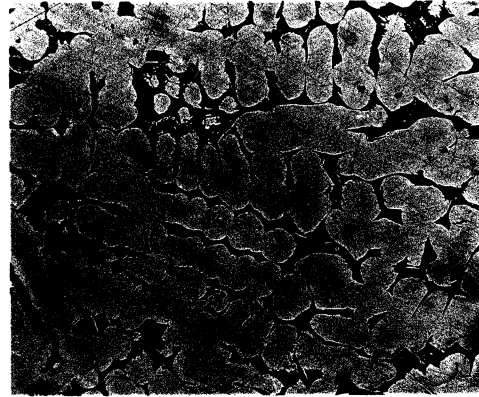
13



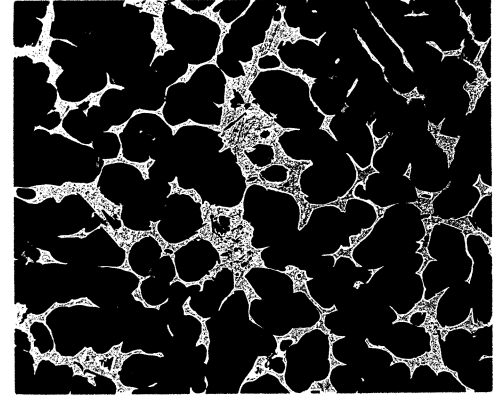
14



15



16



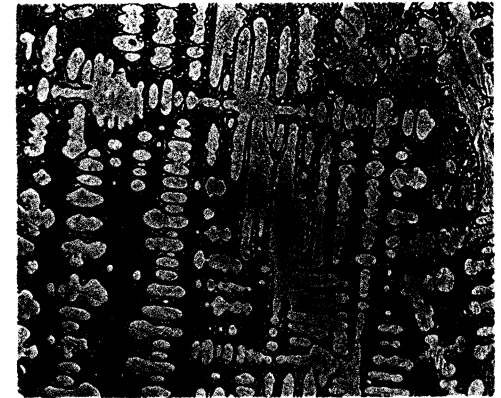
17



18



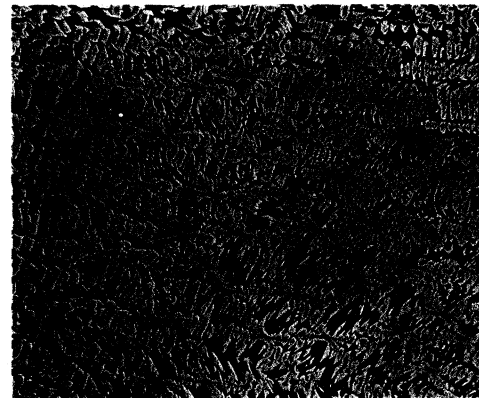
19



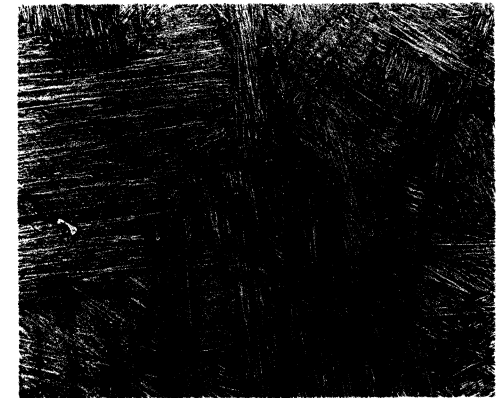
20



21



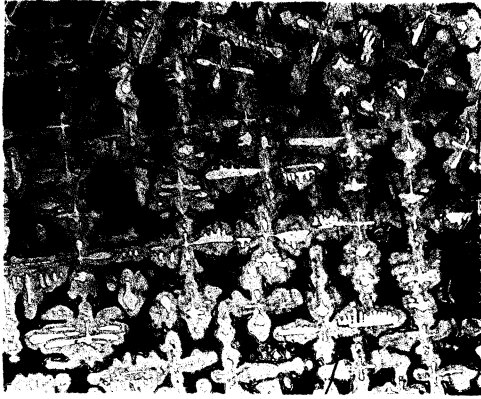
22



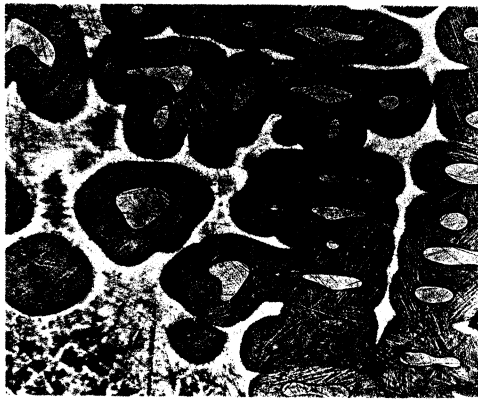
23

PLATE 3.

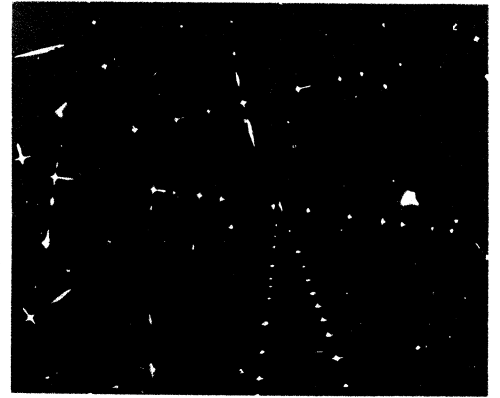
Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
24	Sn 13·5	22·5	× 18	C. 765°	HCl + FeCl ₃	Residue of α , white, in β combs, darker. Liquid darkest.
25	„	22·5	× 45	C. 775°	„	Residue of α in darker striated β . Dark chill primary of β . Liquid light.
26	„	22·5	× 18	C. 740°	NH ₃ (negative)	Residual α , light. β , dark.
27	„	22·5	× 18	C. 558°	HCl + FeCl ₃	New α , light. Uniform β , dark.
28	Sn 14	23·3	× 18	V.s.c.c. 800°	„	Primary α , light. Liquid and chill primary of β , dark.
29	„	23·3	× 18	V.s.c.c. 675°	„	Striated β only.
30	„	23·3	× 18	V.s.c.c. 600°	„	New α , white. Dark and striated β .
31	„	23·3	× 18	V.s.c.c. 530°	„	New α , white. Uniform β , dark.
32	„	23·3	× 18	V.s.c.c. 470°	„	α , dark. C' complex ($\alpha + \delta$), light.
33	Sn 15	24·75	× 18	V.s.c.c. 600	„	Grains of uniform β .
34	Sn 15·5	25·5	× 45	C. 750°	„	Dark primary crystals of β , chill primary of β . Tin-rich liquid, white.
35	„	25·5	× 45	C. 552°	„	Uniform β . <i>Oblique illumination.</i>



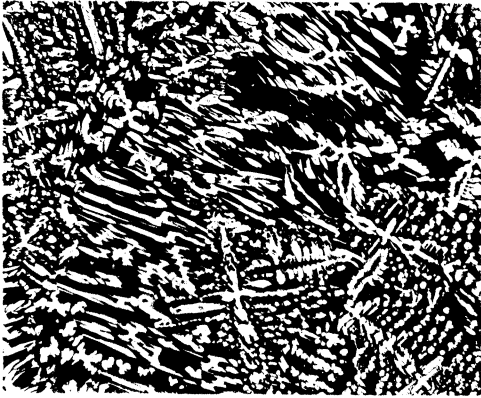
24



25



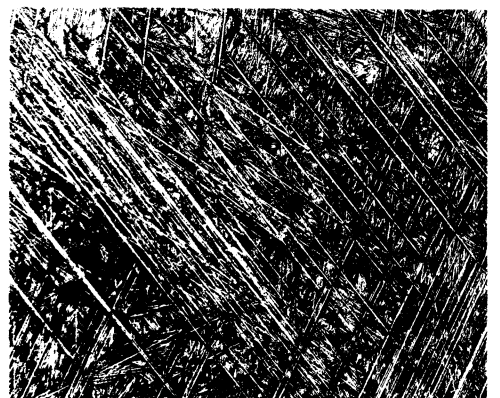
26



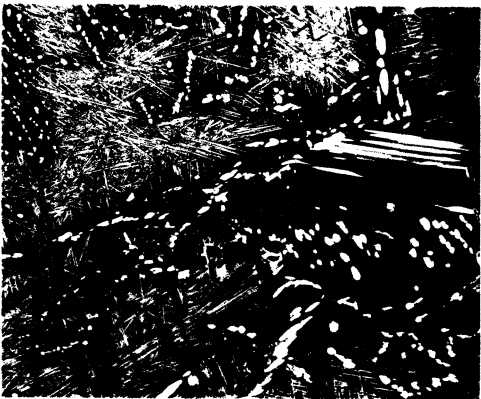
27



28



29



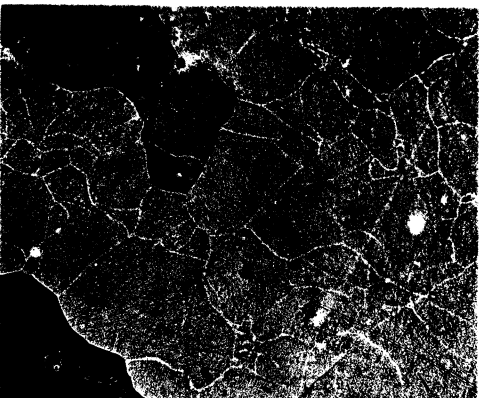
30



31



32



33



34



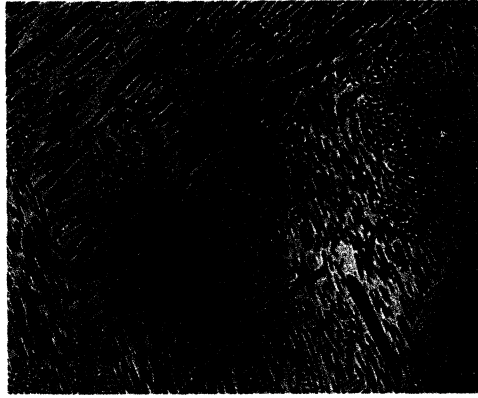
35

PLATE 4.

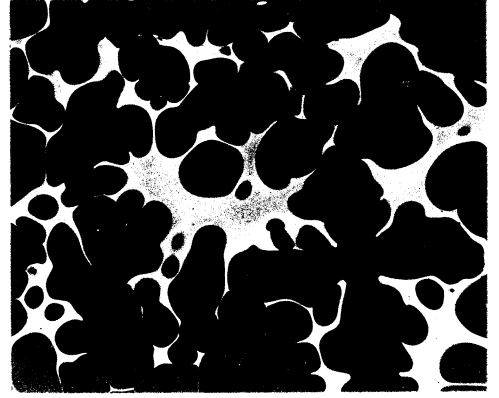
Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
36	Sn 15.5	25.5	× 45	C. 452°	HCl + FeCl ₃	C' complex. <i>Oblique illumination.</i>
37	„	25.5	× 550	C. 452°	„	C' complex. Vertical illumination.
38	Sn 16	26.25	× 18	V.s.c.c. 752°	„	Dark β. Tin-rich liquid white.
39	„	26.25	× 18	V.s.c.c. 738°	„	β filling ingot.
40	„	26.25	× 280	Not chilled	„	Crystals of δ in C' complex.
41	Sn 17	27.65	× 45	V.s.c.c. 745°	„	Maximum of β in liquid.
42	„	27.65	× 18	C. 731°	NH ₃	Dark β in tin-rich matrix.
43	Sn 18	29.05	× 18	C. 734°	HCl + FeCl ₃	β decomposing (D. reaction).
44	Sn 19	30.4	× 125	C. 733°	„	„ „
45	Sn 18	29.05	× 45	V.s.c.c. 728°	„	Homogeneous. Probably γ.
46	Sn 17	27.65	× 45	C. 495°	„	Commencement of δ crystals.
47	„	27.65	× 250	C. 450°	„	White δ in C' complex.



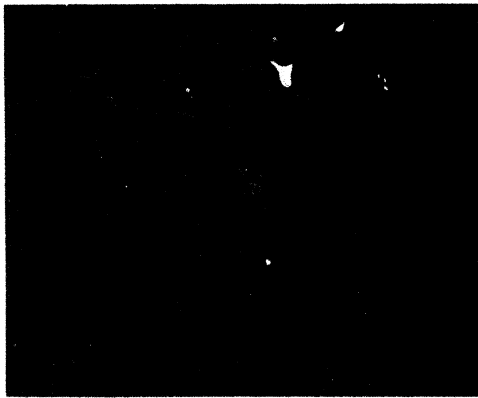
36



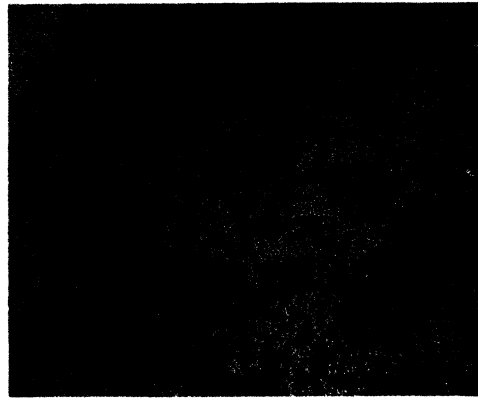
37



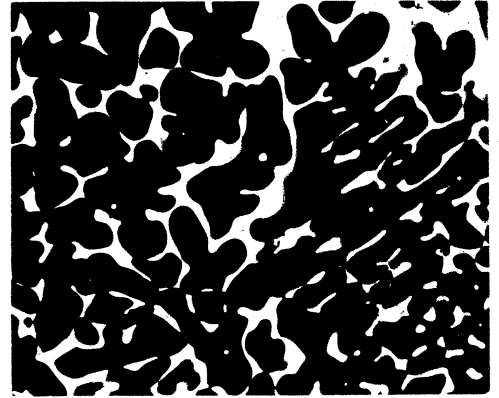
38



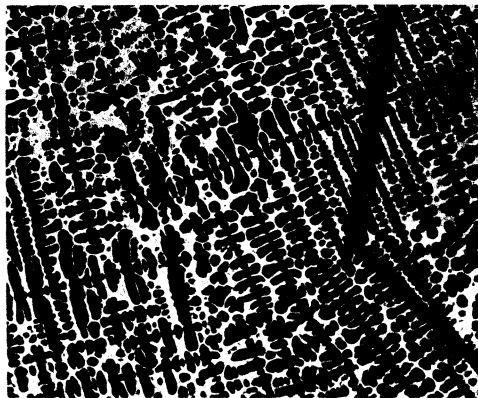
39



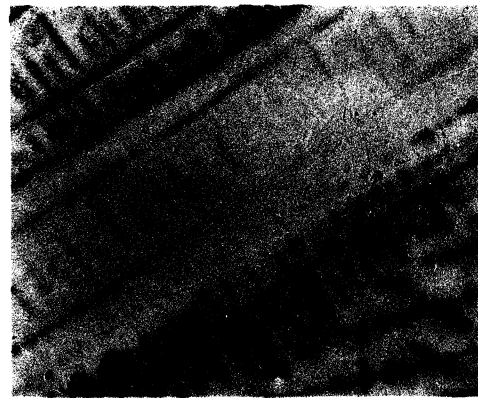
40



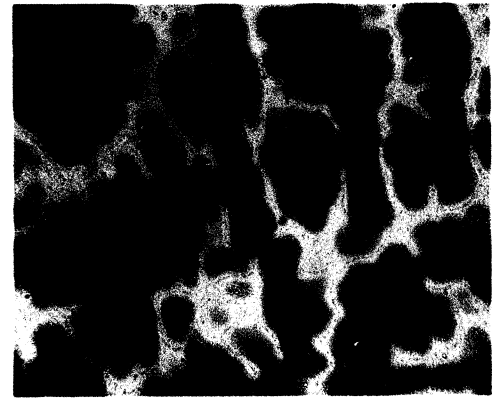
41



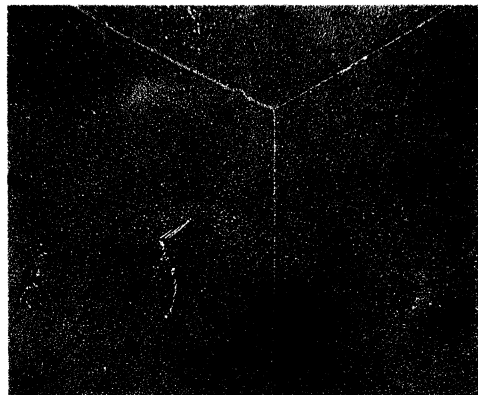
42



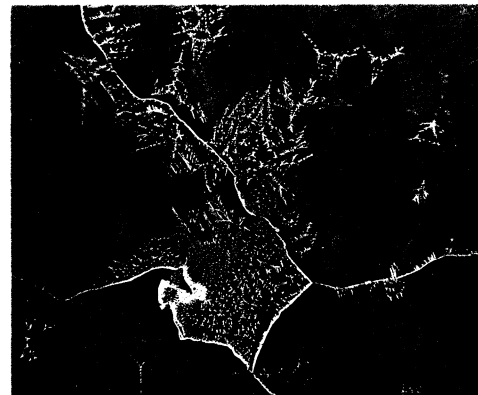
43



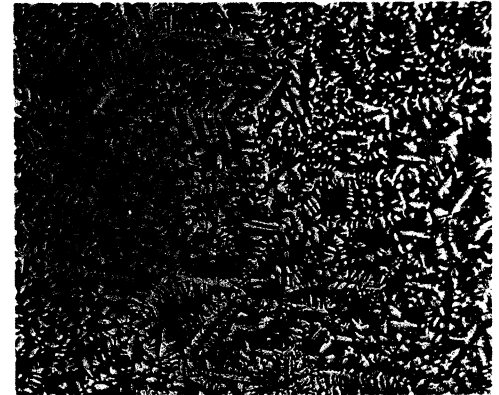
44



45



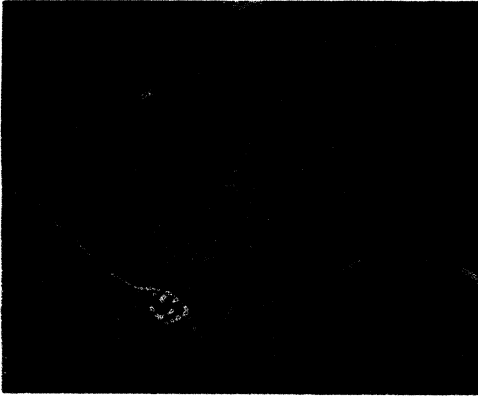
46



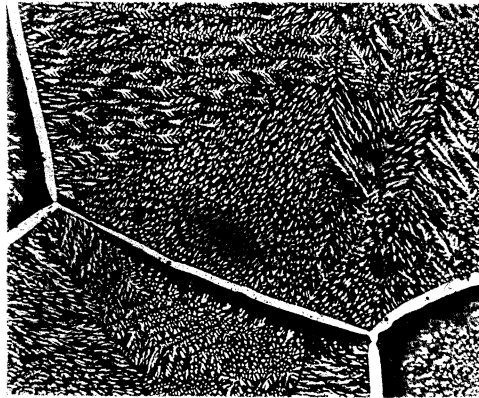
47

PLATE 5.

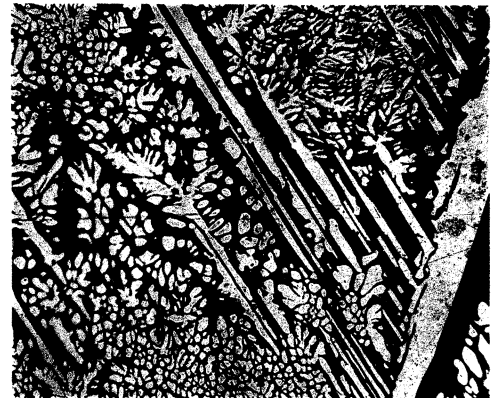
Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
48	Sn 18	29.05	× 45	S.c.c. 550°	HCl + FeCl ₃	Uniform solid.
49	Sn 19	30.4	× 45	S.c.c. 550°	„	White crystallisation of δ .
49A	„	30.4	× 45	S.c.c. 550°	„	„ „
50	Sn 18	29.05	× 45	C. 501°	„	„ „
51	Sn 20	31.8	× 18	C. 726°	„	Decomposing β in a white tin-rich matrix.
52	„	31.8	× 45	Not chilled	„	White δ . Traces of C' complex.
53	Sn 19	30.4	× 800	„	„	Patches of C' complex in lighter α .
53A	Sn 20	31.8	× 600	„	„	Patches of C' complex in lighter α .
54	Sn 21	33.15	× 45	S.c.c. 725°	„	γ primary and chill primary.
55	„	33.15	× 45	C. 650°	„	Uniform γ .
56	„	33.15	× 45	S.c.c. 590°	„	Dark η . Light δ .
57	„	33.15	× 45	C. 580°	„	Twinned plates of η .
58	Sn 22	34.45	× 45	C. 733°	„	Primary combs of γ .
59	„	34.45	× 18	C. 690°	„	Uniform γ and slender dark bars of η .



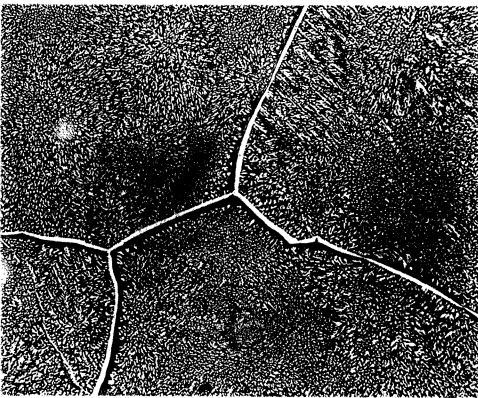
48



49



49A



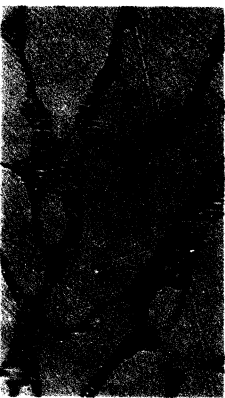
50



51



52



53



53A



54



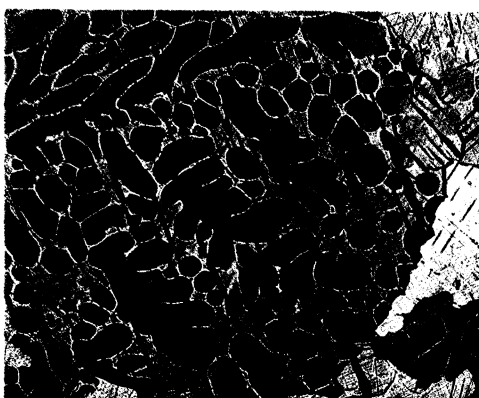
55



56



57



58



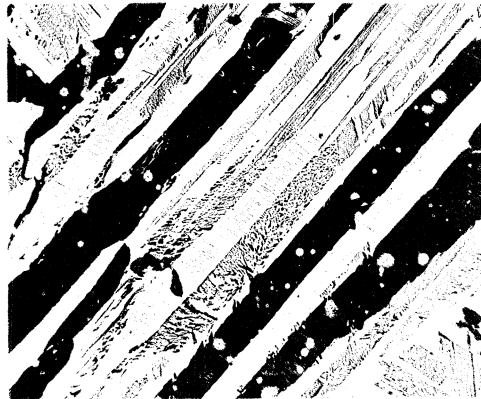
59

PLATE 6.

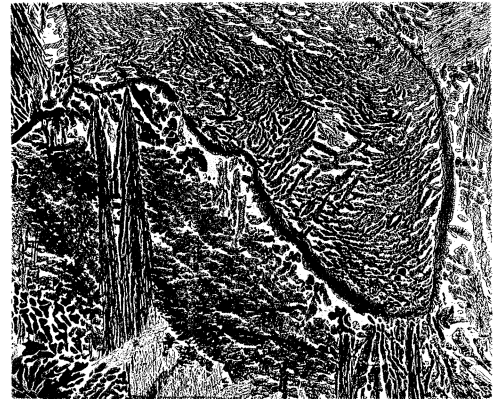
Figure	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
60	Sn 22	34.45	× 18	S.c.c. 565°	HCl + FeCl ₃	Dark bands of η and lace complex of $\delta + \eta$.
61	„	34.45	× 45	C. 495°	„	Dark bars of η and lace bars of $\delta + \eta$.
62	Sn 23	35.8	× 18	V.s.c.c. 620°	„	Crystallisation of η increasing in amount.
63	Sn 24	37.1	× 18	S.c.c. 685°	„	Solid γ (crystallisation of η not wholly prevented by chill).
64	„	37.1	× 18	S.c.c. 635°	„	Dark crystals of η nearly filling the alloy.
65	Sn 25	38.4	× 13	S.c.c. 720°	Ignited to orange	Copper-rich γ combs darker than tin-rich liquid.
65A	„	38.4	× 45	S.c.c. 720°	„	Shows the breaking up of the γ into complex of fig. 64.
66	„	38.4	× 18	Not chilled	HCl + FeCl ₃	Bars of differently oriented η .
67	Sn 26	39.65	× 45	C. 656°	„	Solid solution of γ .
68	„	39.65	× 45	C. 612°	„	Plates of η .
69	Sn 27	40.8	× 18	S.c.c. 647°	„	γ with traces of liquid and chill primary of η bars.
70	„	40.8	× 45	S.c.c. 635°	„	Solid solution γ .
71	„	40.8	× 45	C. at 625°	HCl + Br	Plates of η with inclusions of tin-rich liquid.



60



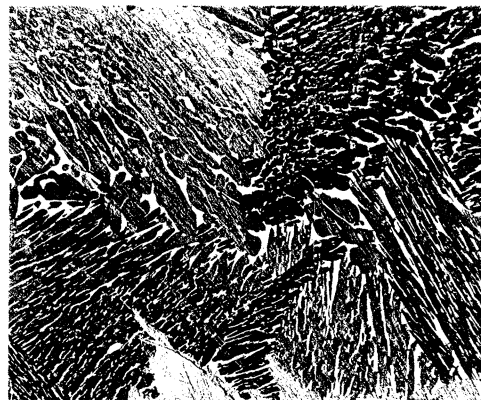
61



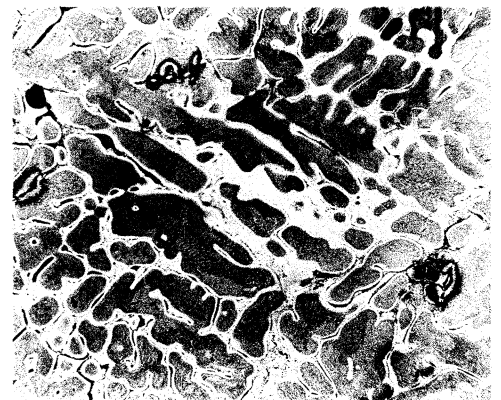
62



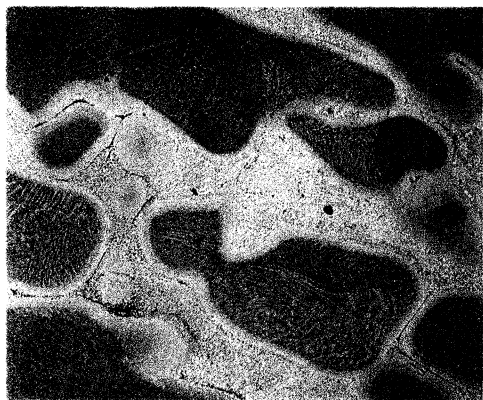
63



64



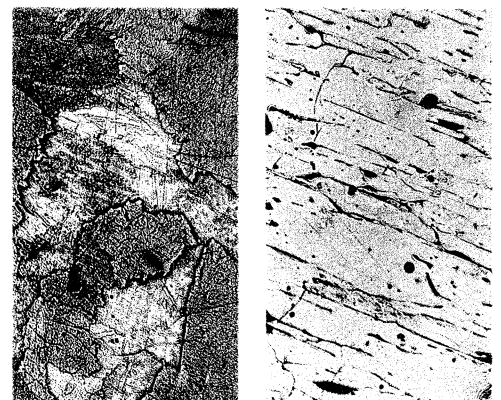
65



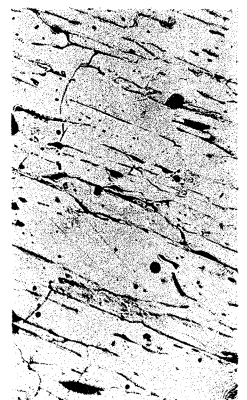
65A



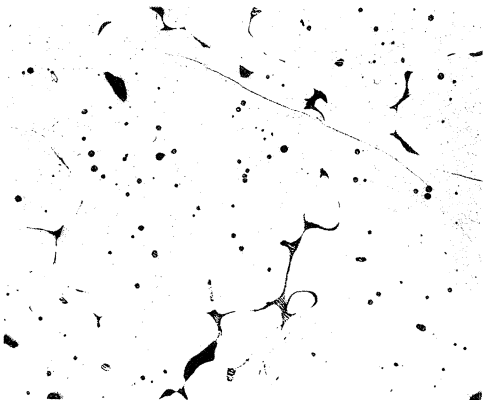
66



67



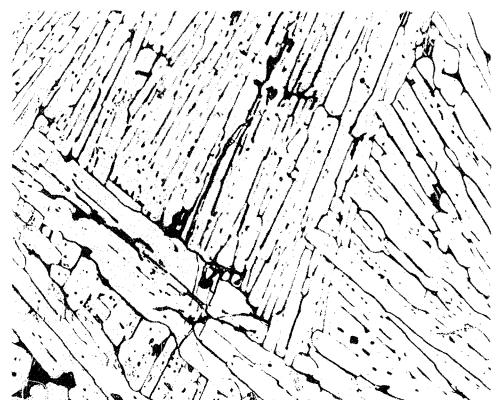
68



69



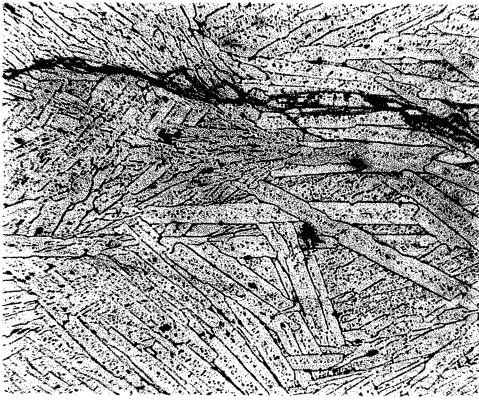
70



71

PLATE 7.

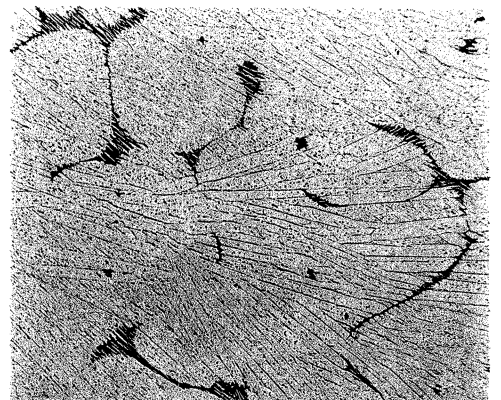
Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
72	Sn 27	40.8	× 18	C. 565°	HCl + FeCl ₃	Plates of η with inclusions of liquid (due to G transformation).
73	Sn 28	42.05	× 45	S.c.c. 650°	„	Uniform lobes of γ . Chill primary of η . Dark tin-rich liquid.
74	„	42.05	× 45	S.c.c. 625°	„	Same as preceding, except that the G reaction has occurred.
75	Sn 33	47.9	× 45	C. 676°	„	Primary γ . γ chill primary.
76	„	47.9	× 18	C. 644°	„	Primary of γ . Chill primary of η .
77	„	47.9	× 45	C. 644°	„	Primary of γ . Chill primary of η .
78	„	47.9	× 45	C. 628°	„	Same, after the G transformation.
79	Sn 38	53.35	× 45	C. 644°	„	Primary γ . Chill primary of η .
80	„	53.35	× 45	C. 628°	„	The incomplete G transformation.
81	„	53.35	× 45	C. 606°	„	The complete G transformation.
82	Sn 42	57.5	× 18	C. 600°	„	Primary and chill primary of η .
83	Sn 38	53.35	× 45	S.c.c. 445°	„	Primary η after 70 hours in boiling sulphur.



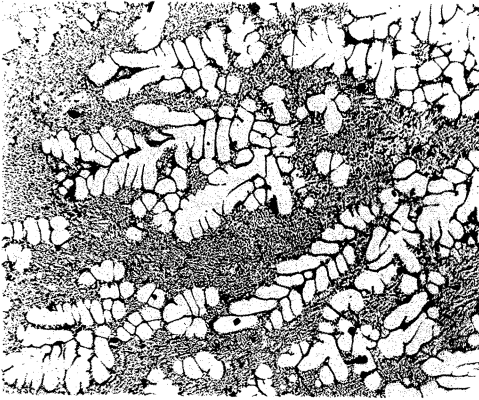
72



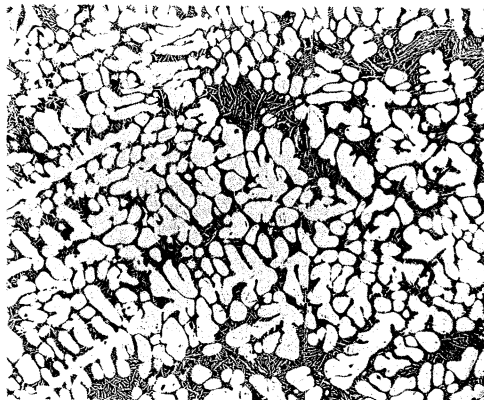
73



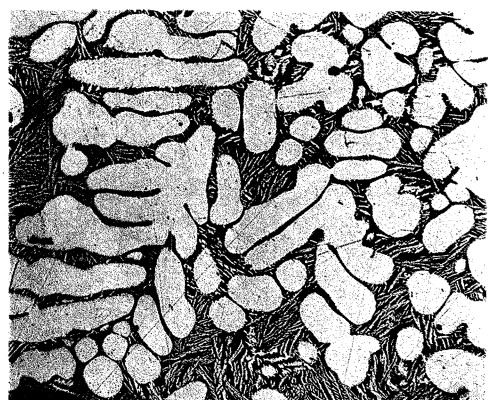
74



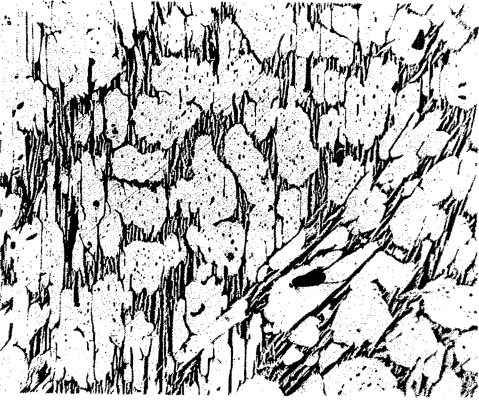
75



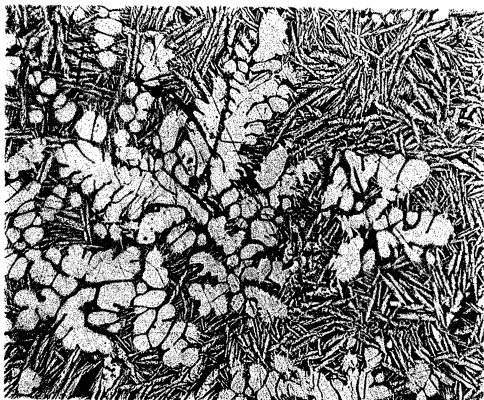
76



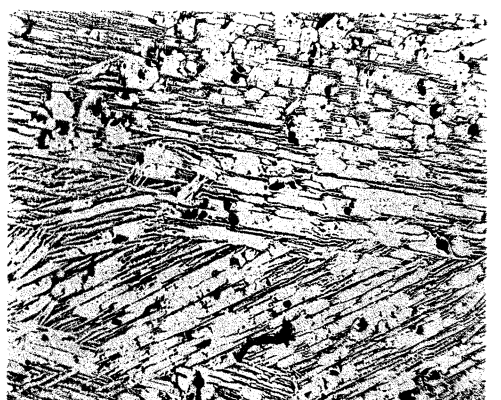
77



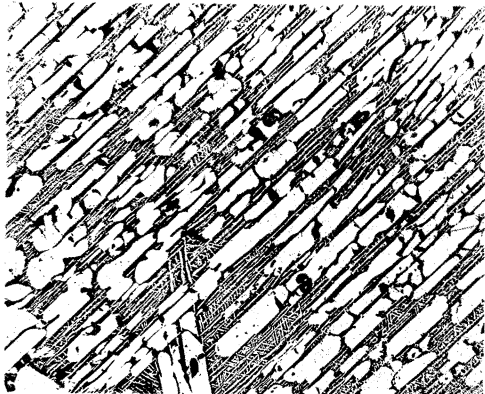
78



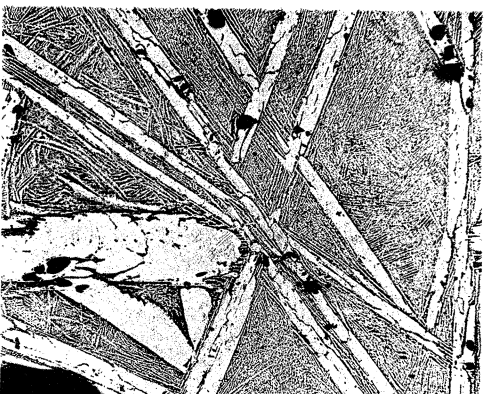
79



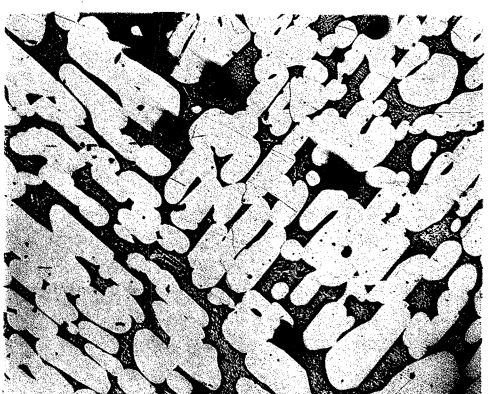
80



81



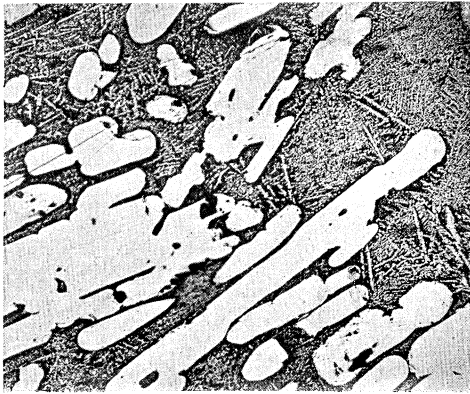
82



83

PLATE 8.

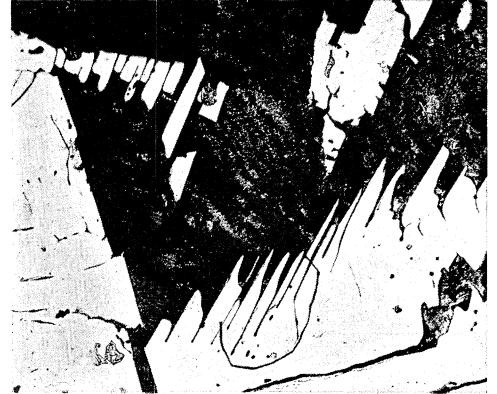
Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
84	Sn 50	65·1	× 45	S.c.c. 445°	HCl + FeCl ₃	Primary η after 70 hours' sulphur boil. Chill primary is H.
85	Sn 80	88·2	× 18	C. 433°	„	Primary plates of η in tin-rich liquid.
86	Sn 50	65·1	× 45	S.c.c. 420°	„	Primary plates of η in tin-rich liquid.
87	Sn 73	83·5	× 45	C. 373°	„	Plates of darkened η , margined by white H. In liquid.
88	Sn 29	43·2	× 45	S.c.c. 380°	„	Plates of darkened η , margined by H. No liquid.
89	Sn 90	94·4	× 45	Not chilled	„	Primary of H in eutectic of H and tin.
90	Sn 95	97·25	× 45	„	„	Primary of H in eutectic of H and tin.
91	Sn 50	65·1	× 45	„	„	Bars of η with narrow margin of H, in H + tin eutectic.
92	„	65·1	× 18	C. after 10 hours at 380°	„	H reaction incomplete. η largely transformed.



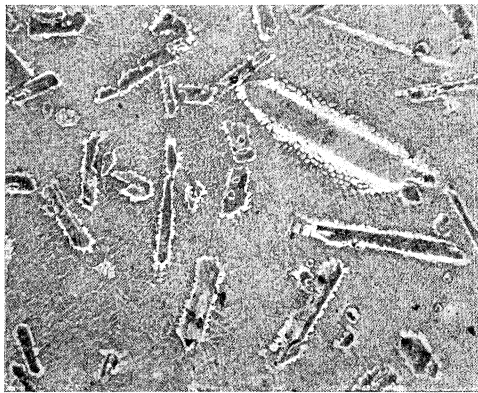
84



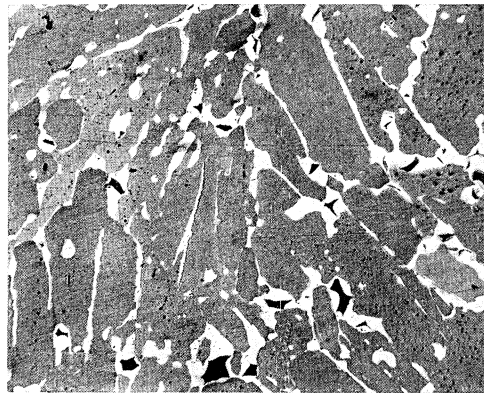
85



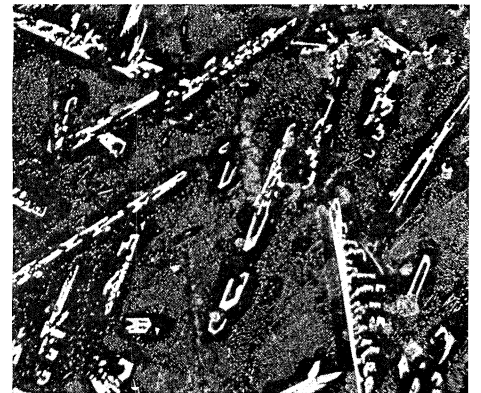
86



87



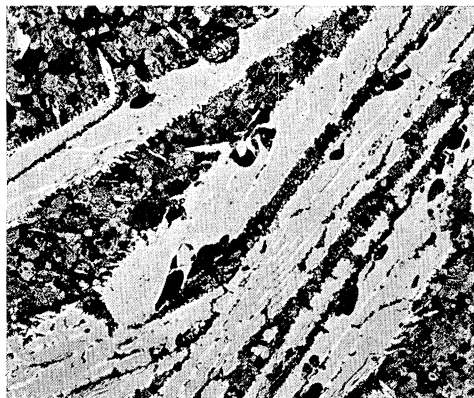
88



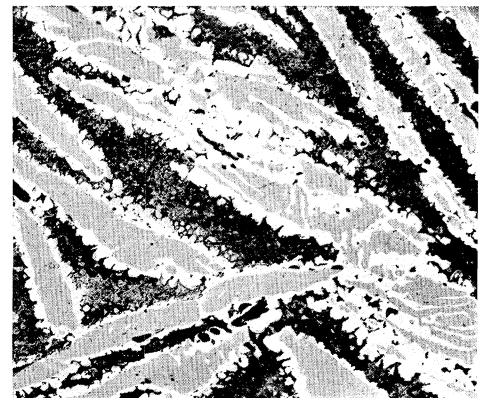
89



90



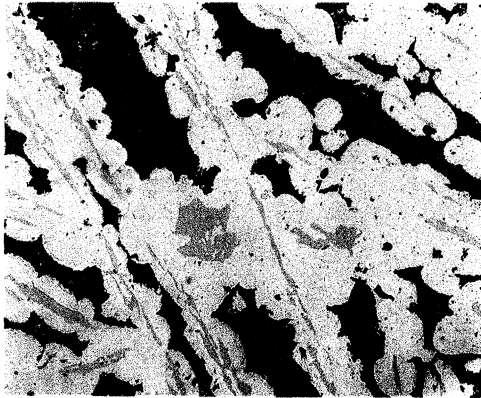
91



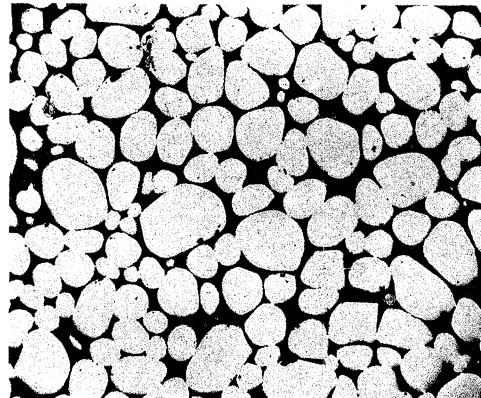
92

PLATE 9.

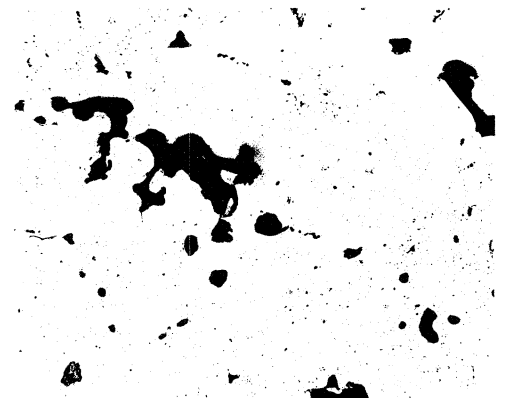
Figure.	Atomic percentage of tin.	Per cent. by weight of tin.	Magnification.	Method of cooling the ingot.	Method of etching.	Description.
93	Sn 50	65·1	× 18	After 60 hours at 350°	HCl + FeCl ₃	Traces of η in bands of H. Tin-rich liquid dark.
94	„	65·1	× 18	After 21 days at 350°	„	η entirely gone. Polyhedra of H. Dark tin-rich matrix.
95	Sn 45	60·4	× 45	After 21 days at 350°	„	Uniform H, with holes. No liquid. No η .
96	Sn 42	57·5	× 18	24 days at 350°	„	Compact H, containing η . Many cavities (black).
97	Sn 40	55·4	× 45	21 days at 350°	„	Compact H, containing η .
98	Sn 60	73·7	× 45	21 days at 350°	„	Light polyhedra of H in the H + tin eutectic.
99	Sn 85	91·3	× 45	21 days at 350°	„	Two types of H crystals in the eutectic.
100	Sn ?	?	× 45	—	„	H made by prolonged stirring of Sn 90 at 350° by means of a copper stirrer.
101	Sn 50	65·1	× 18	10 days at 350° then heated to 400°	„	η and liquid produced from H by heating for a short time to above 400°.



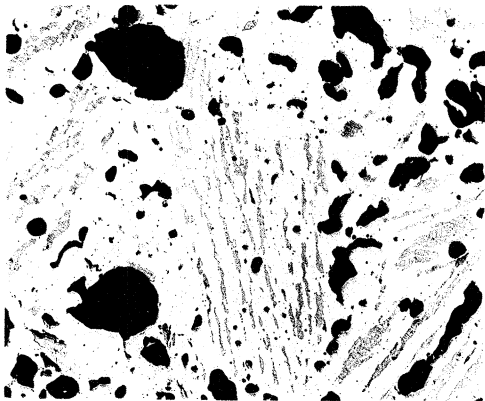
93



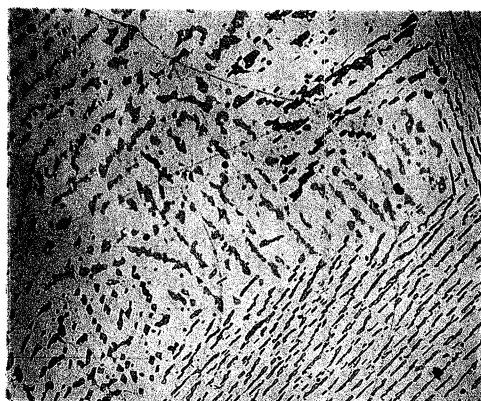
94



95



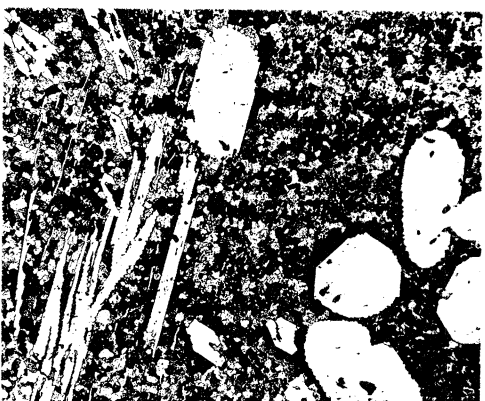
96



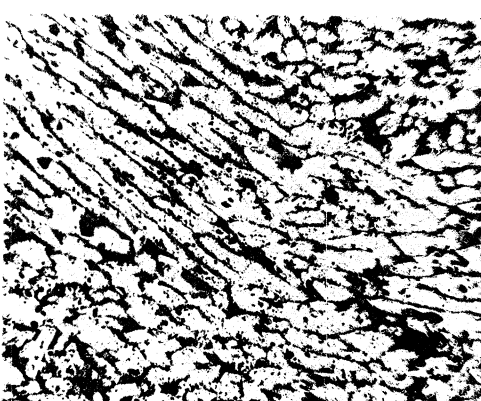
97



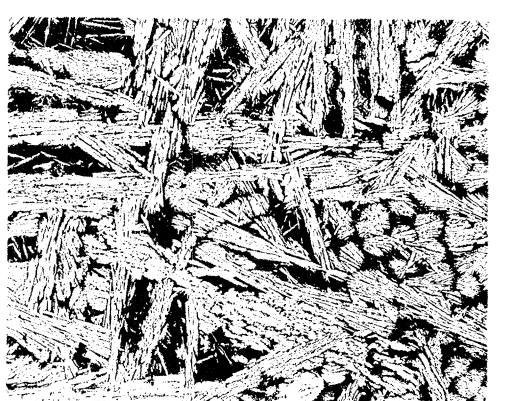
98



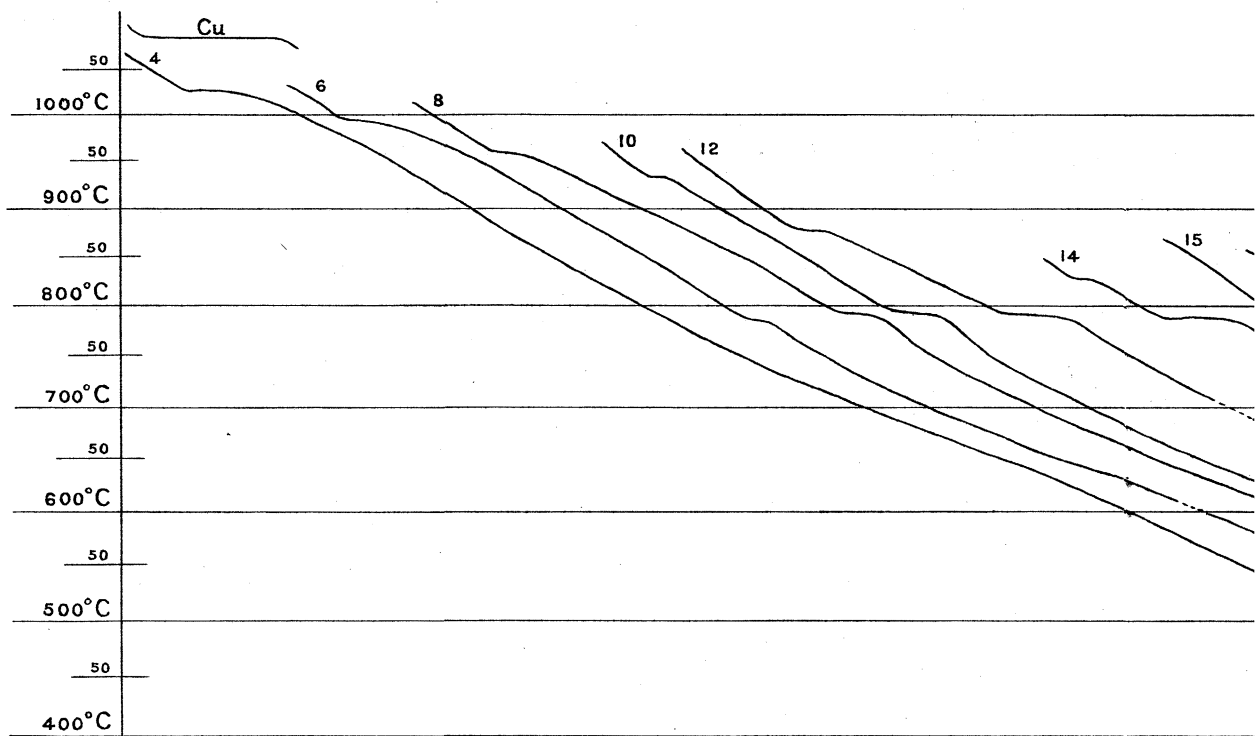
99



100

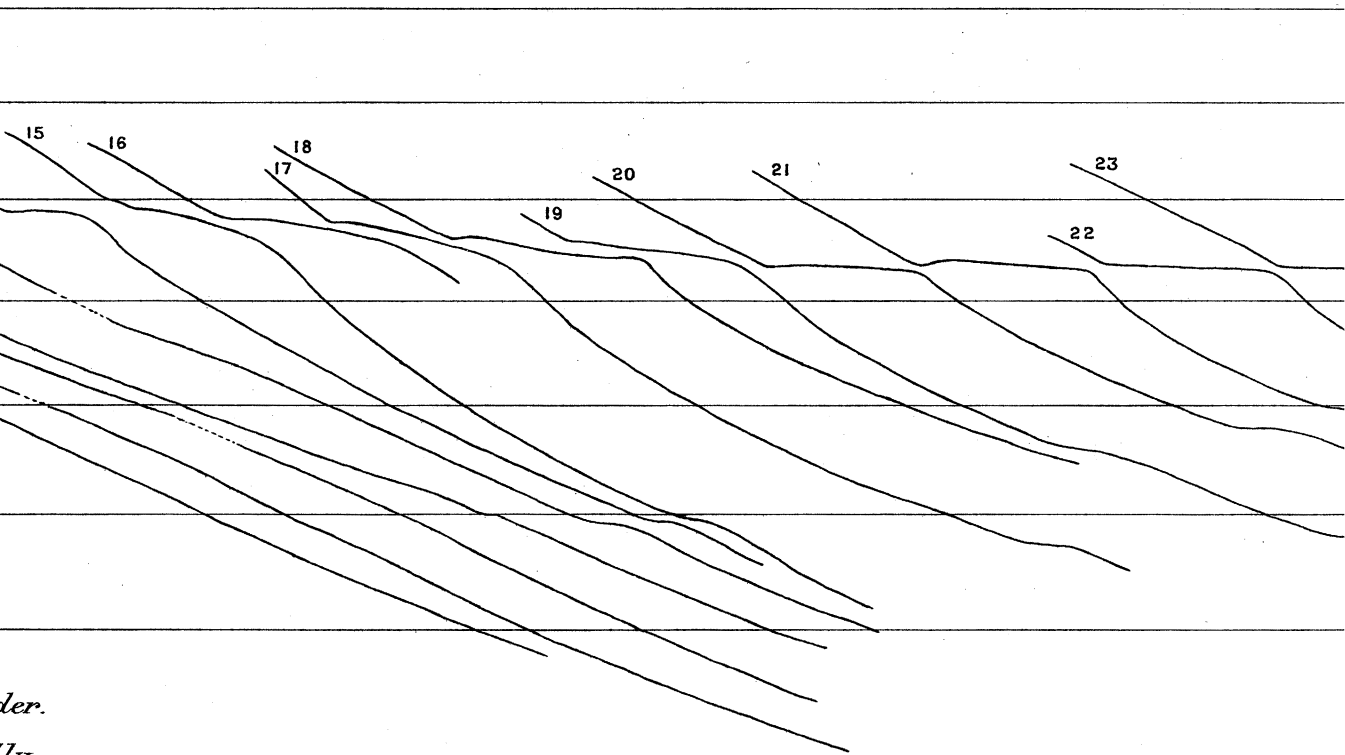


101



*Cooling Curves of Copper. Tin Alloys, taken with Callendar Recorder.
 Time is measured horizontally, Centigrade Temperature vertically.
 The numerals near beginning of each Cooling Curve give Atomic Percent
 Curves are given for Alloys between Sn₄ and Sn₂₇.
 Equal vertical distances correspond to equal differences of Temperature.*

COOLING CURVES
OF
COPPER-TIN ALLOYS.

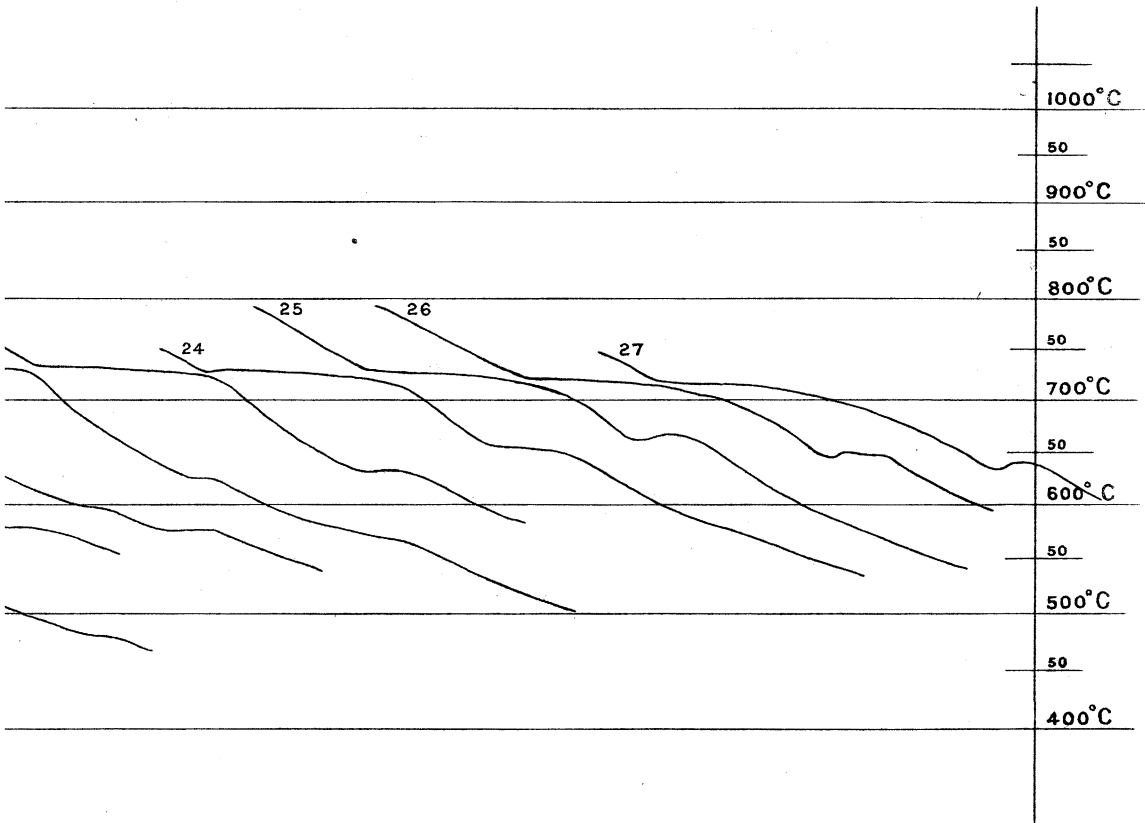


der.

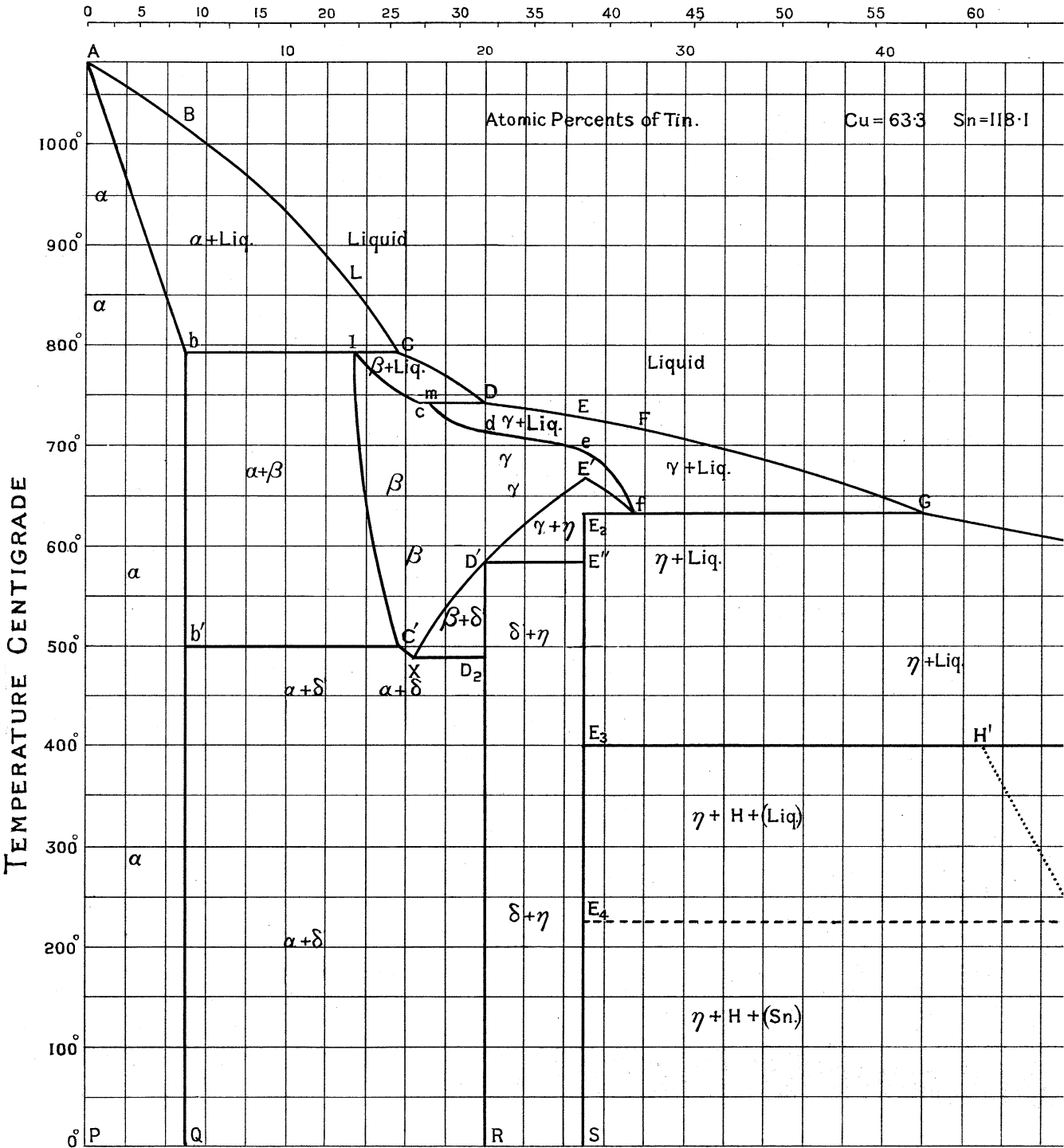
ly.

ic Percentage of Tin in the Alloy of the Curve.

Temperature on the Platinum Scale.

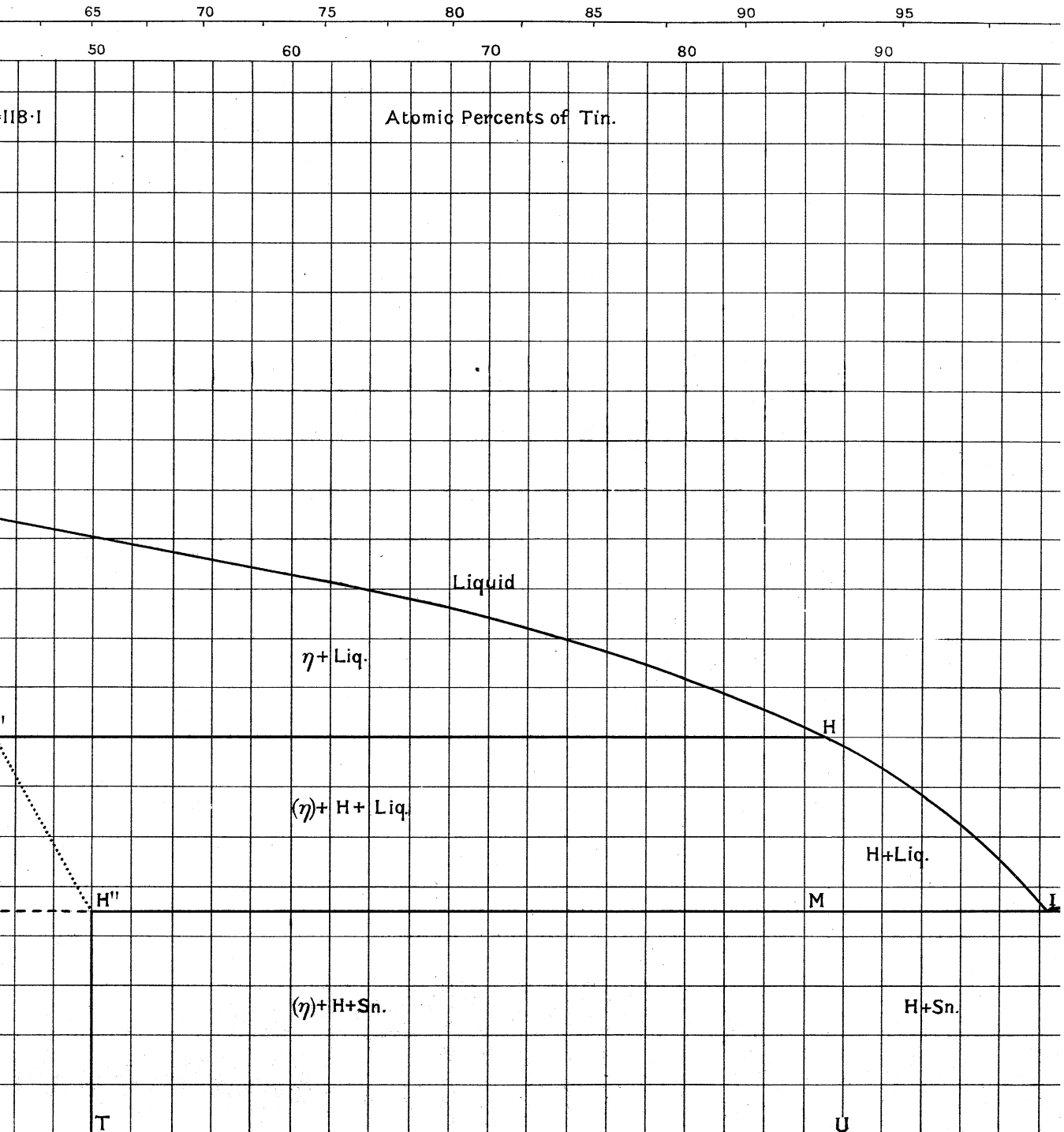


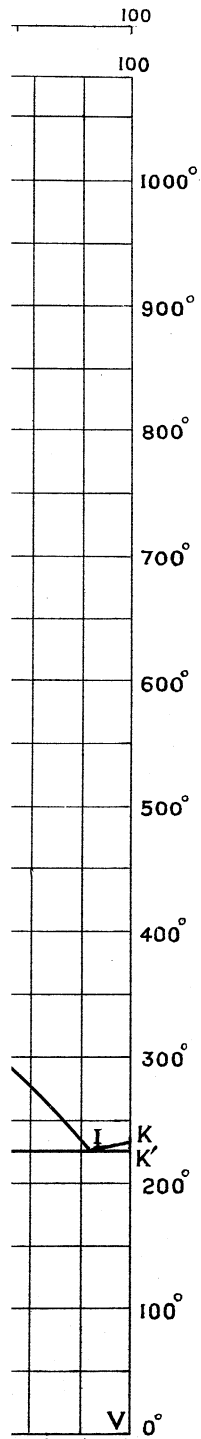
Percentage



OF THE COPPER-TIN ALLOYS.

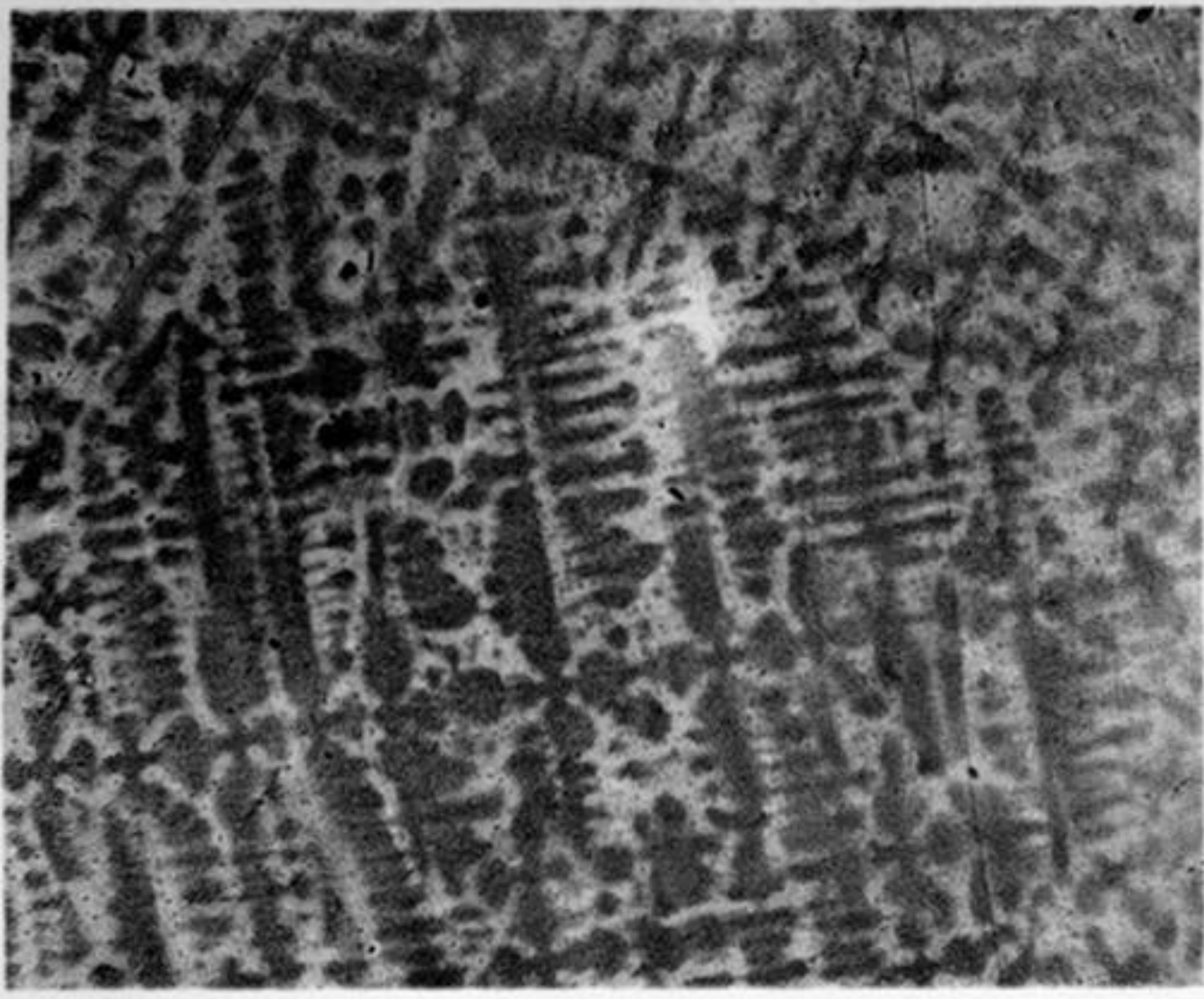
Percentage by Weight of Tin.



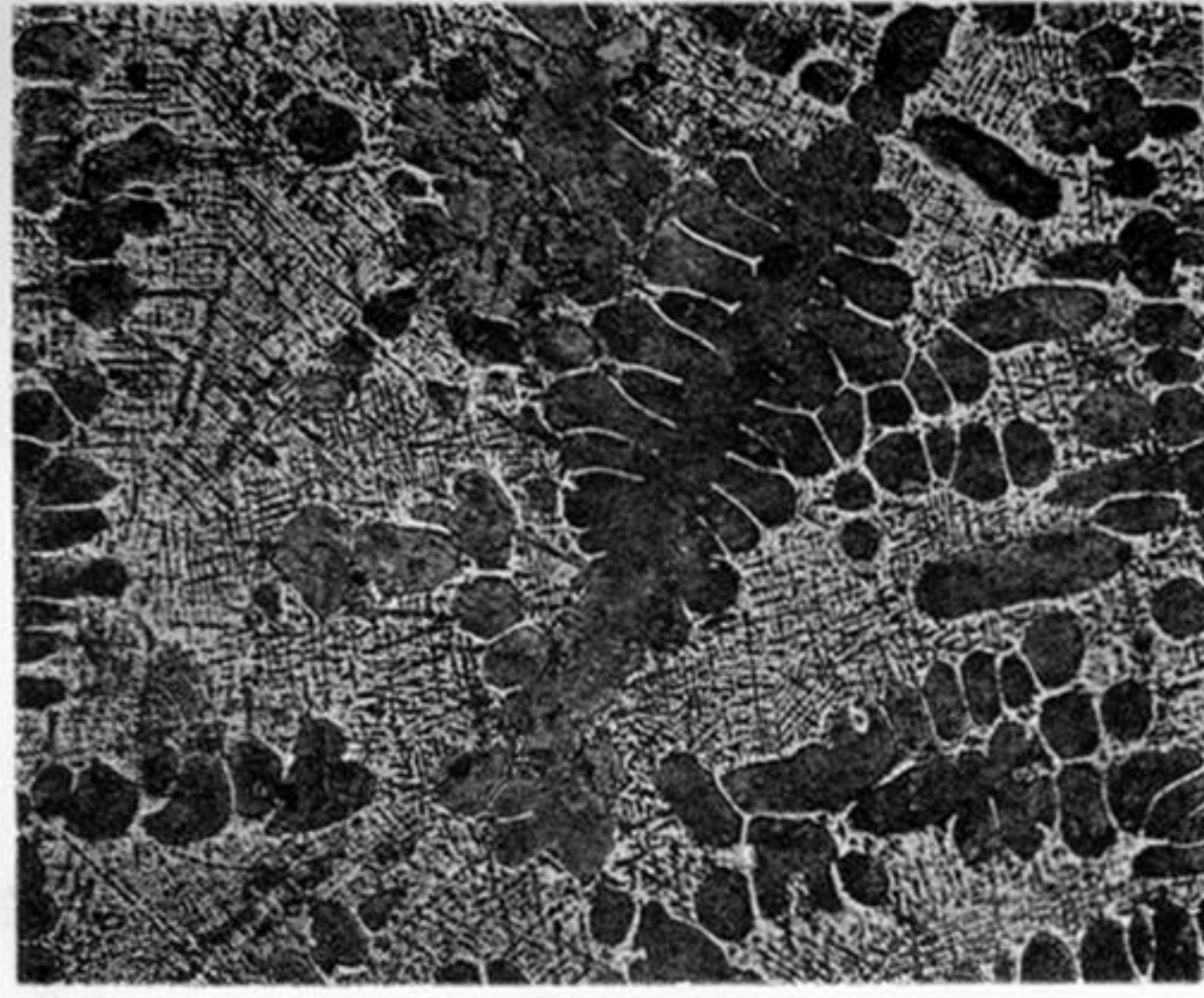


Edwin Wilson, Car

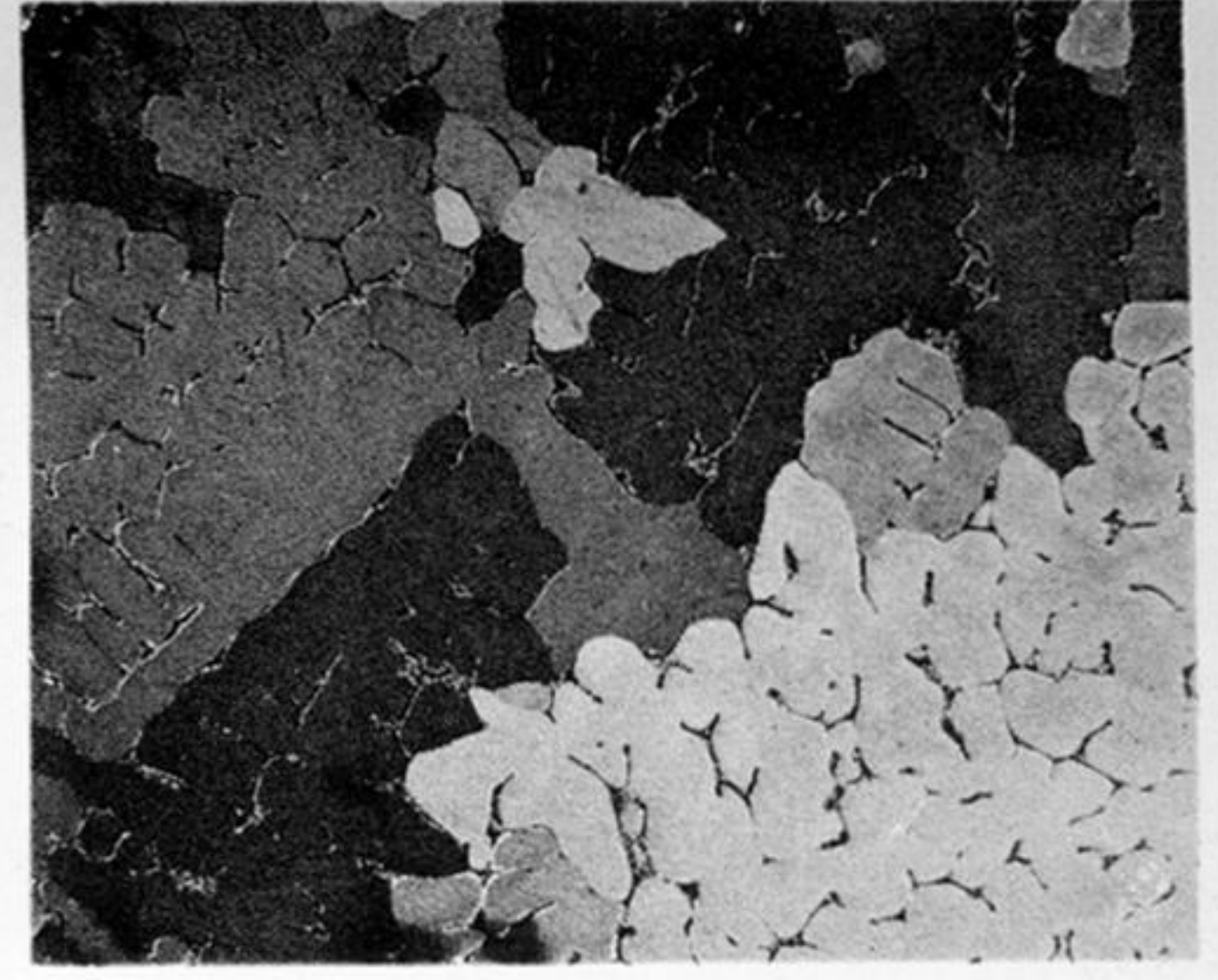
Wilson, Cambridge.



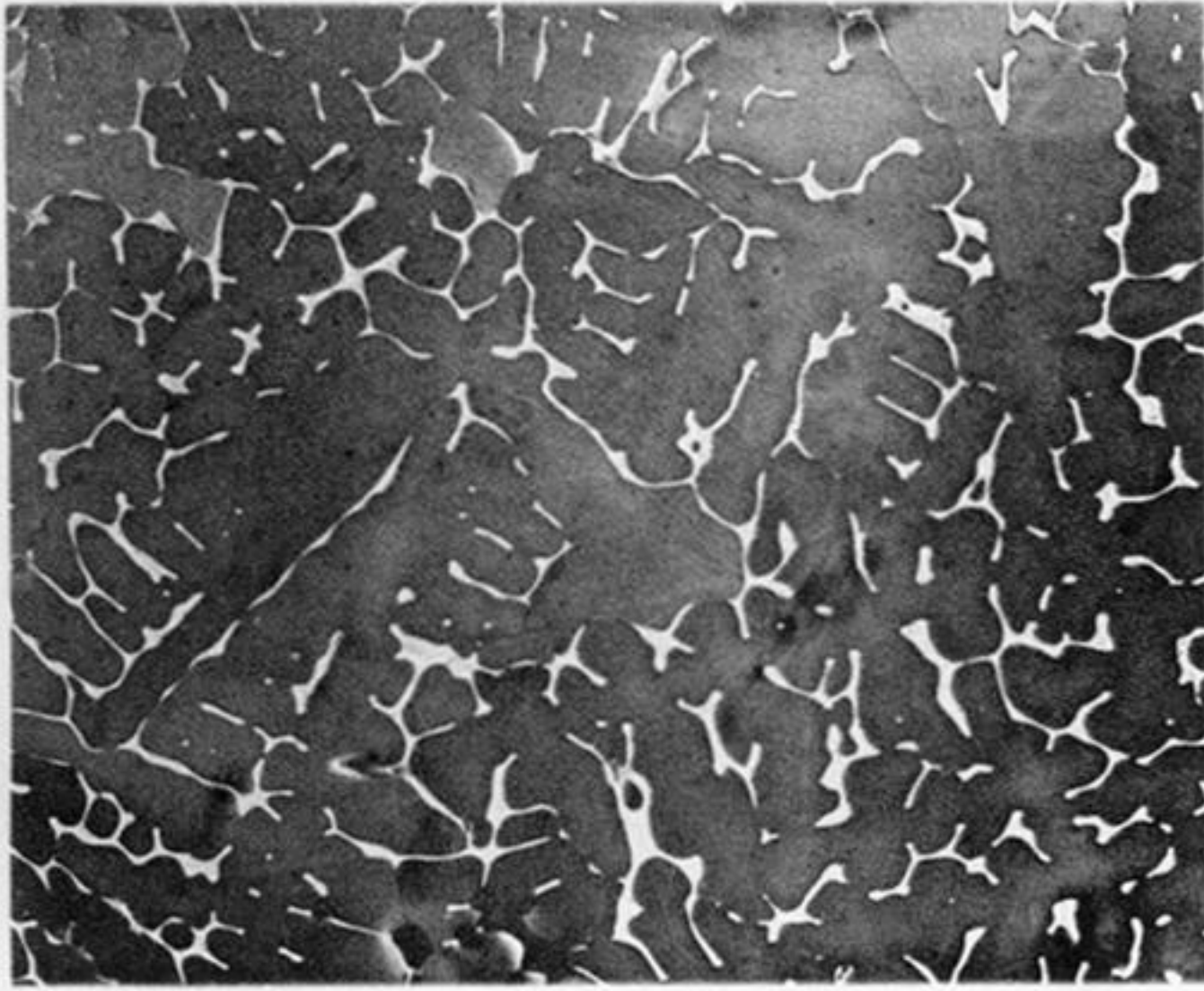
1



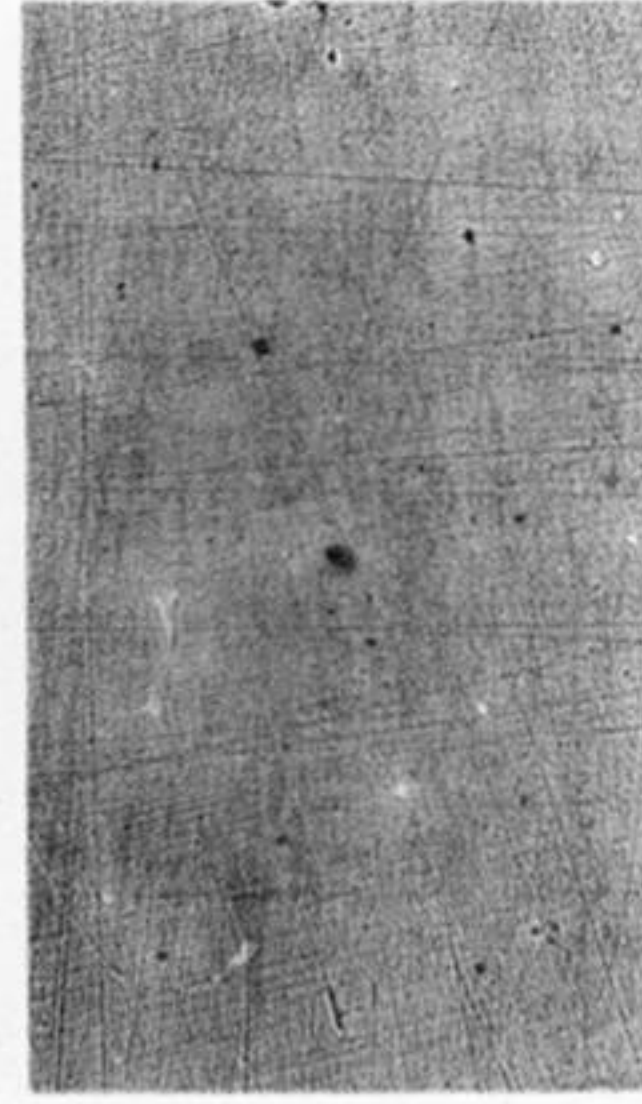
2



3



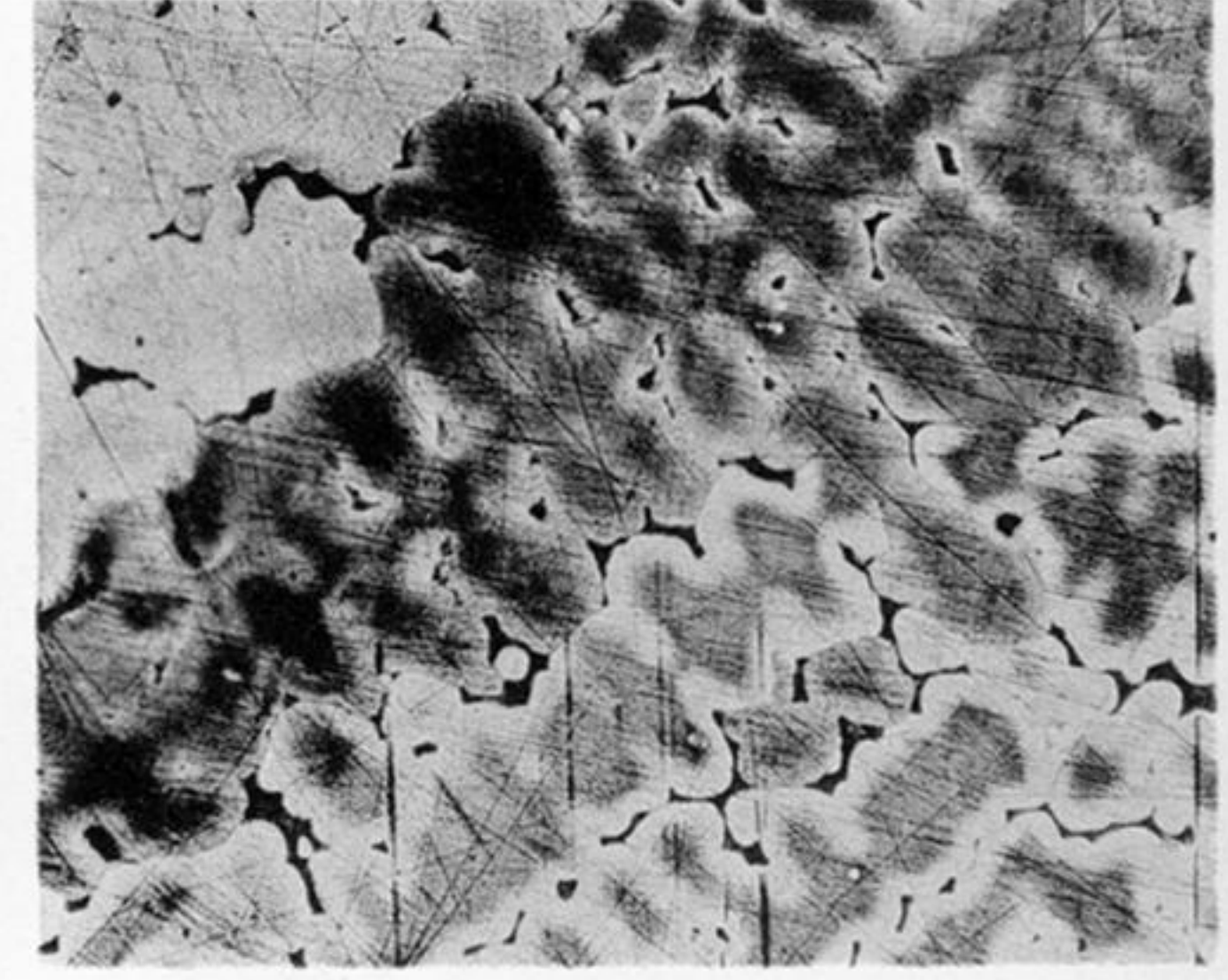
3A



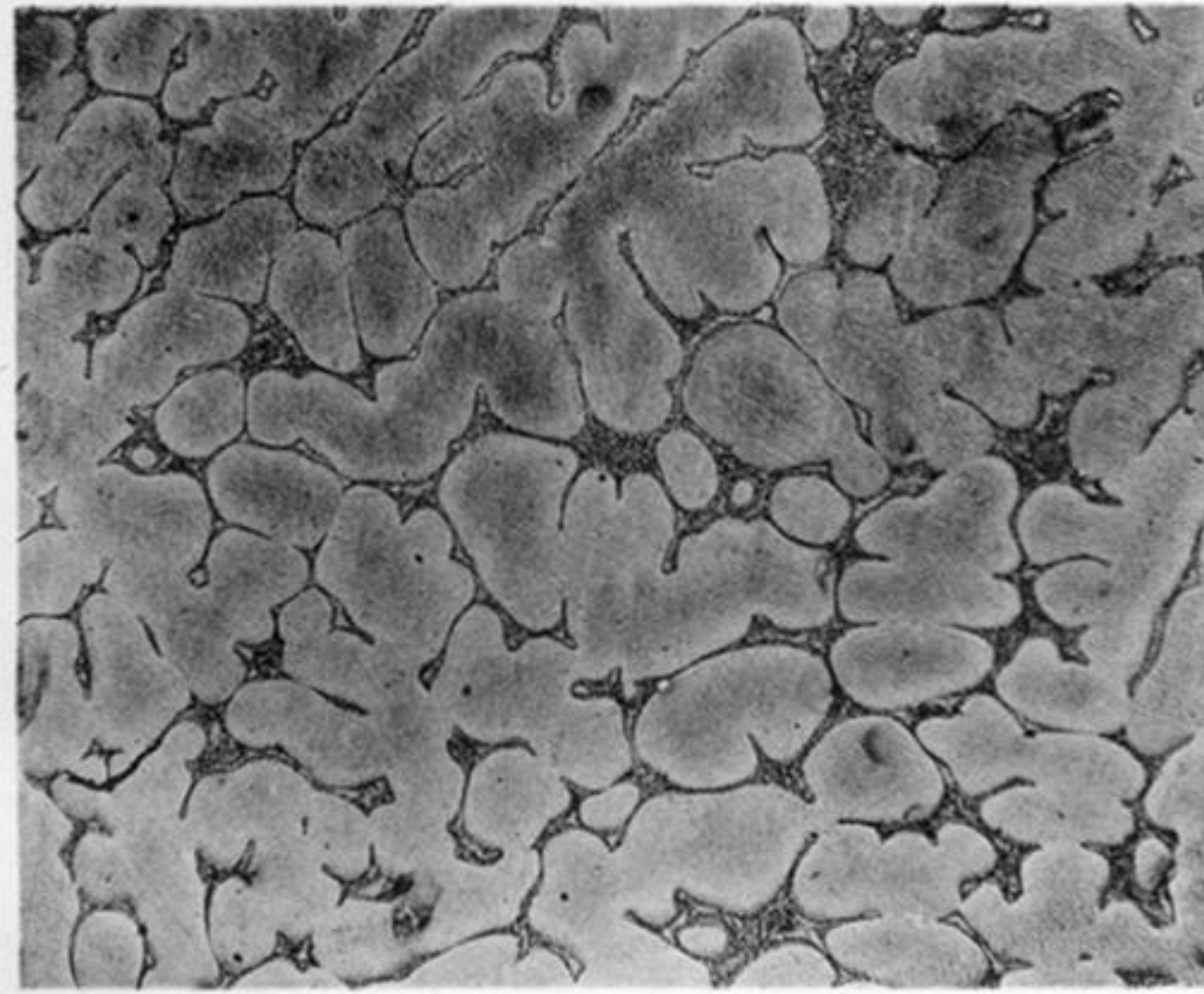
4



5



5A



6



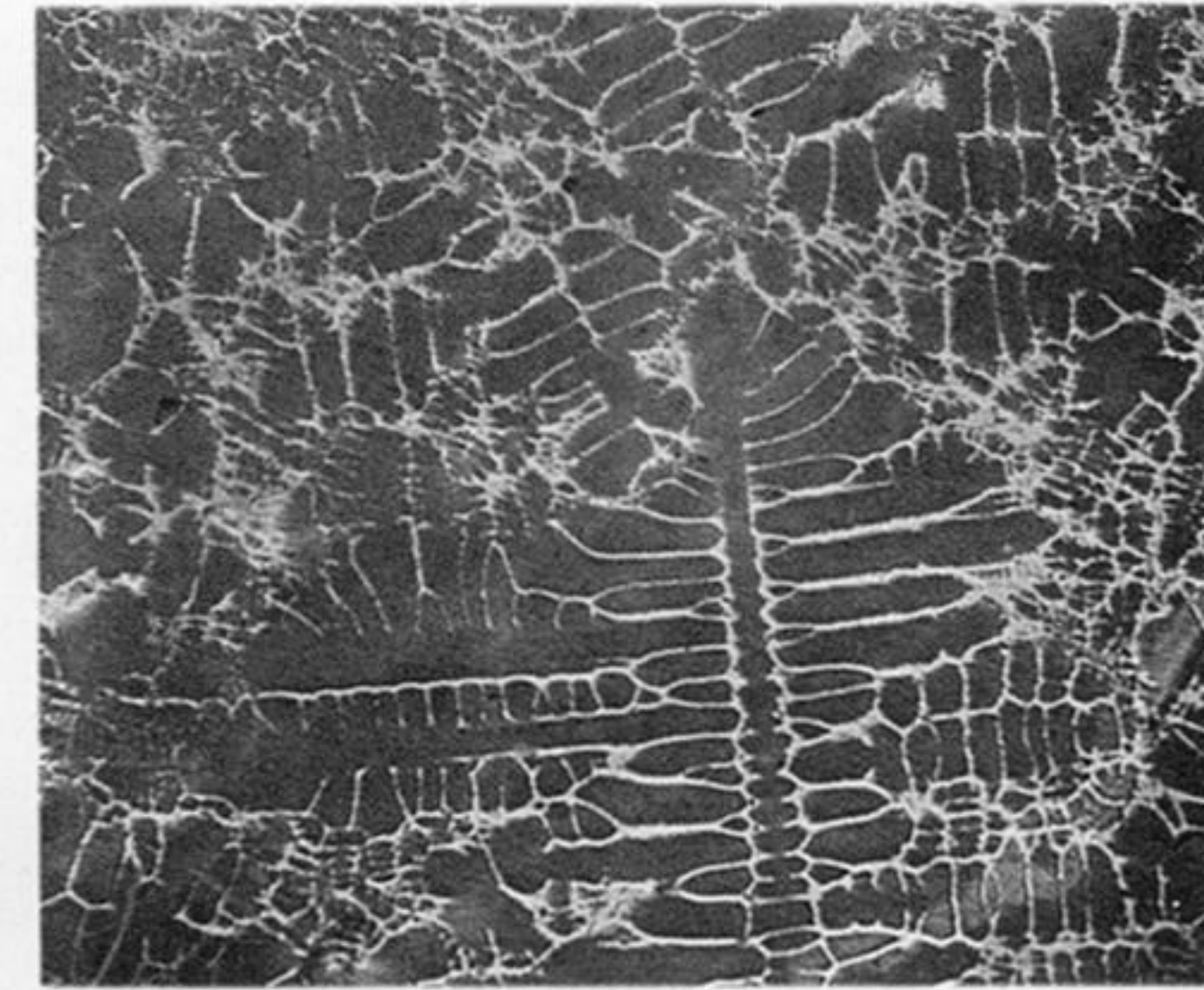
7



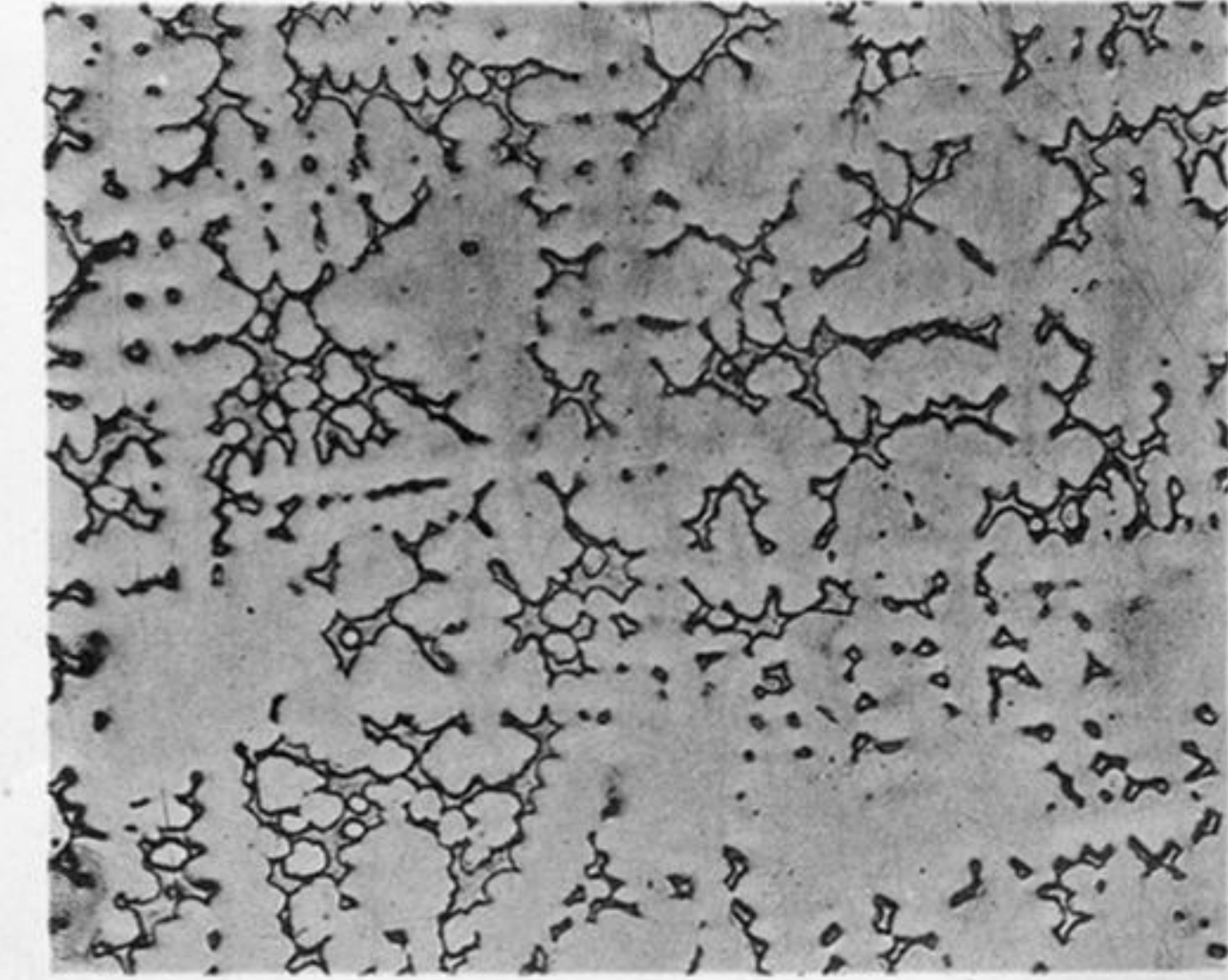
8



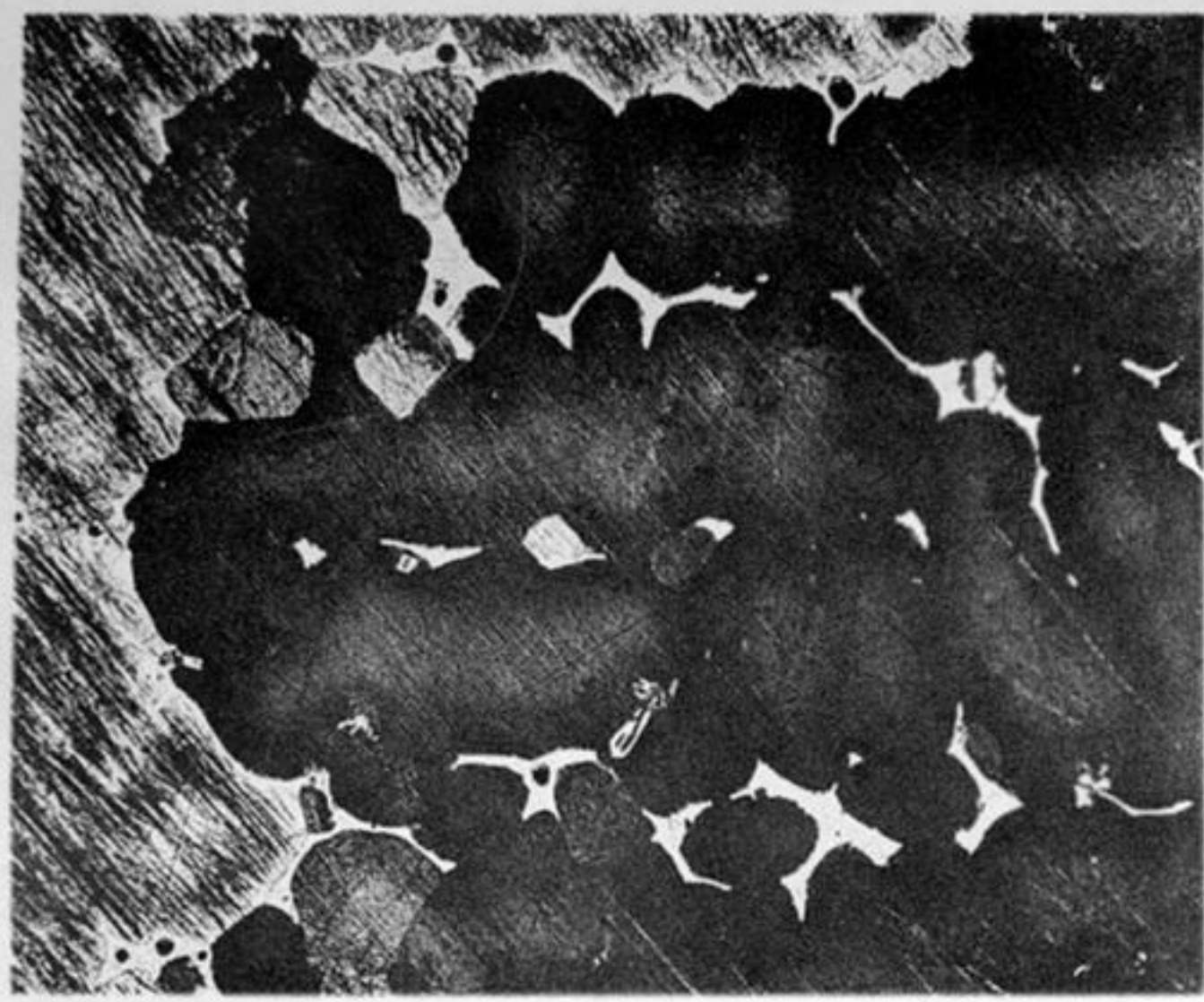
9



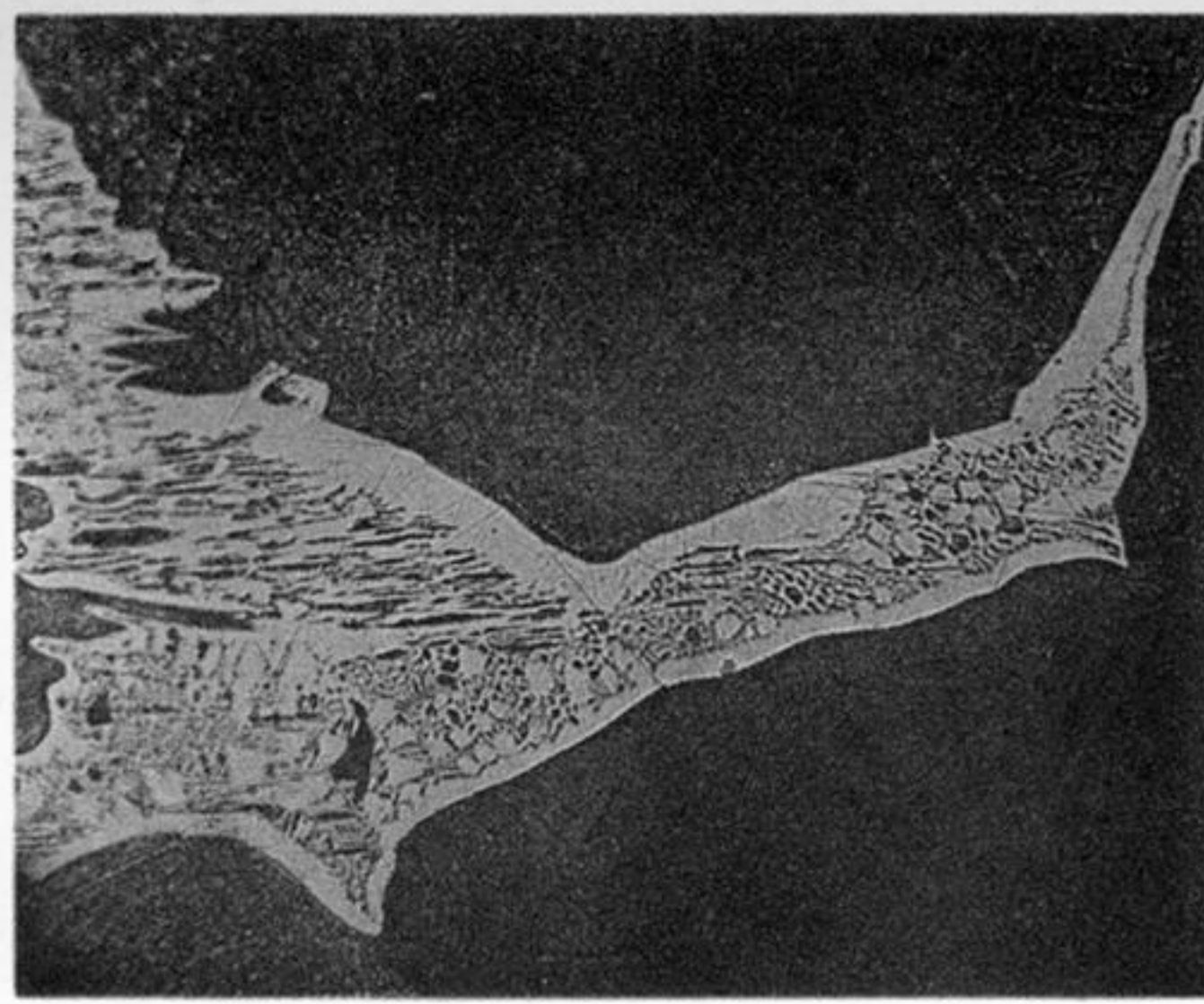
10



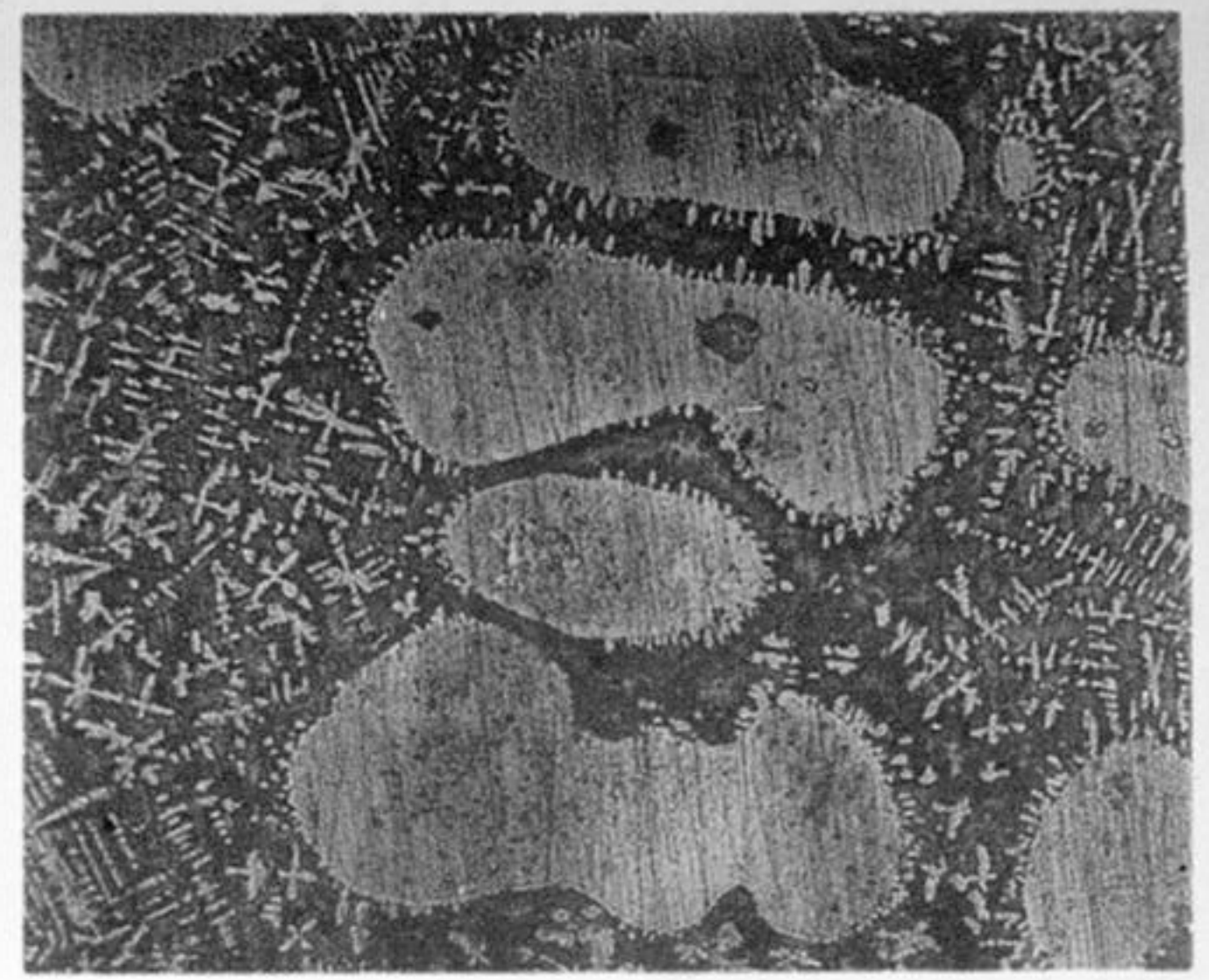
11



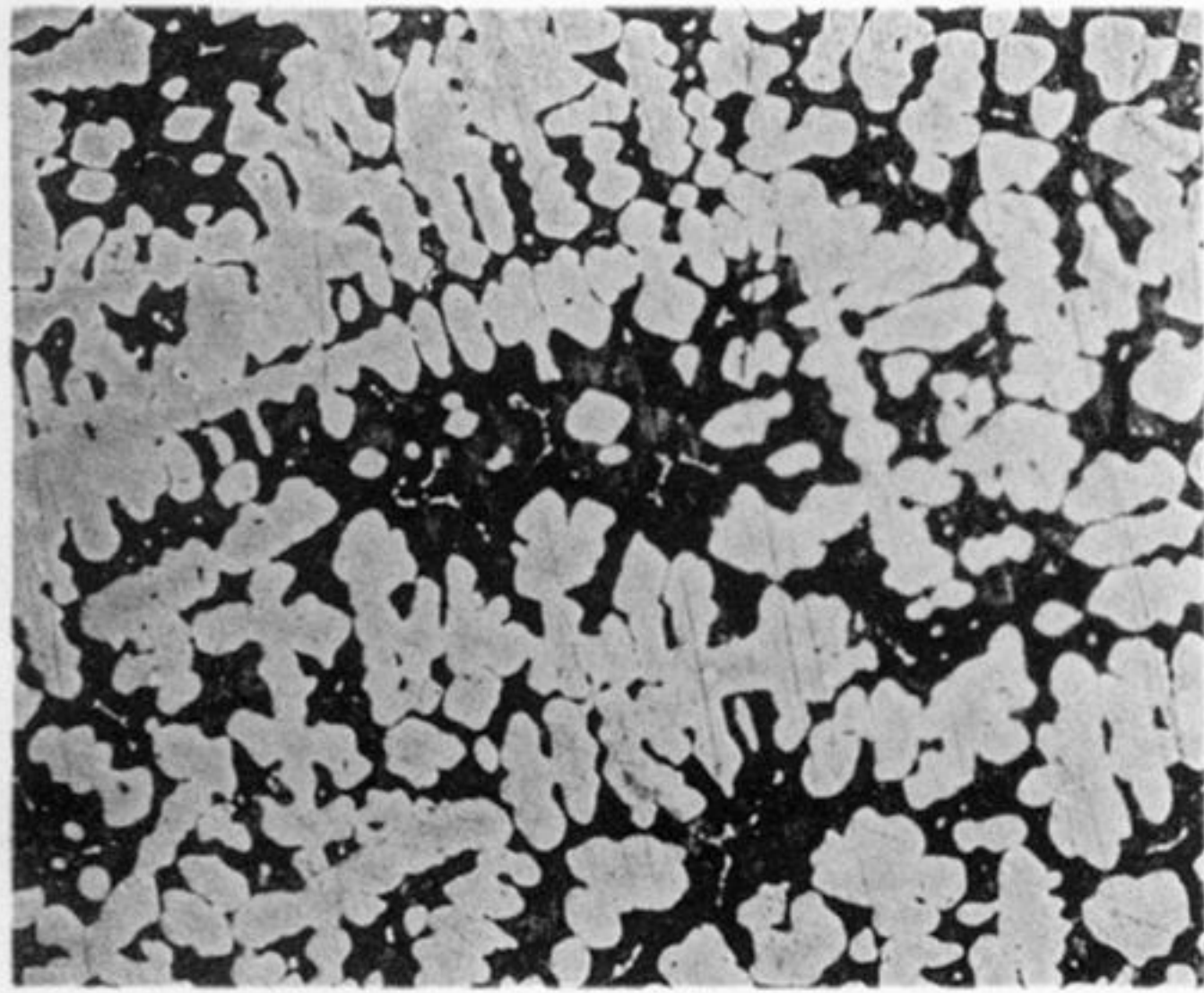
12



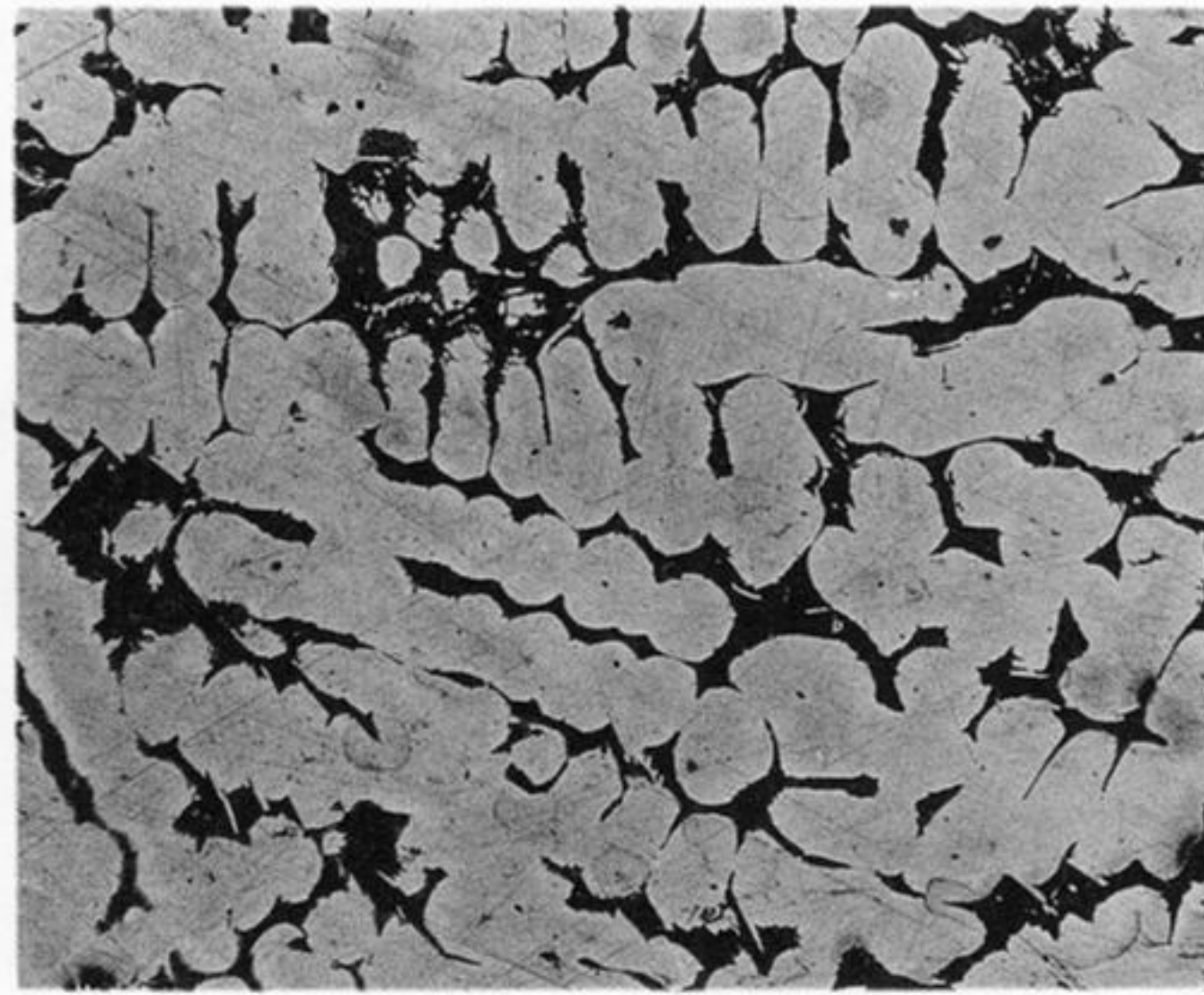
13



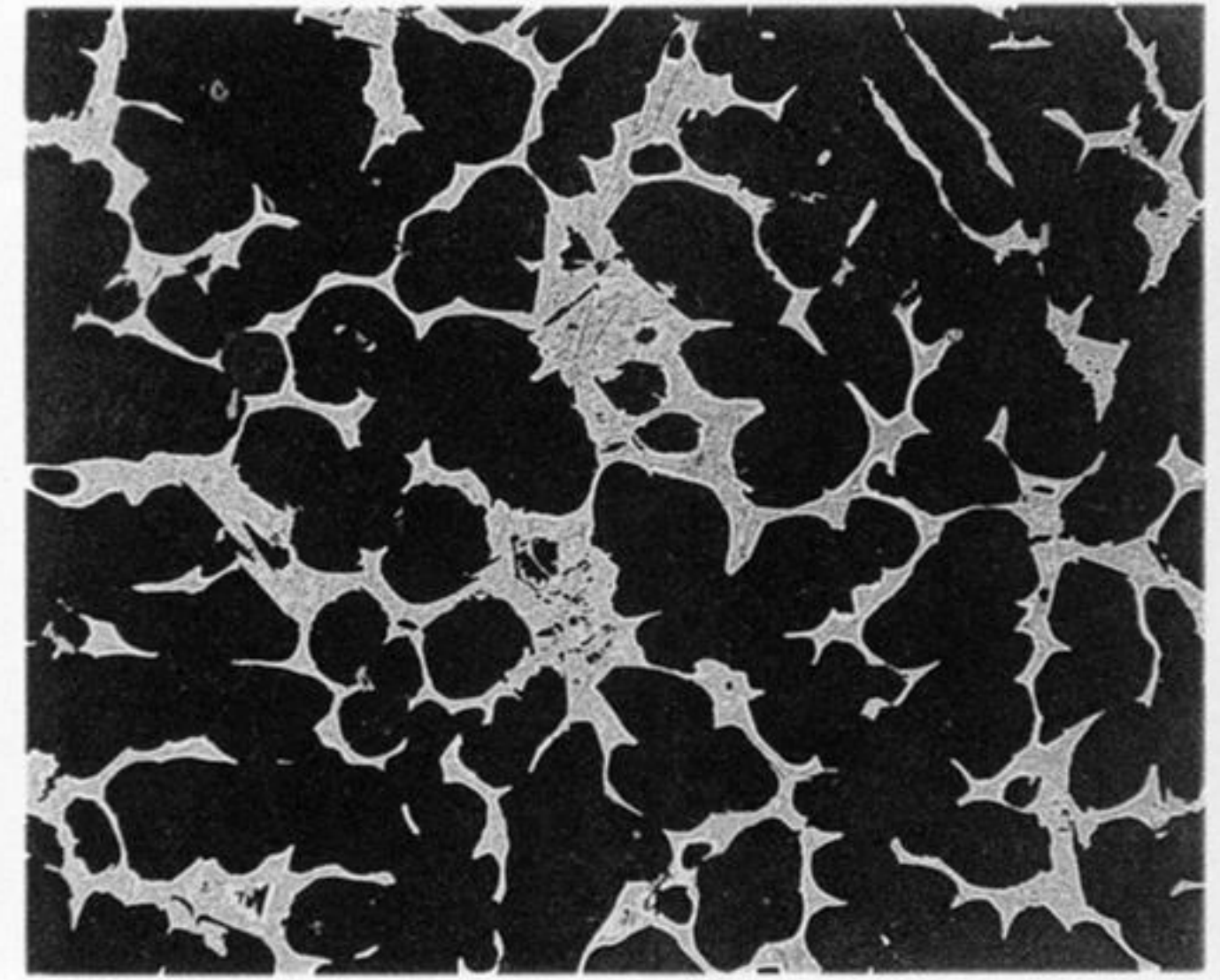
14



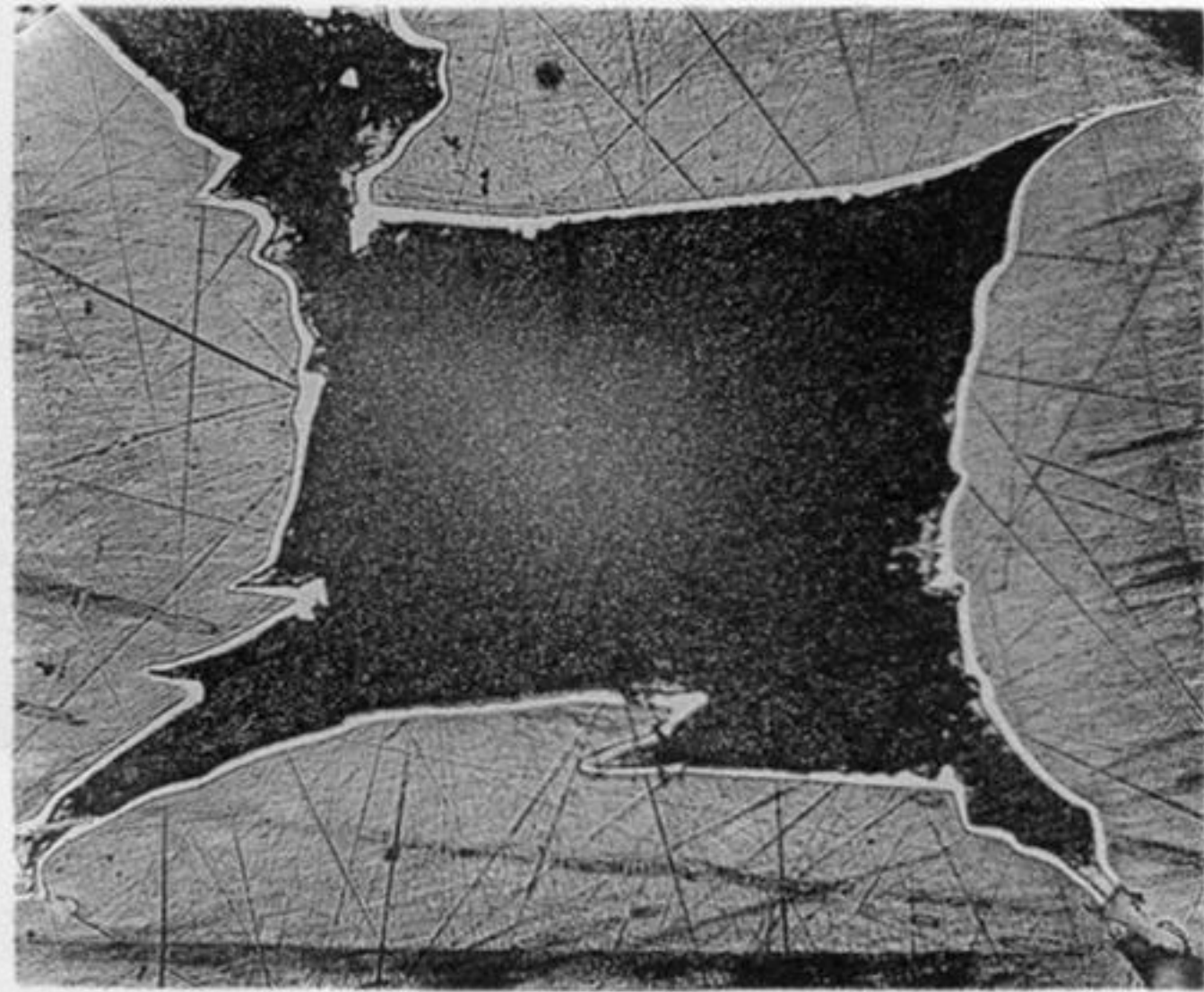
15



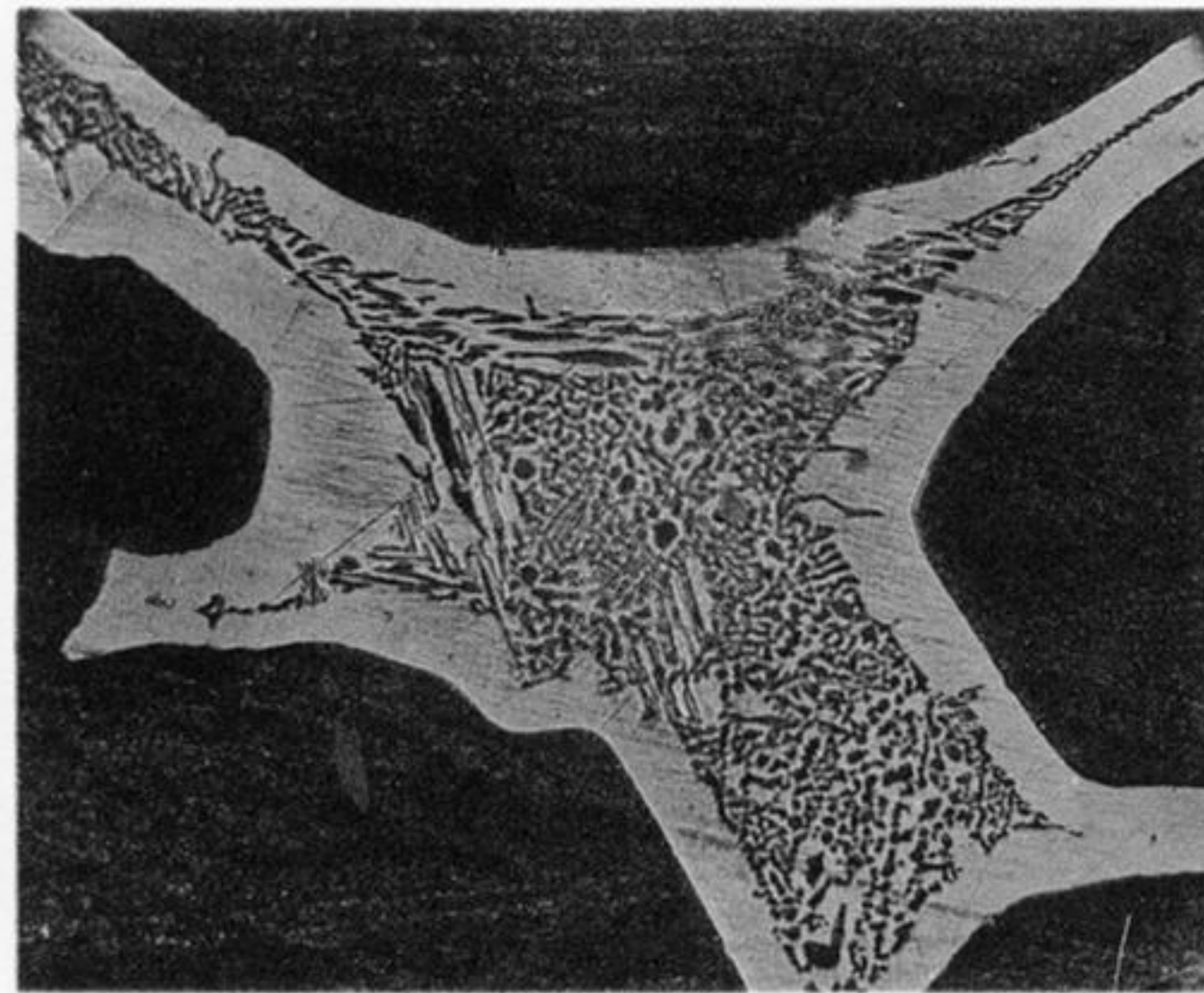
16



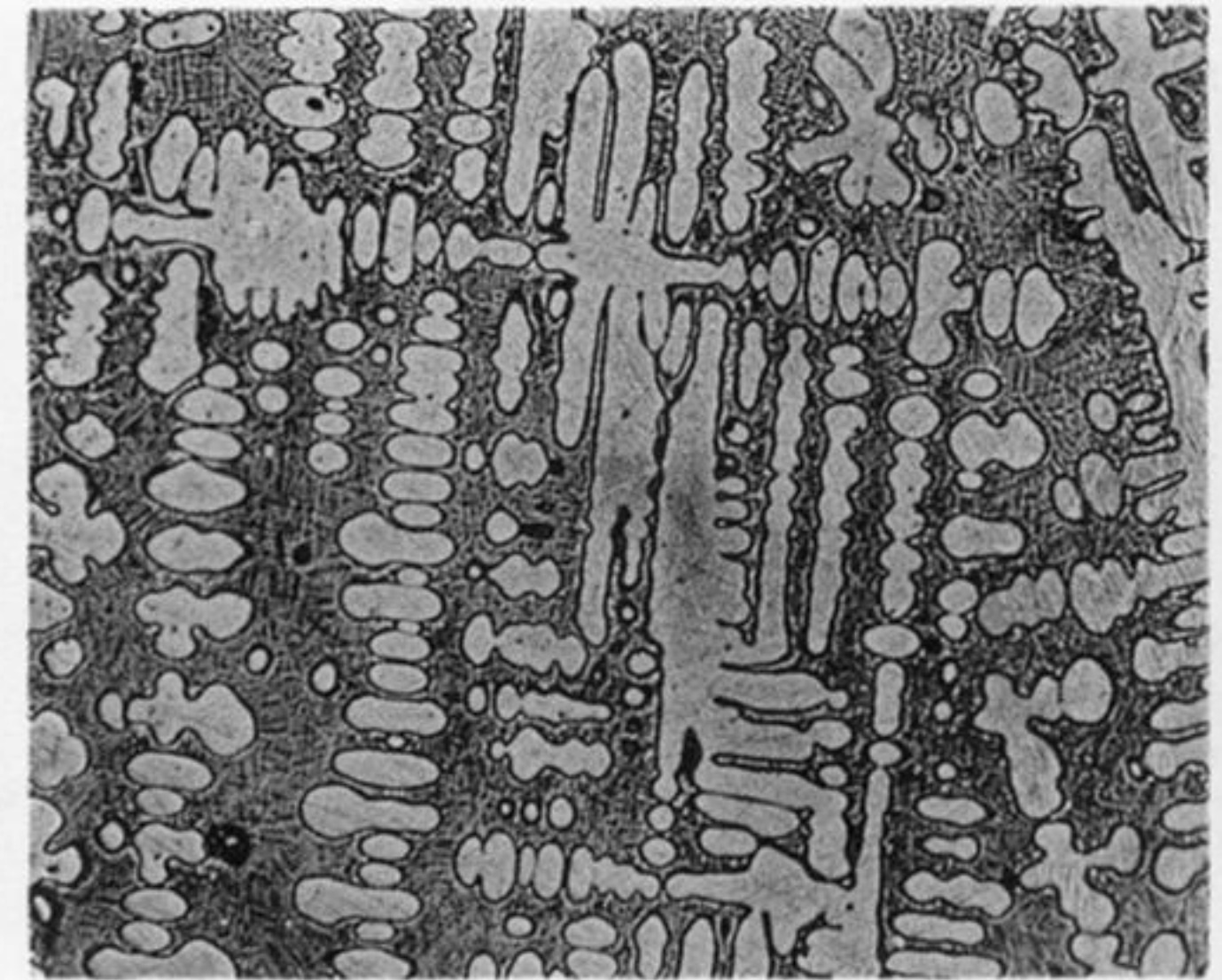
17



18



19



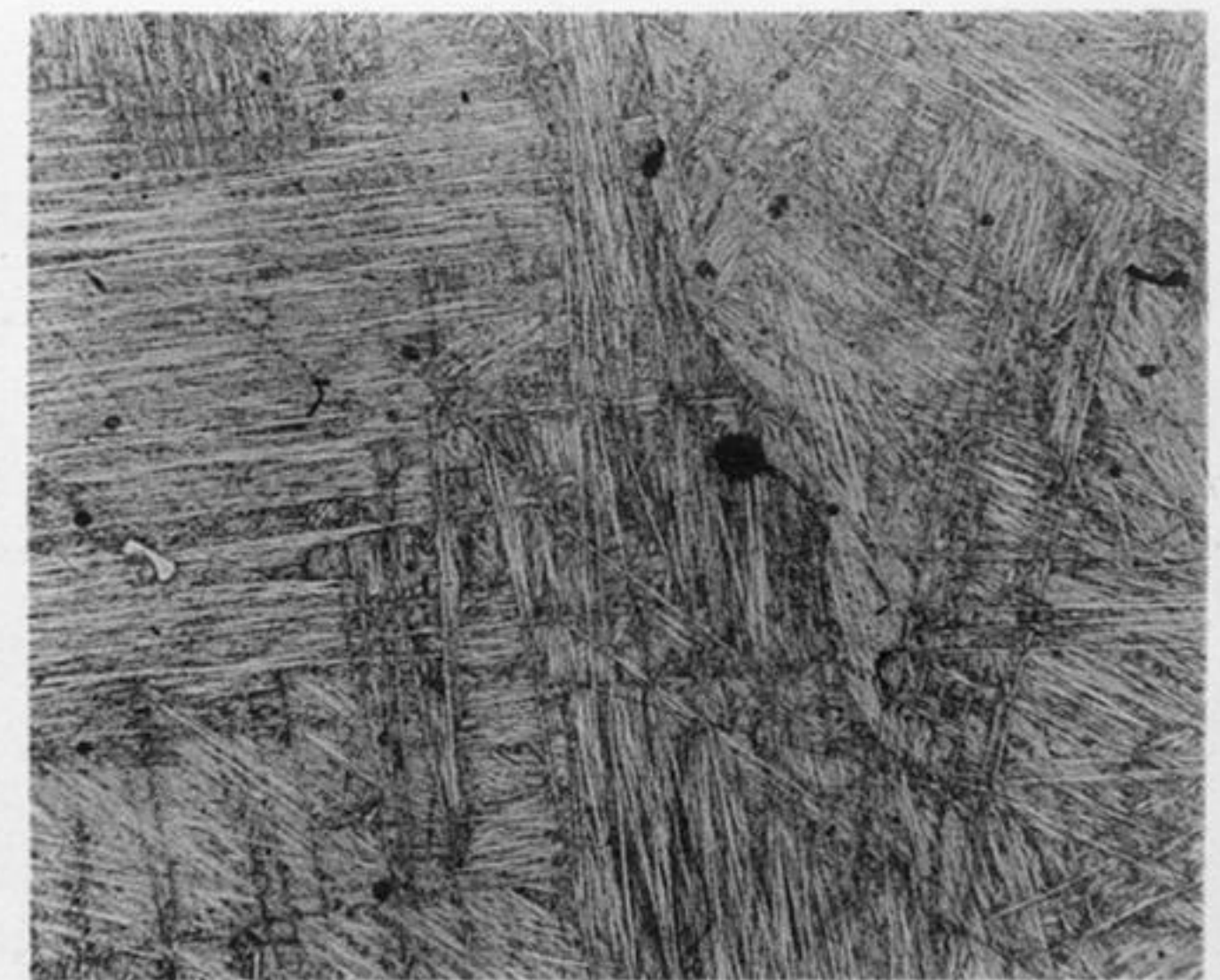
20



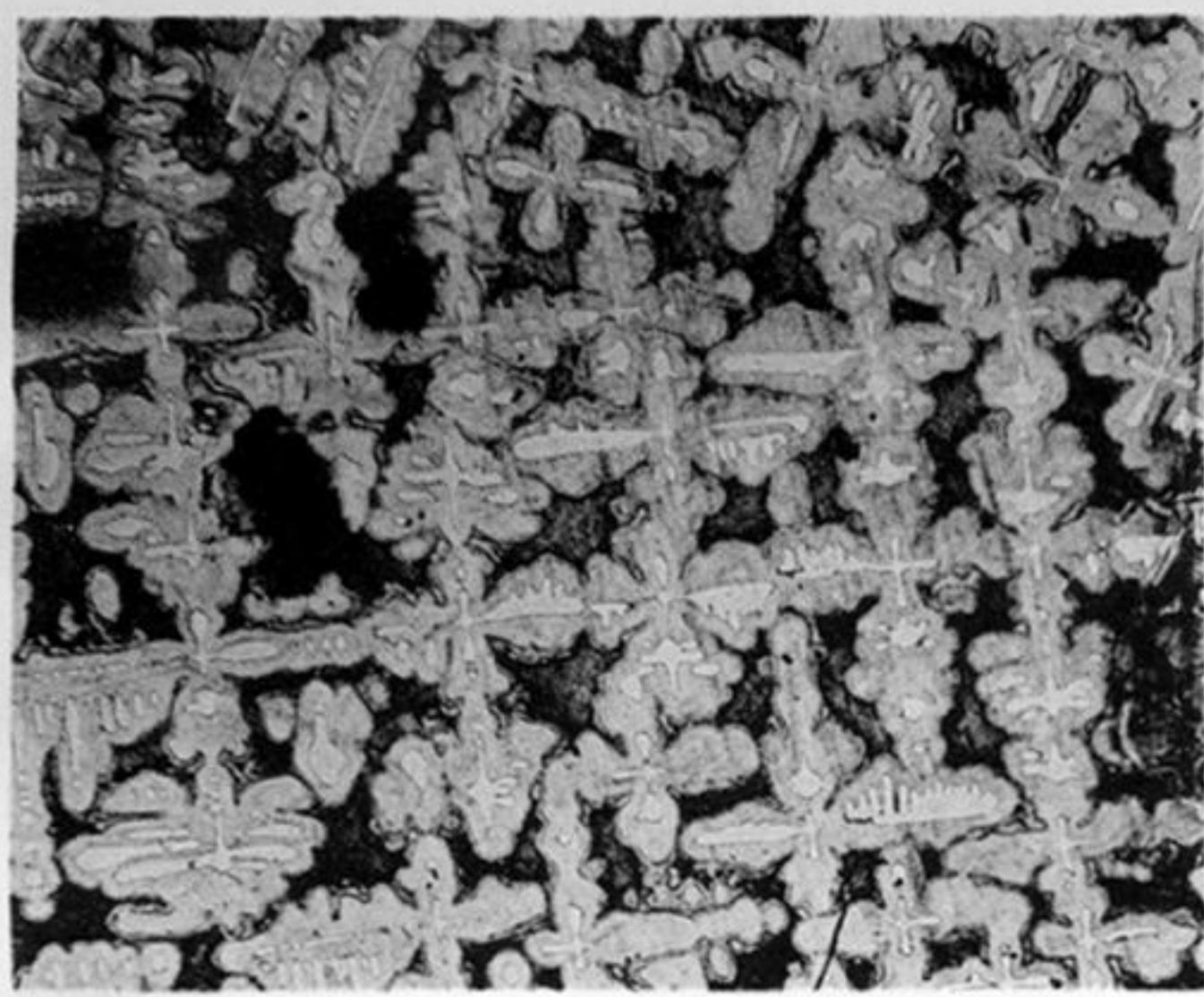
21



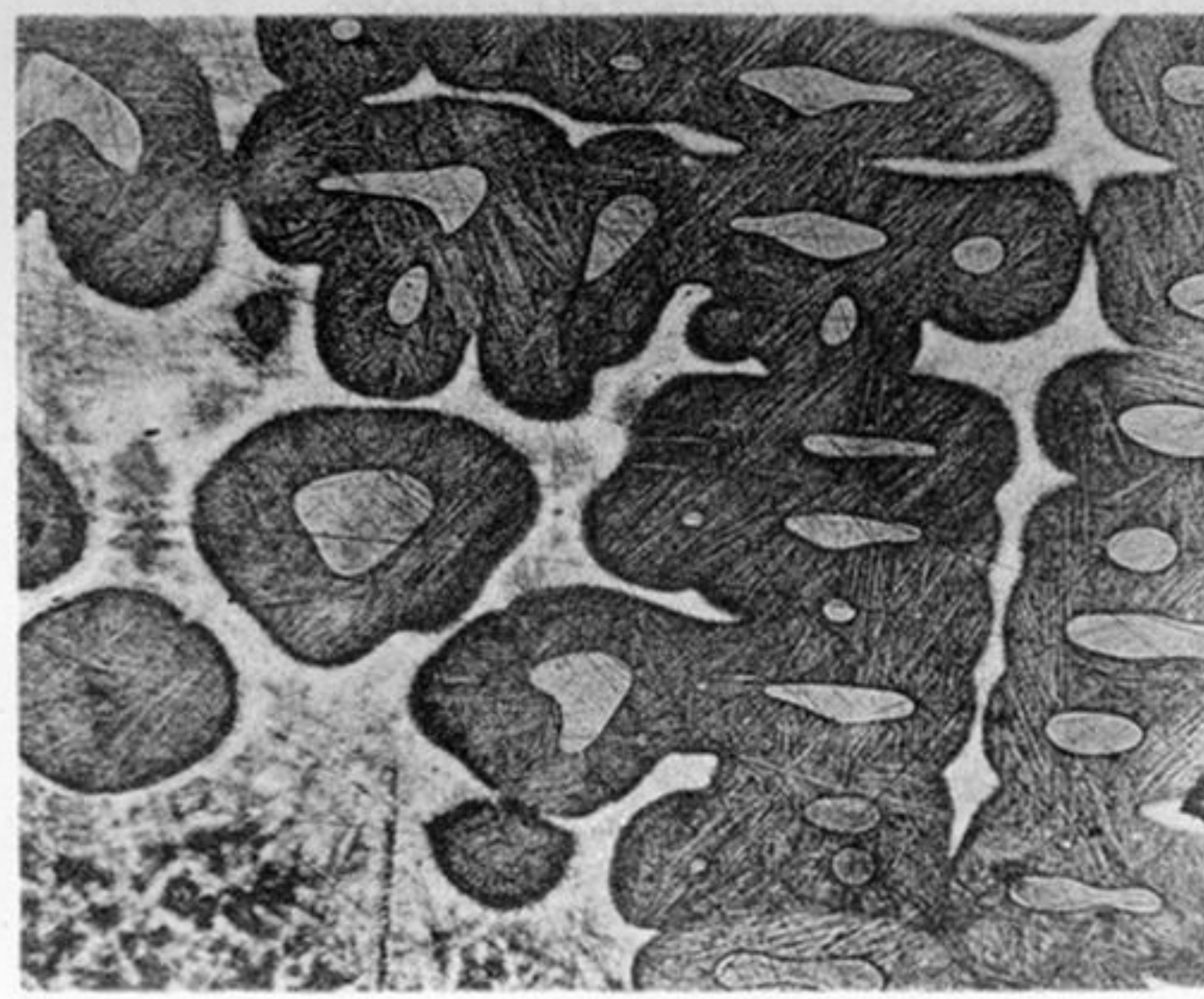
22



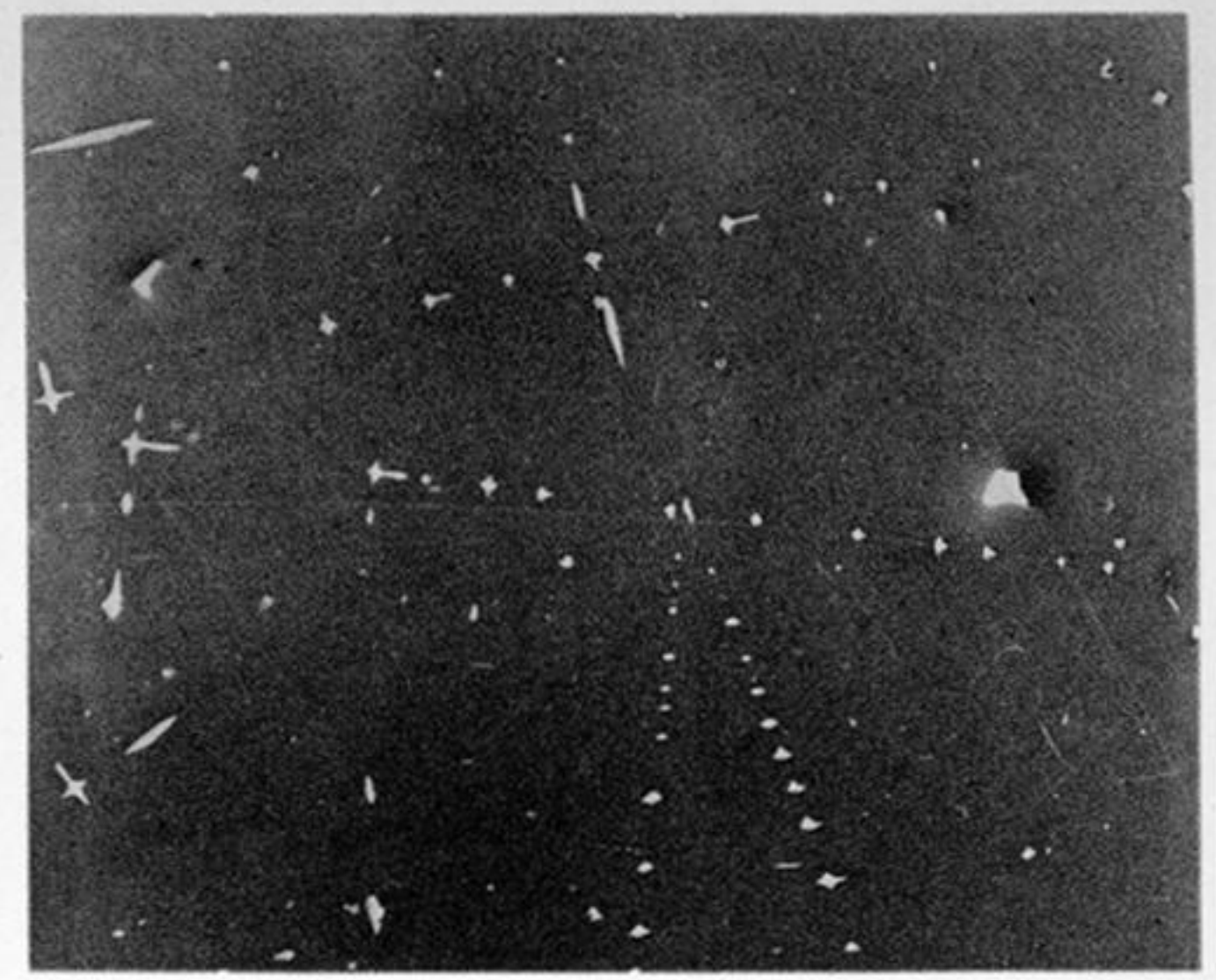
23



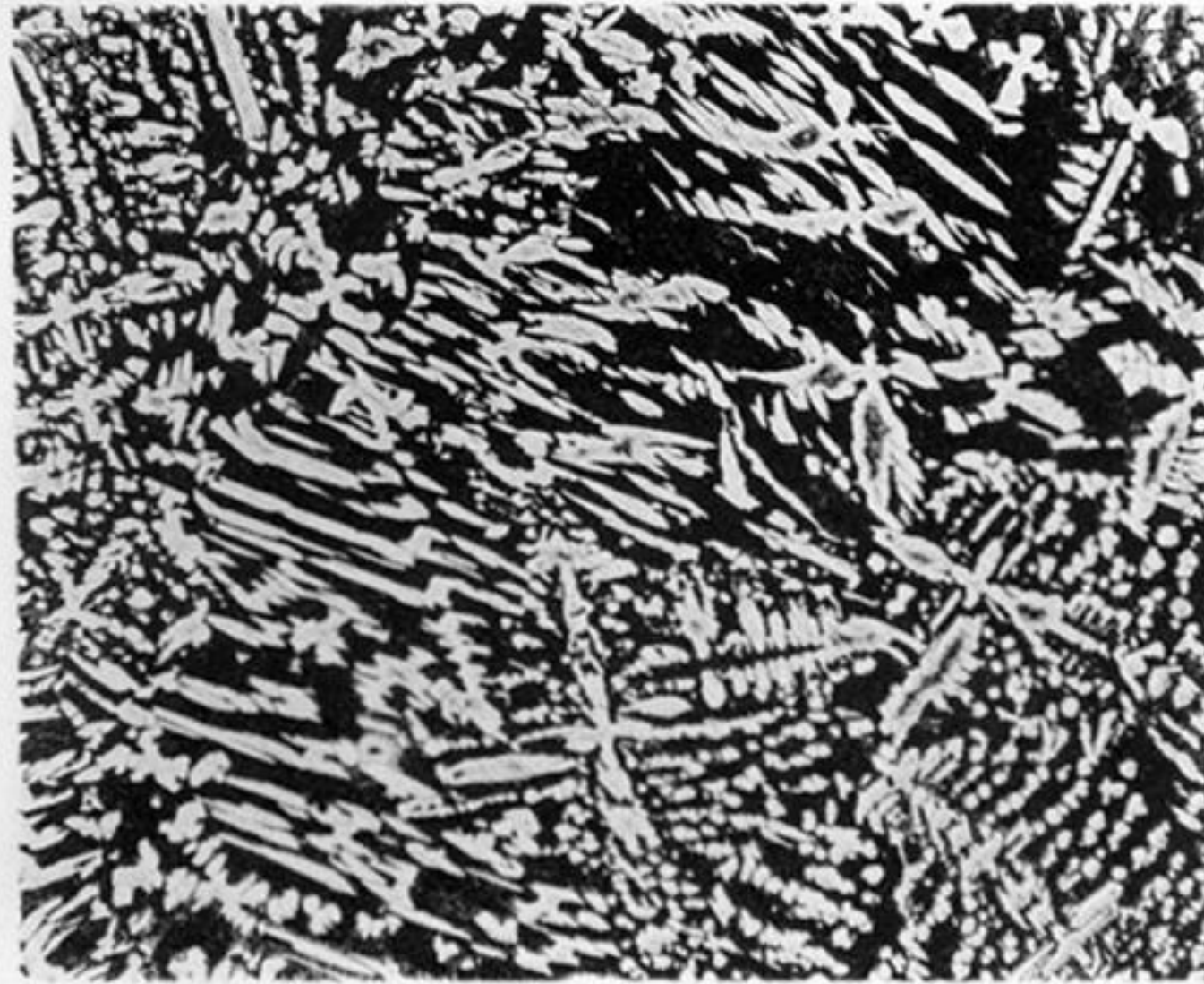
24



25



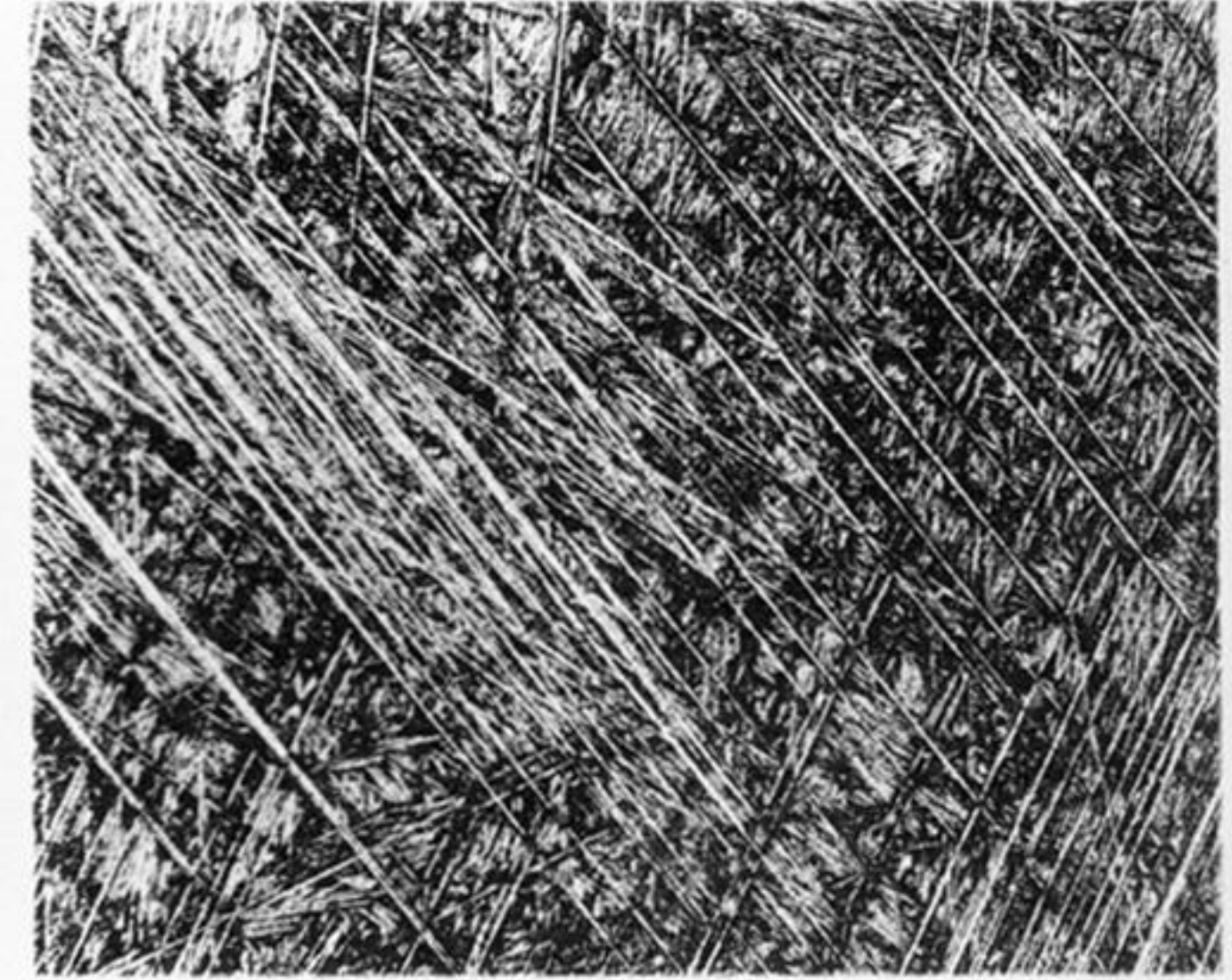
26



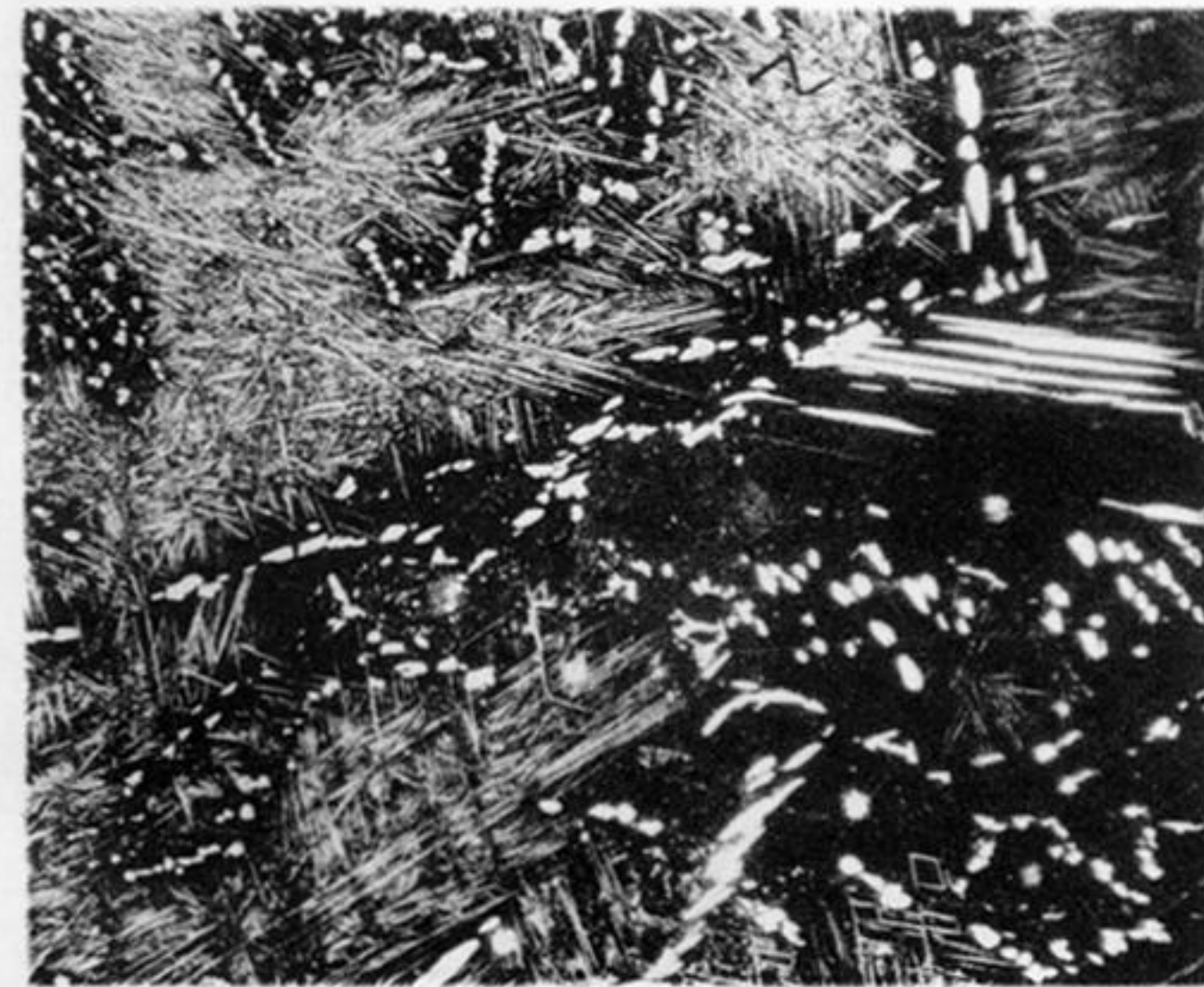
27



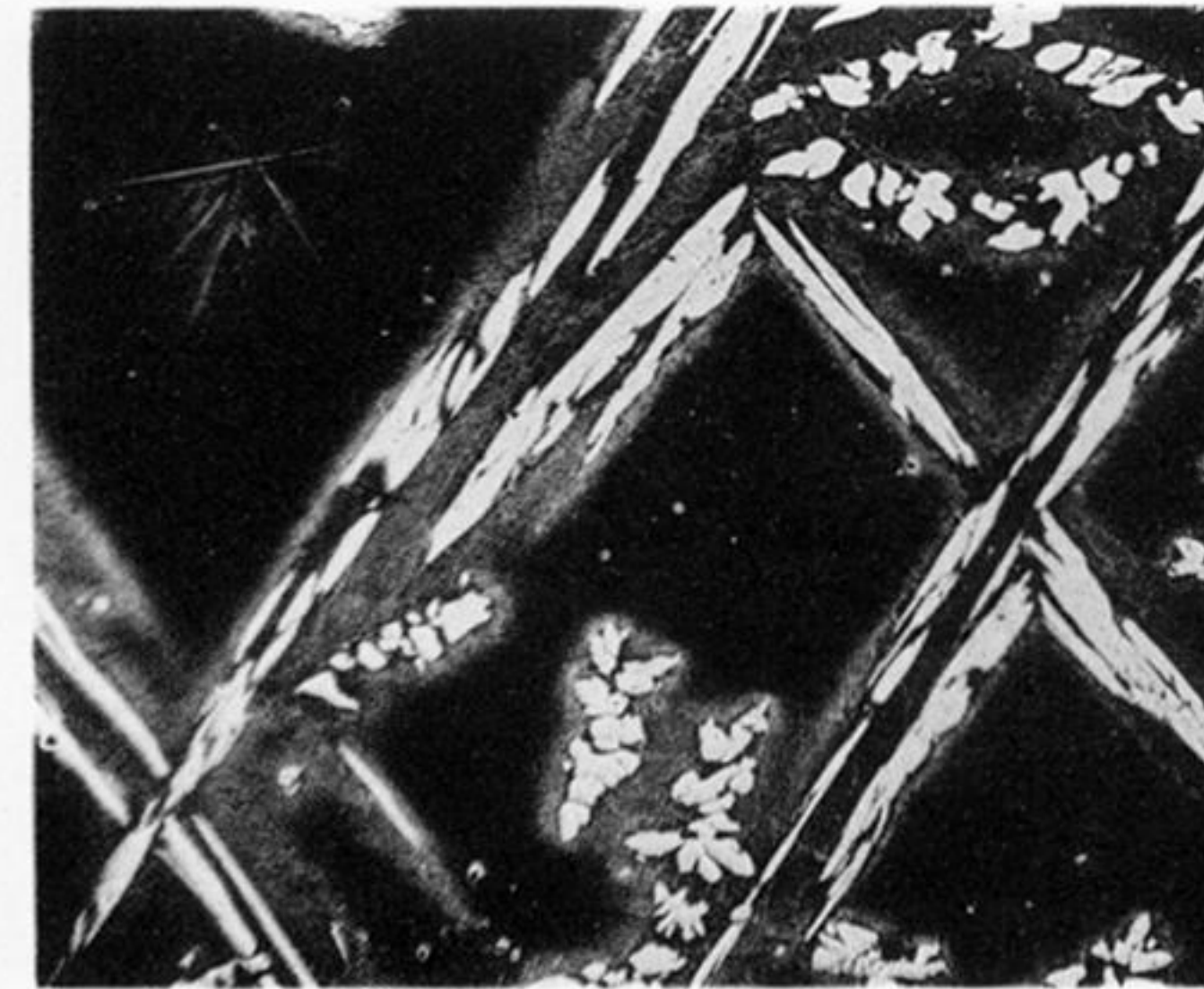
28



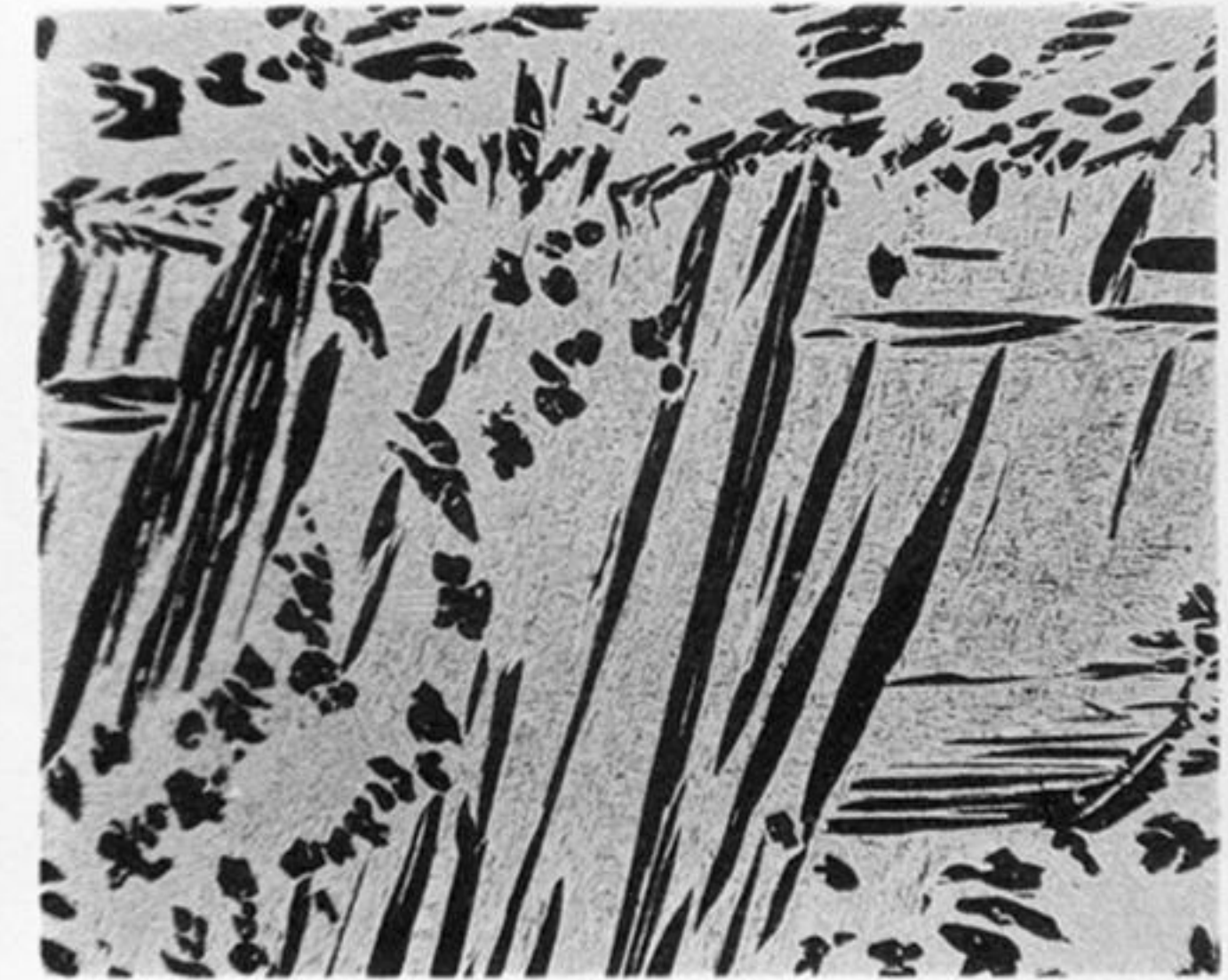
29



30



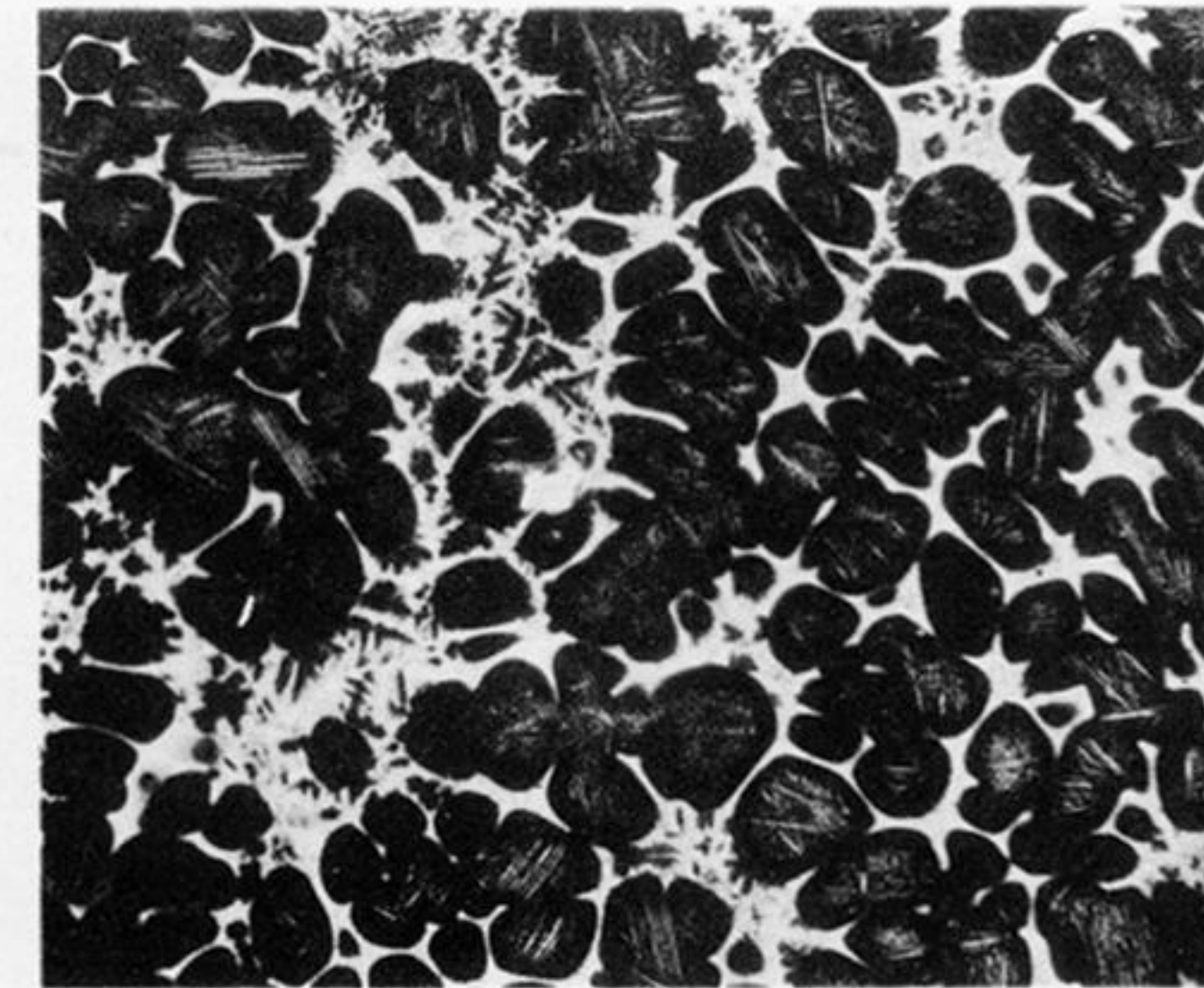
31



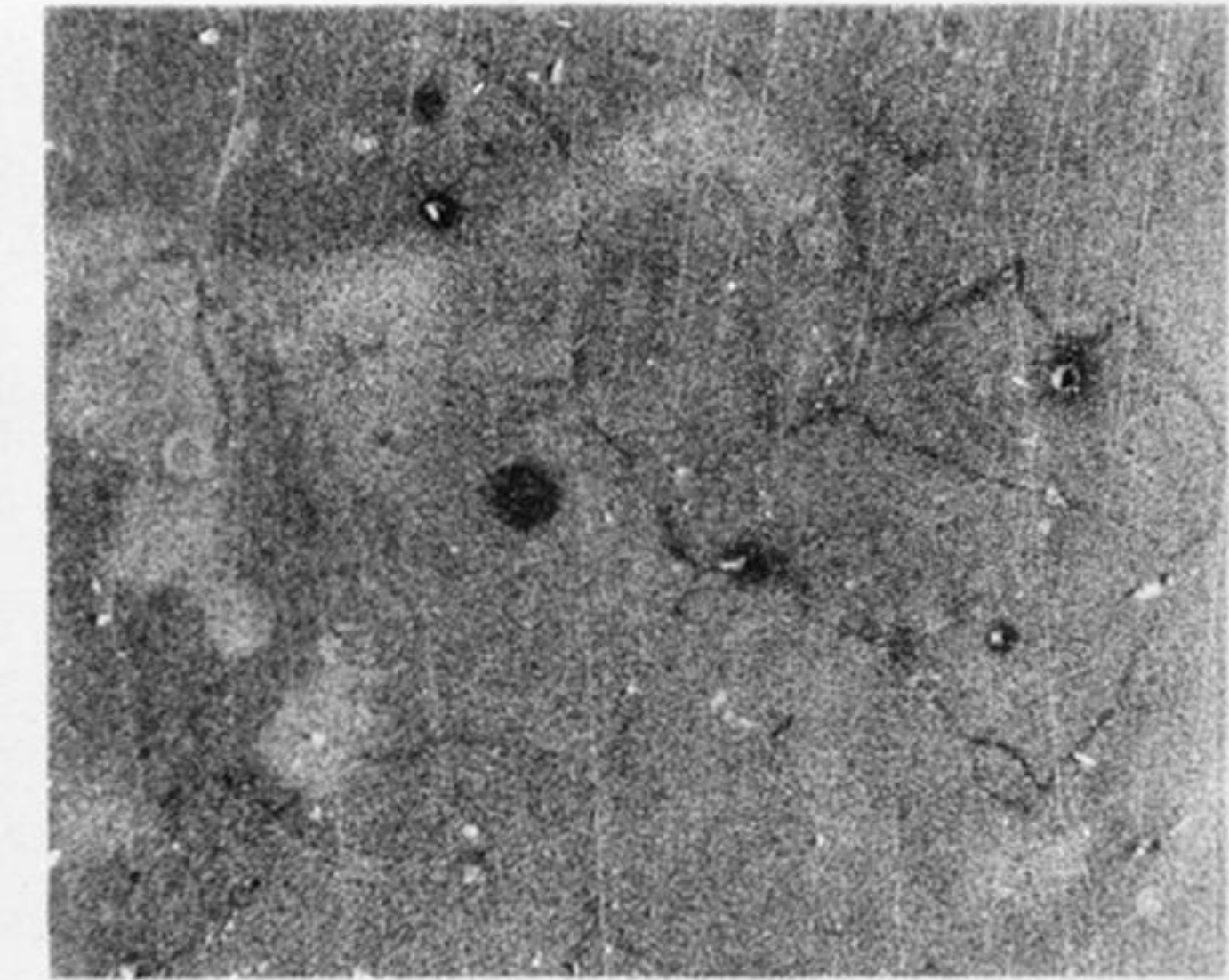
32



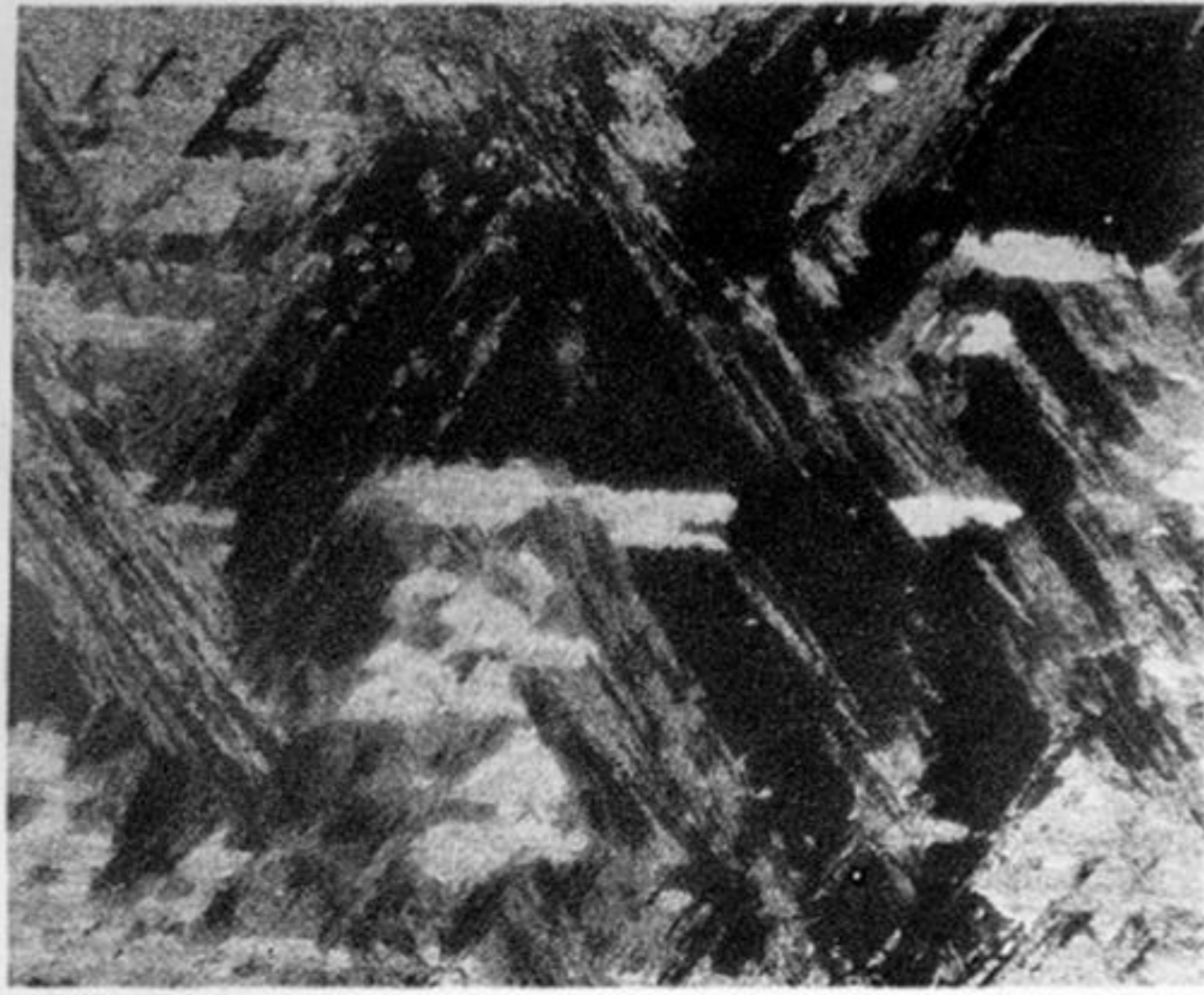
33



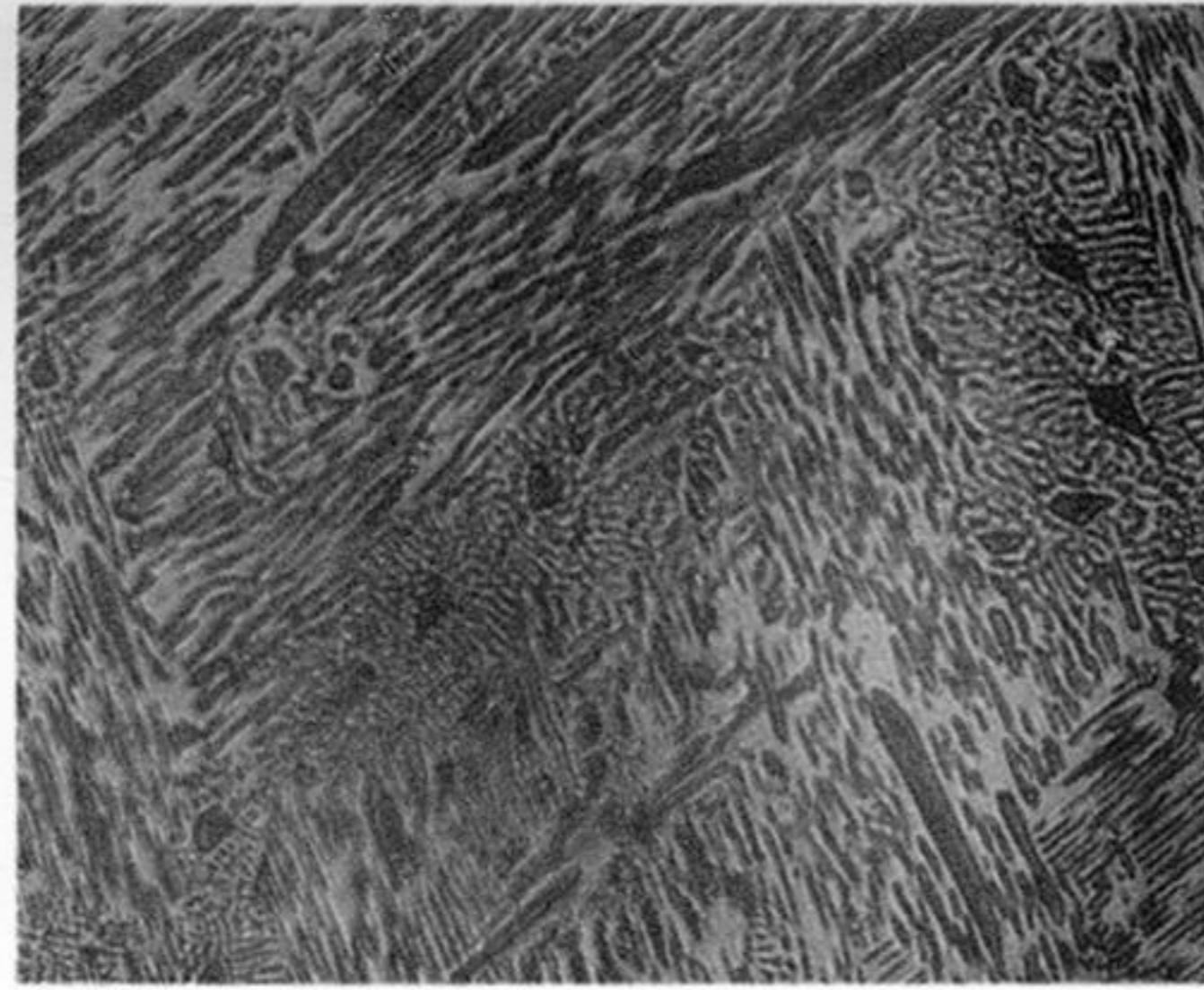
34



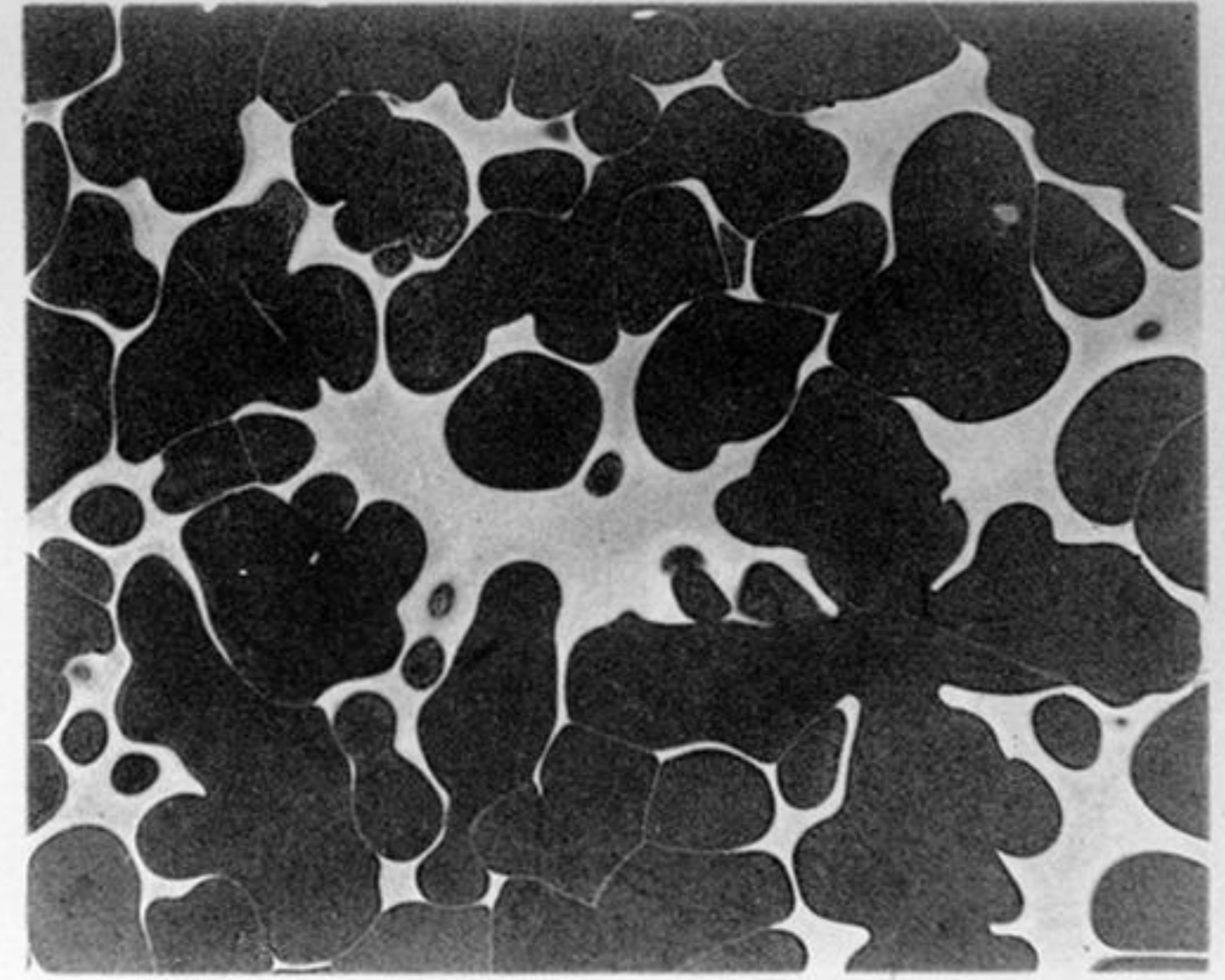
35



36



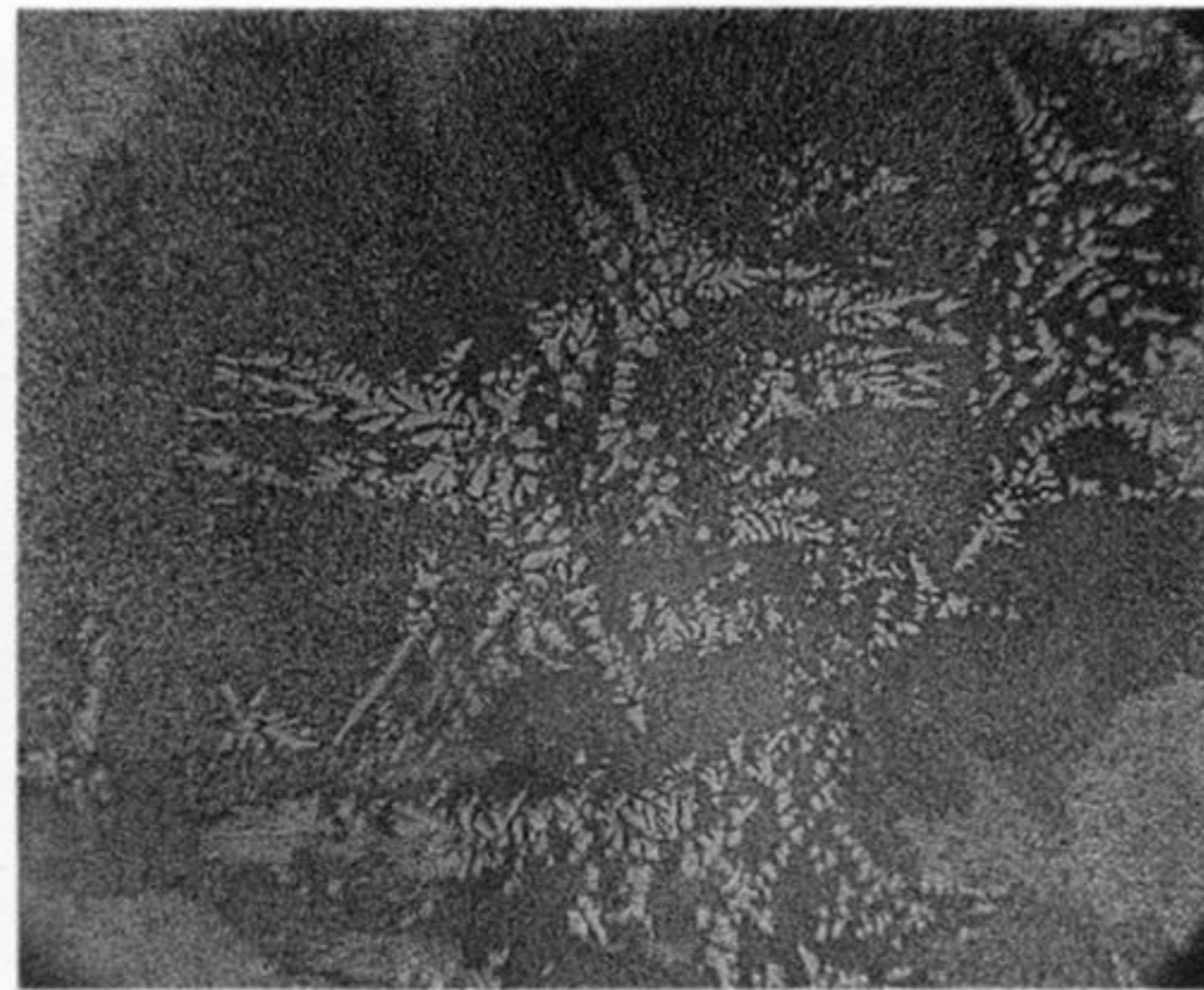
37



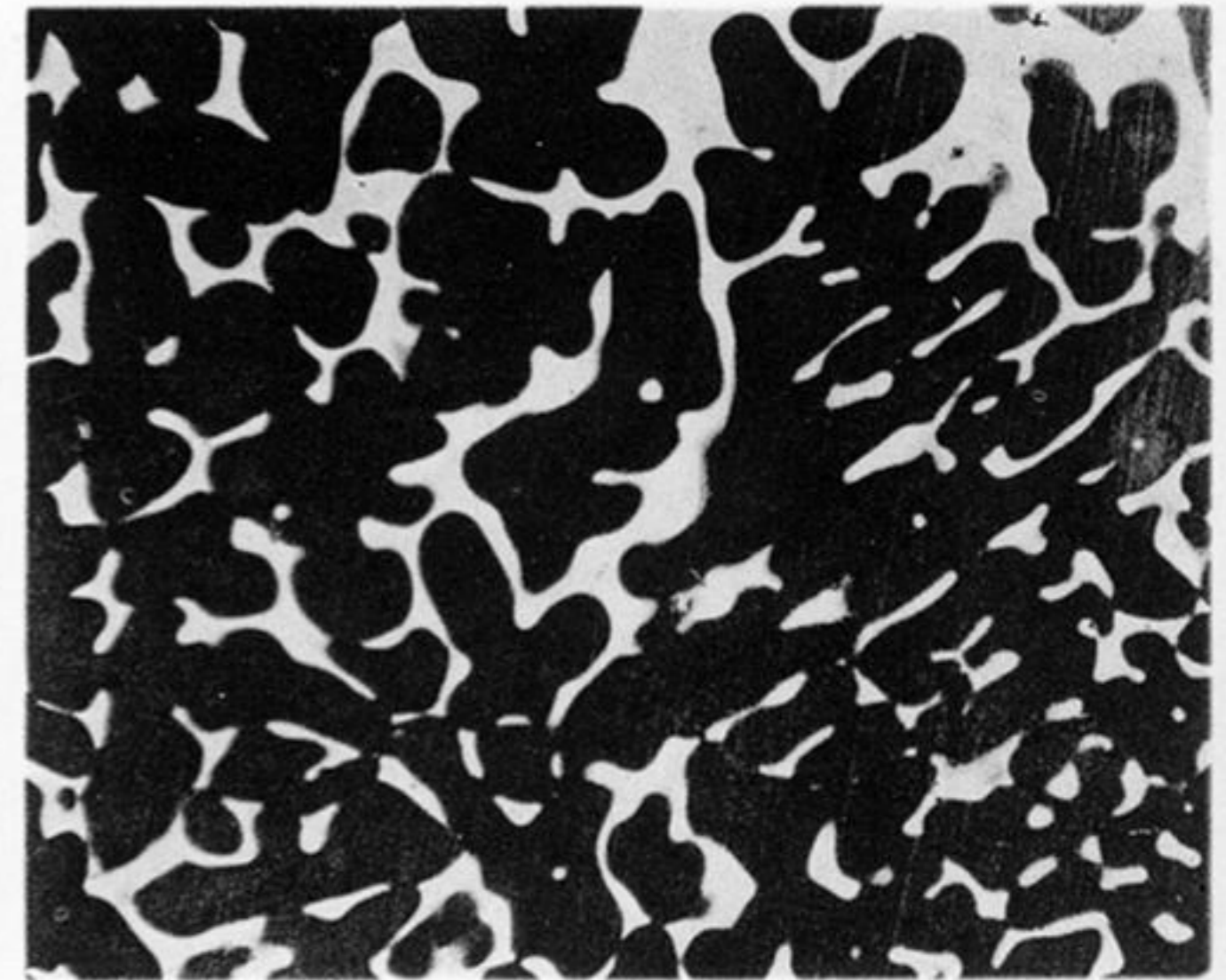
38



39



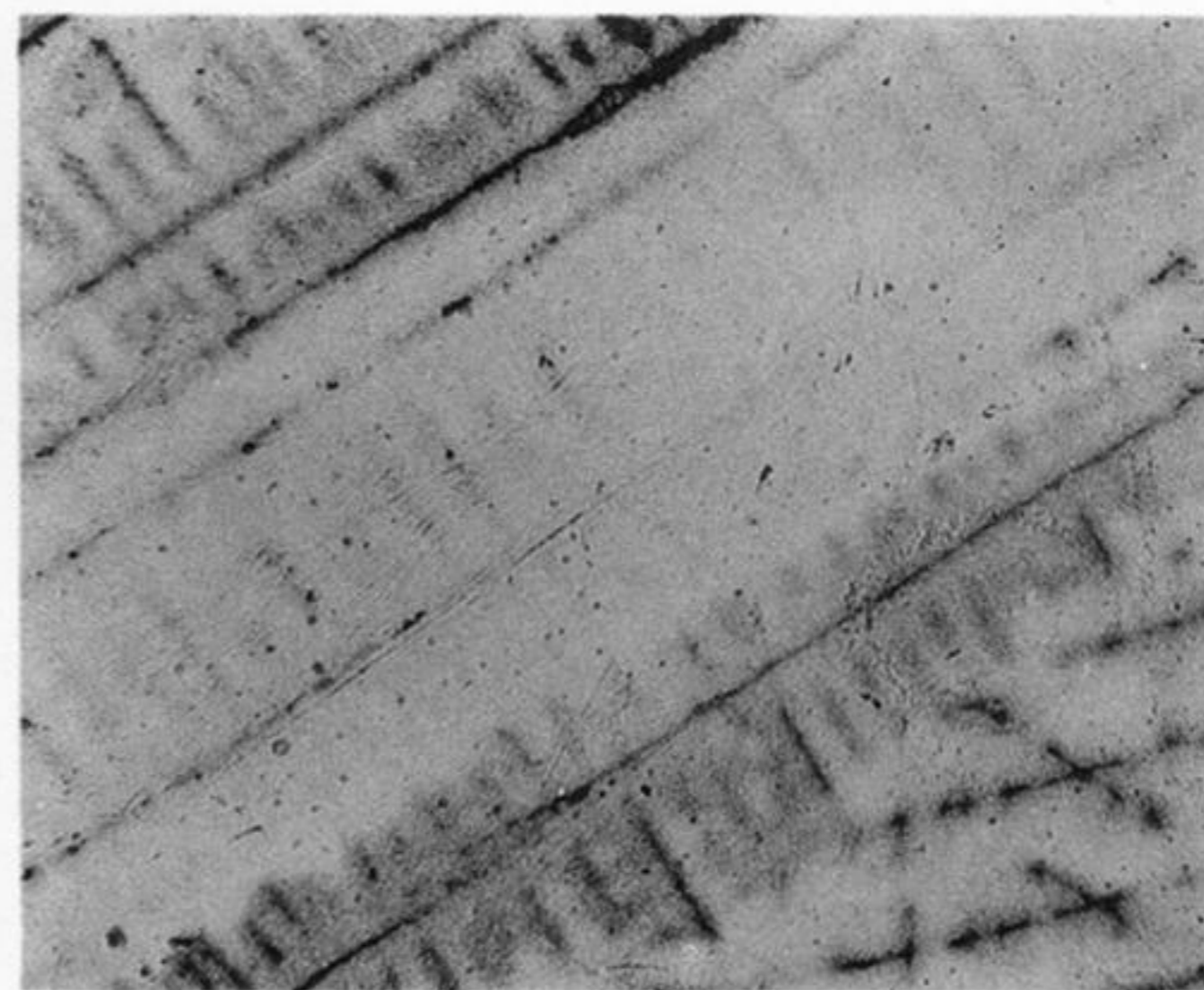
40



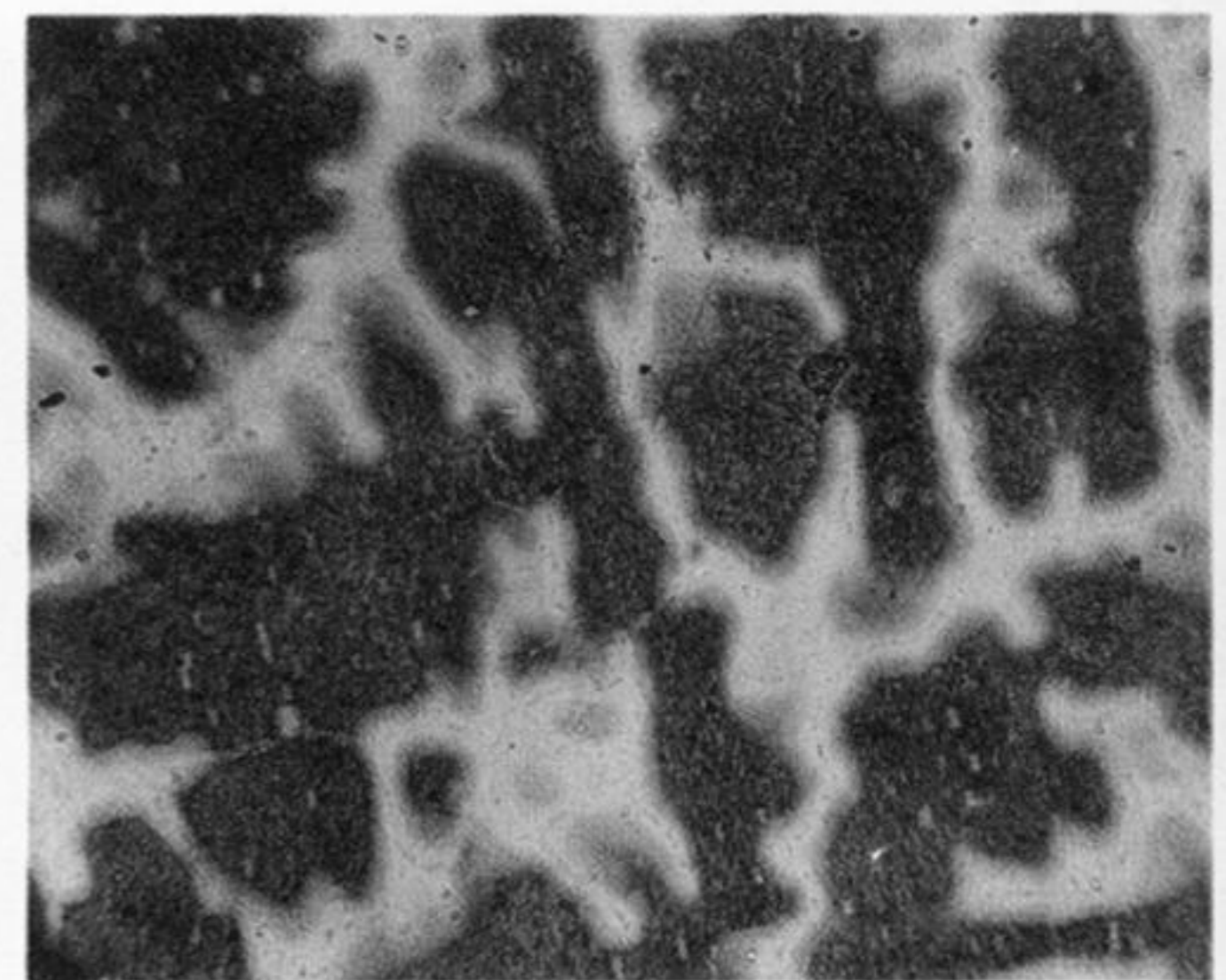
41



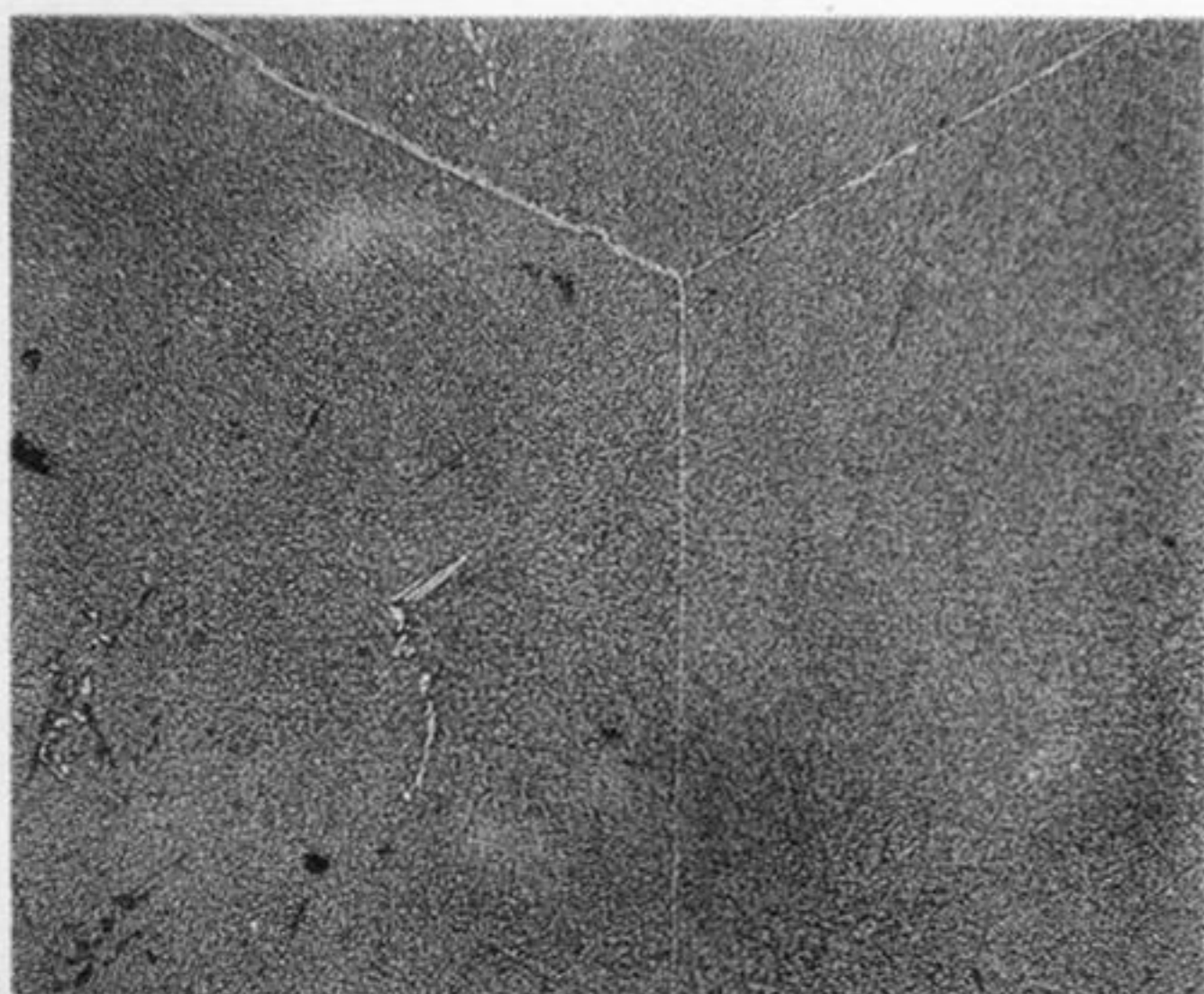
42



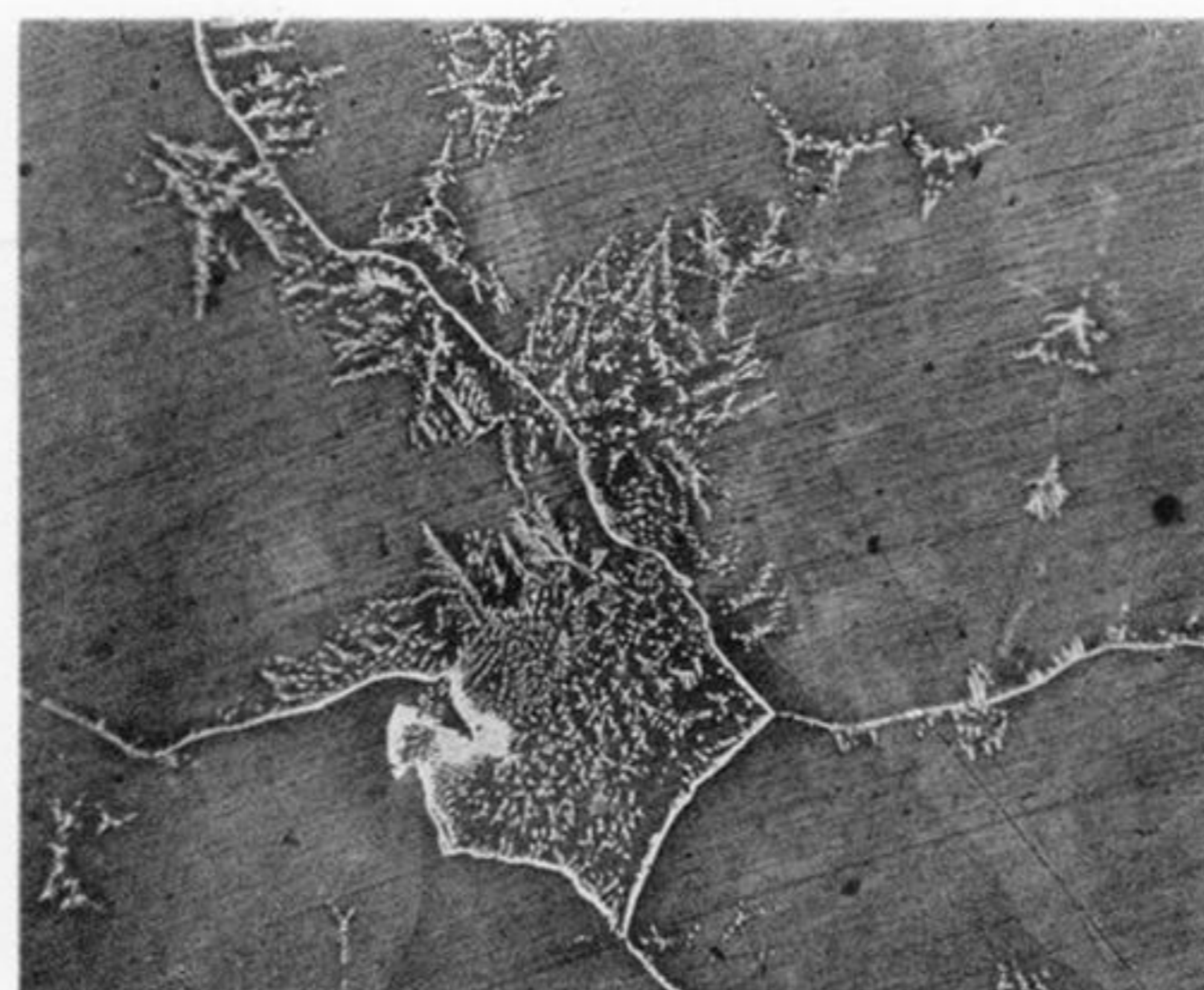
43



44



45



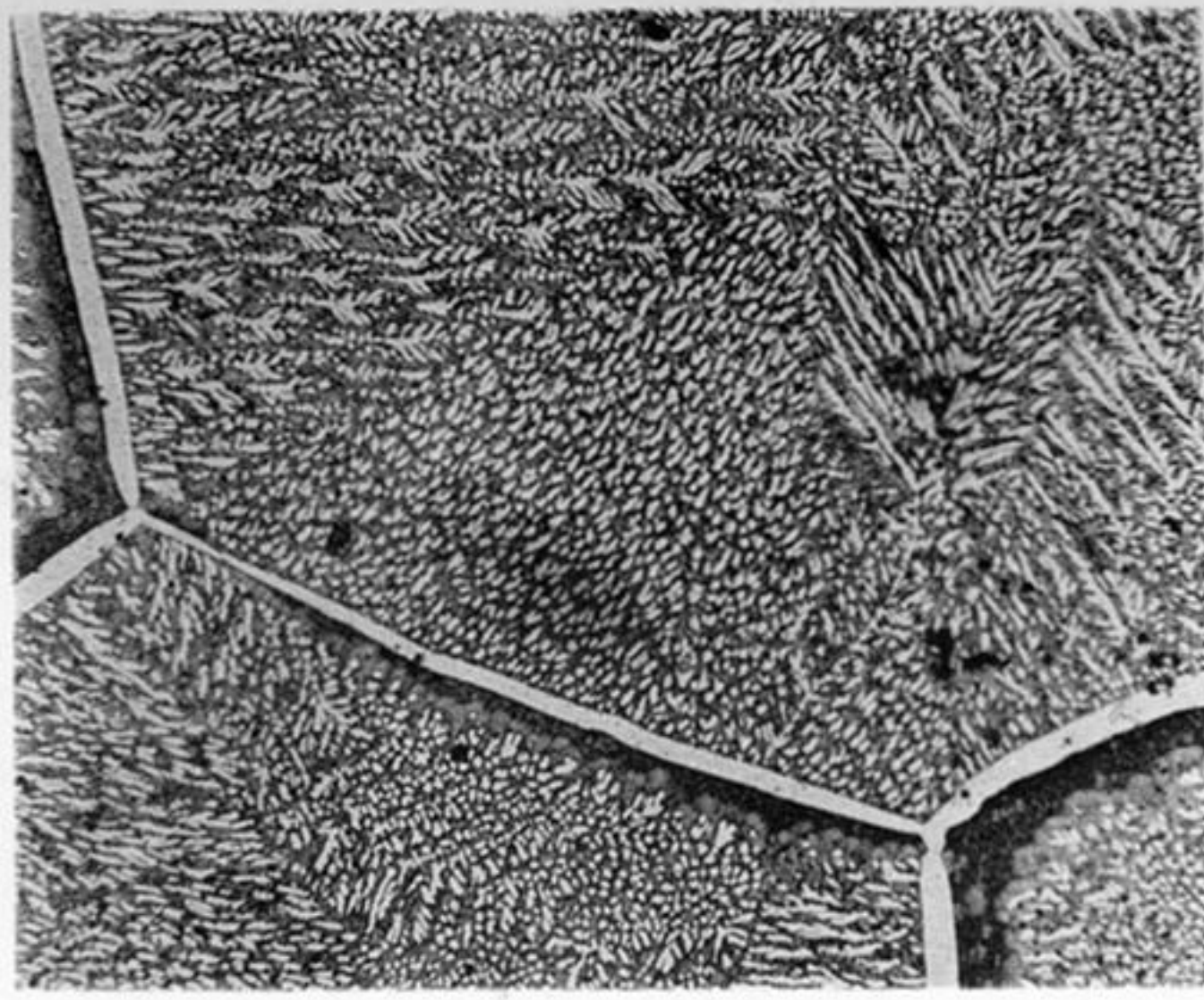
46



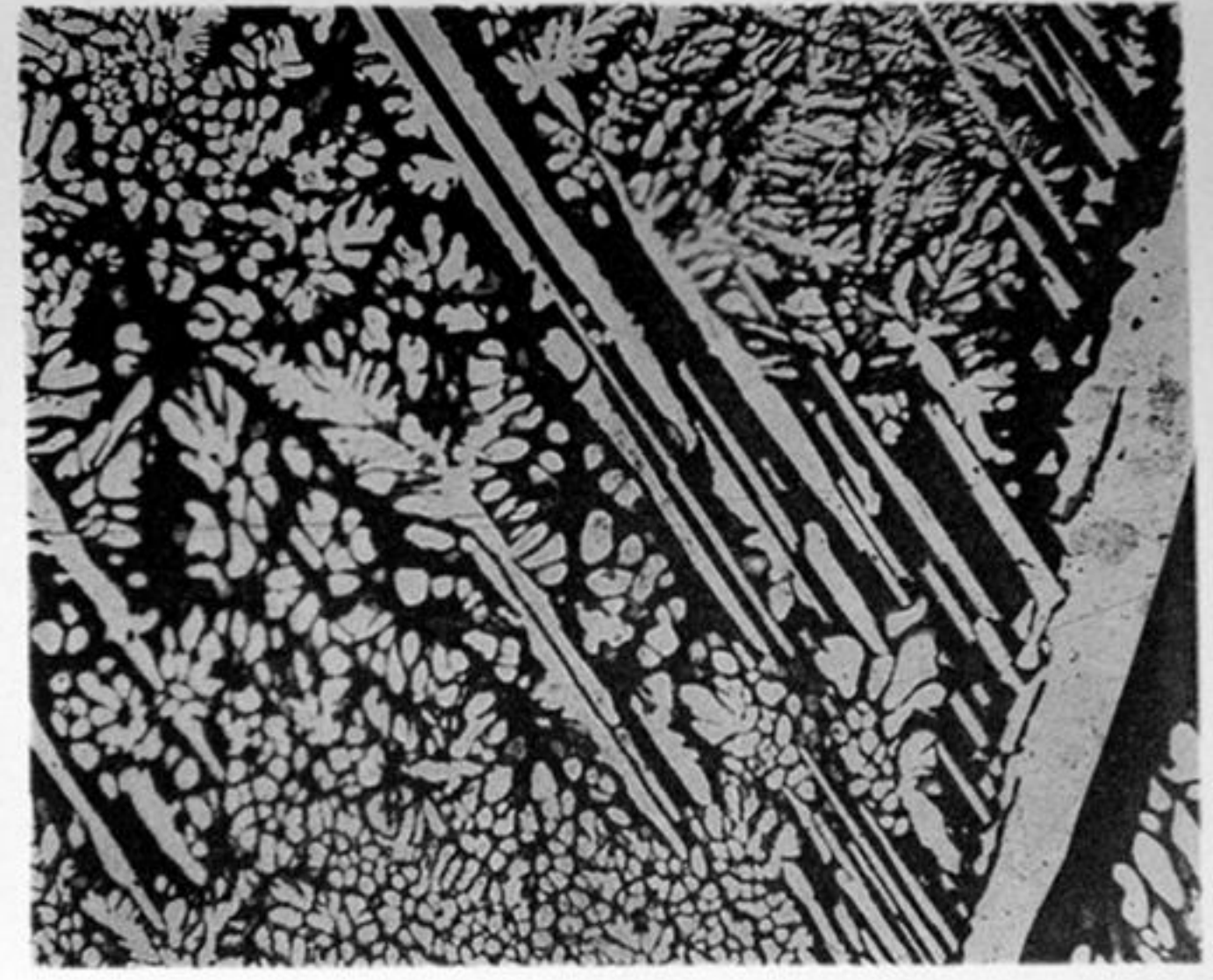
47



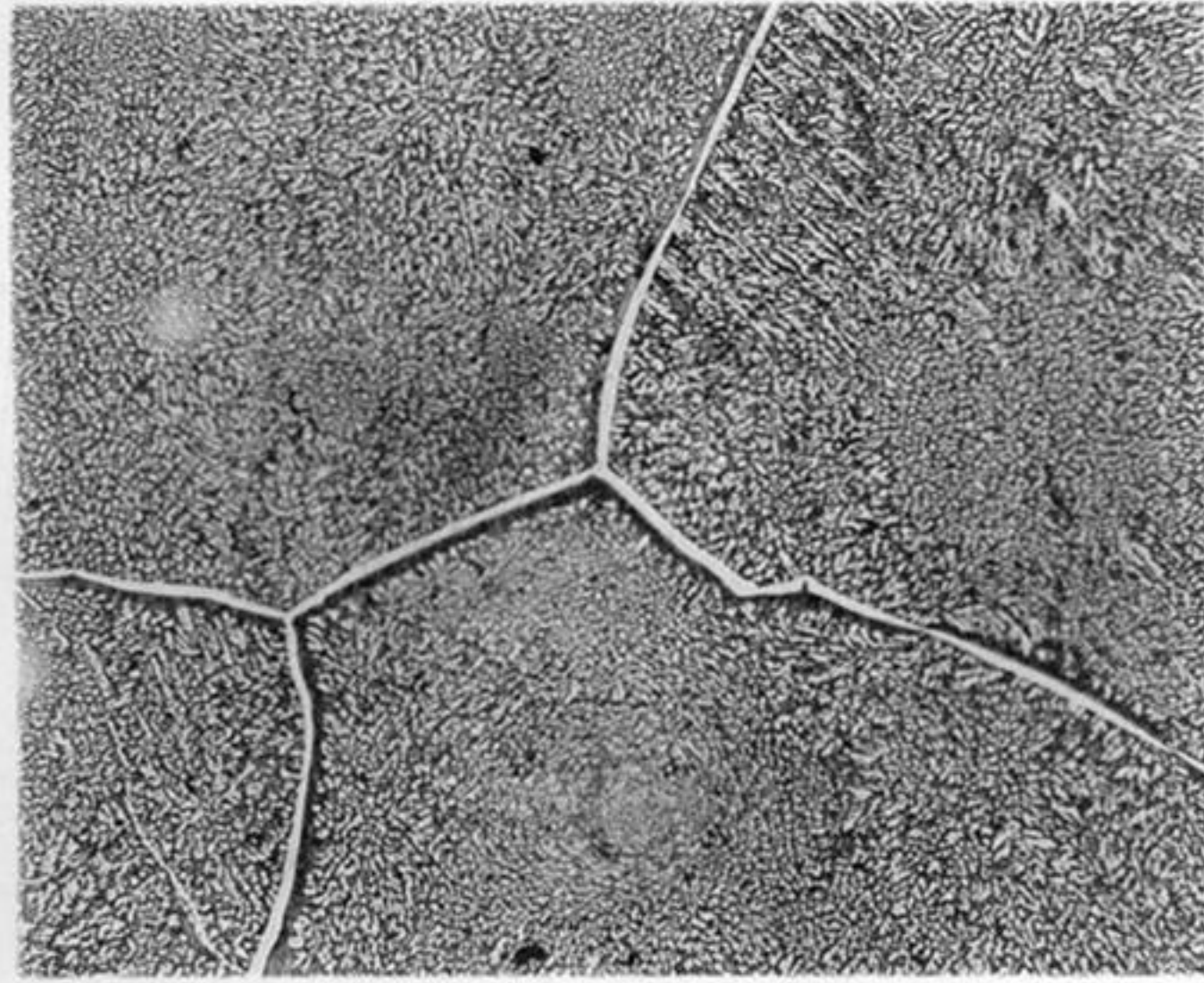
48



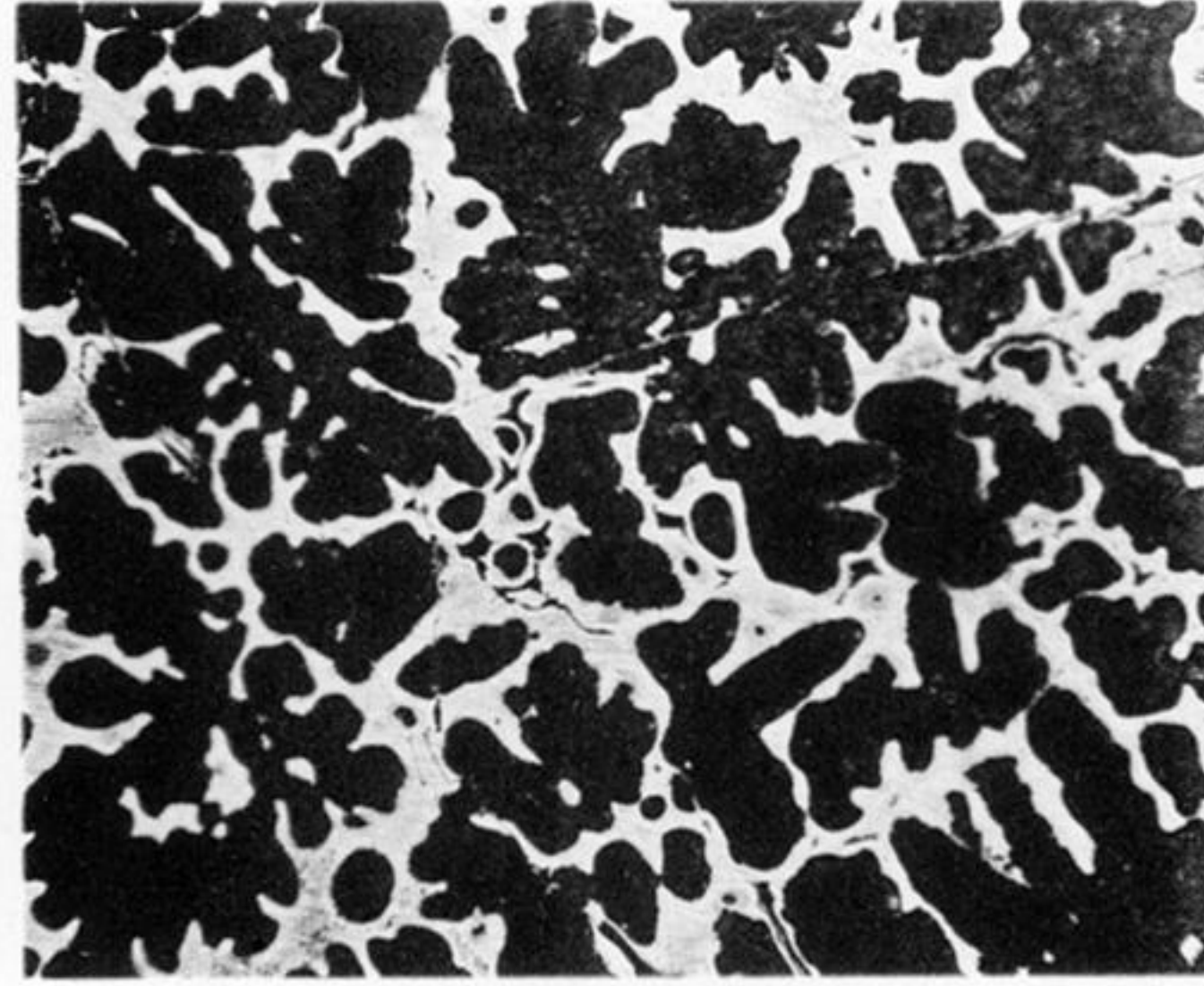
49



49A



50



51



52



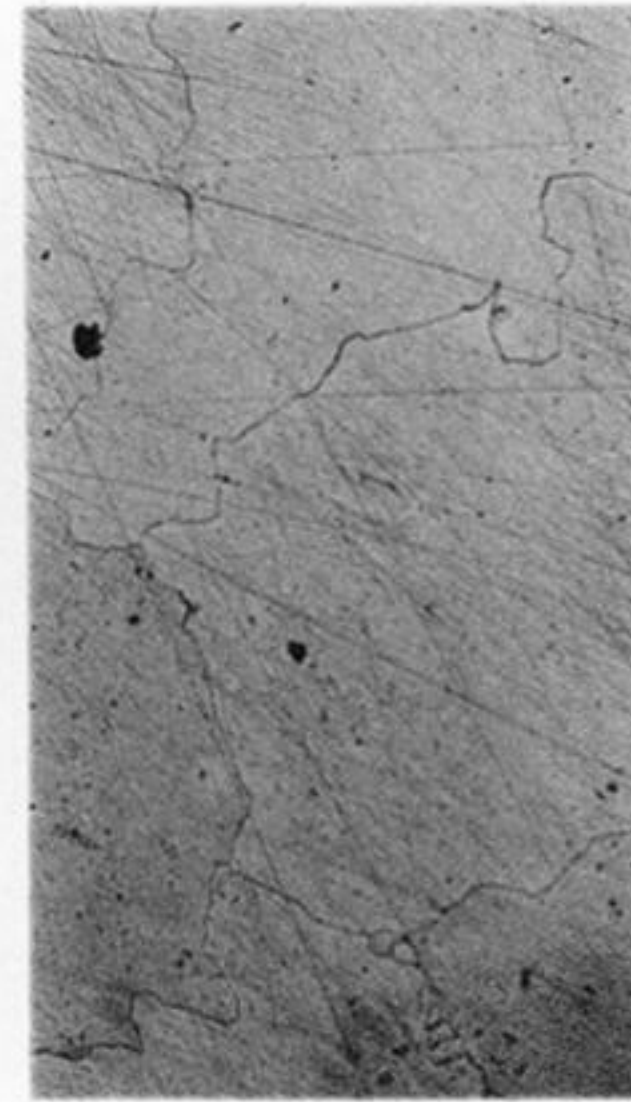
53



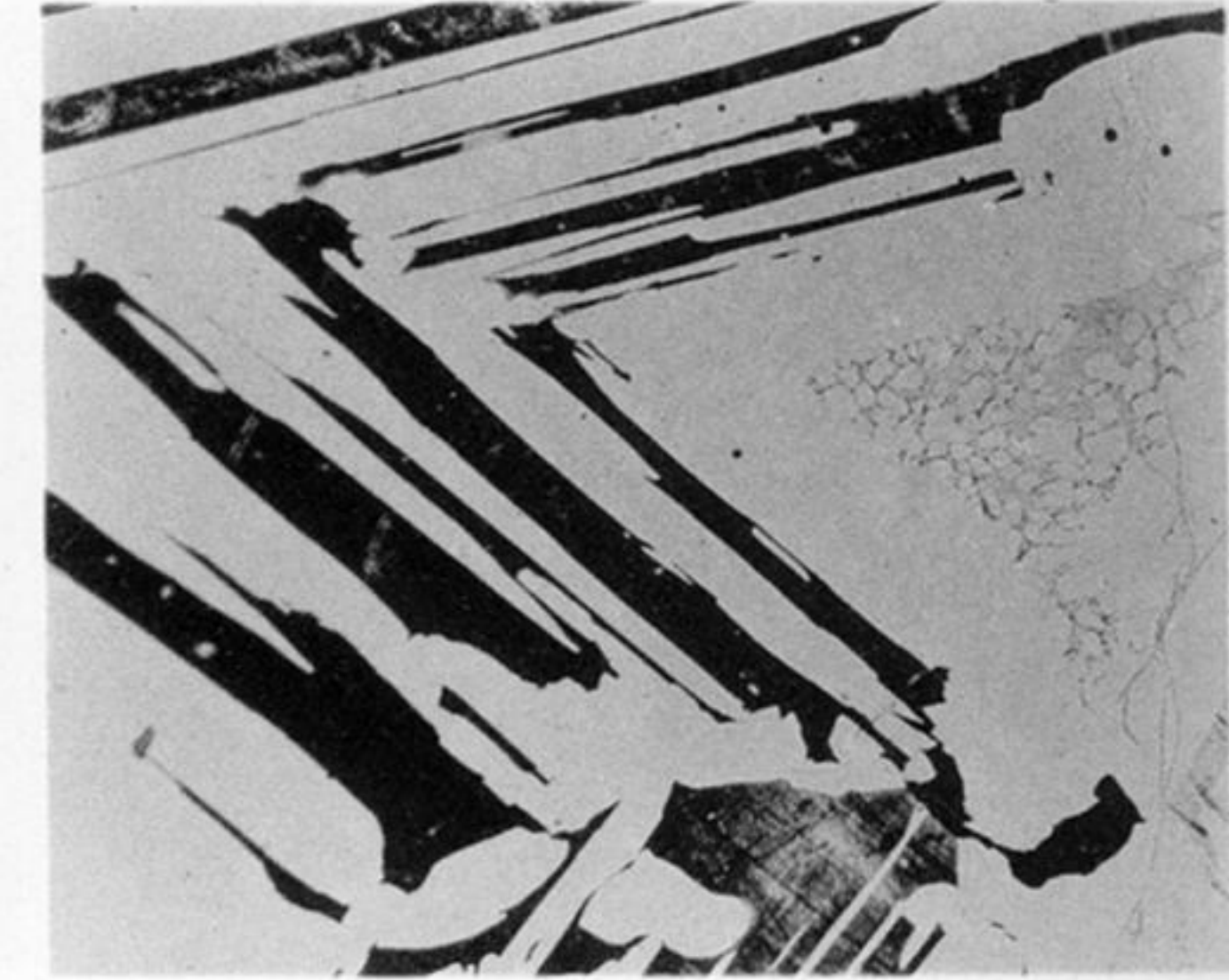
53A



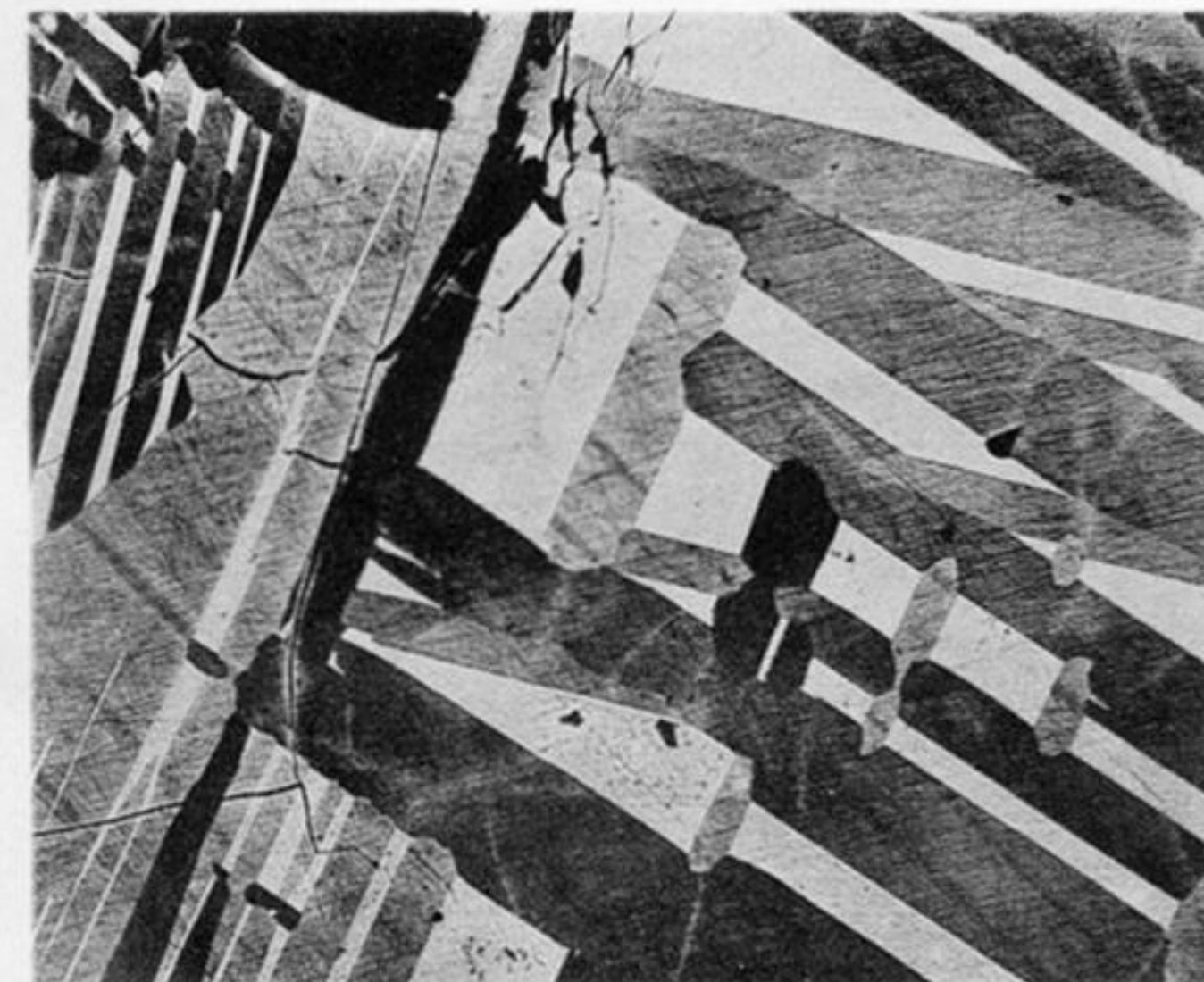
54



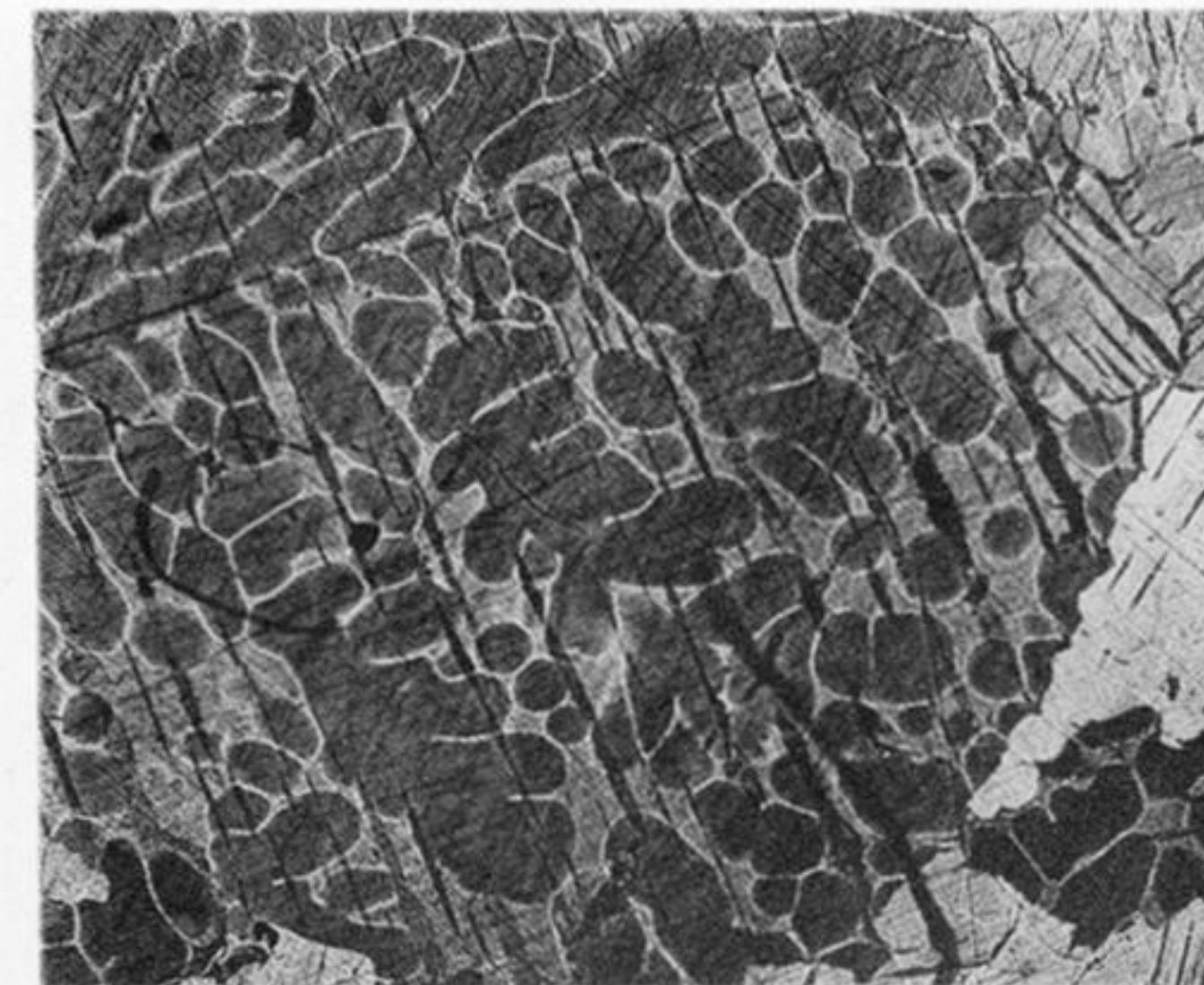
55



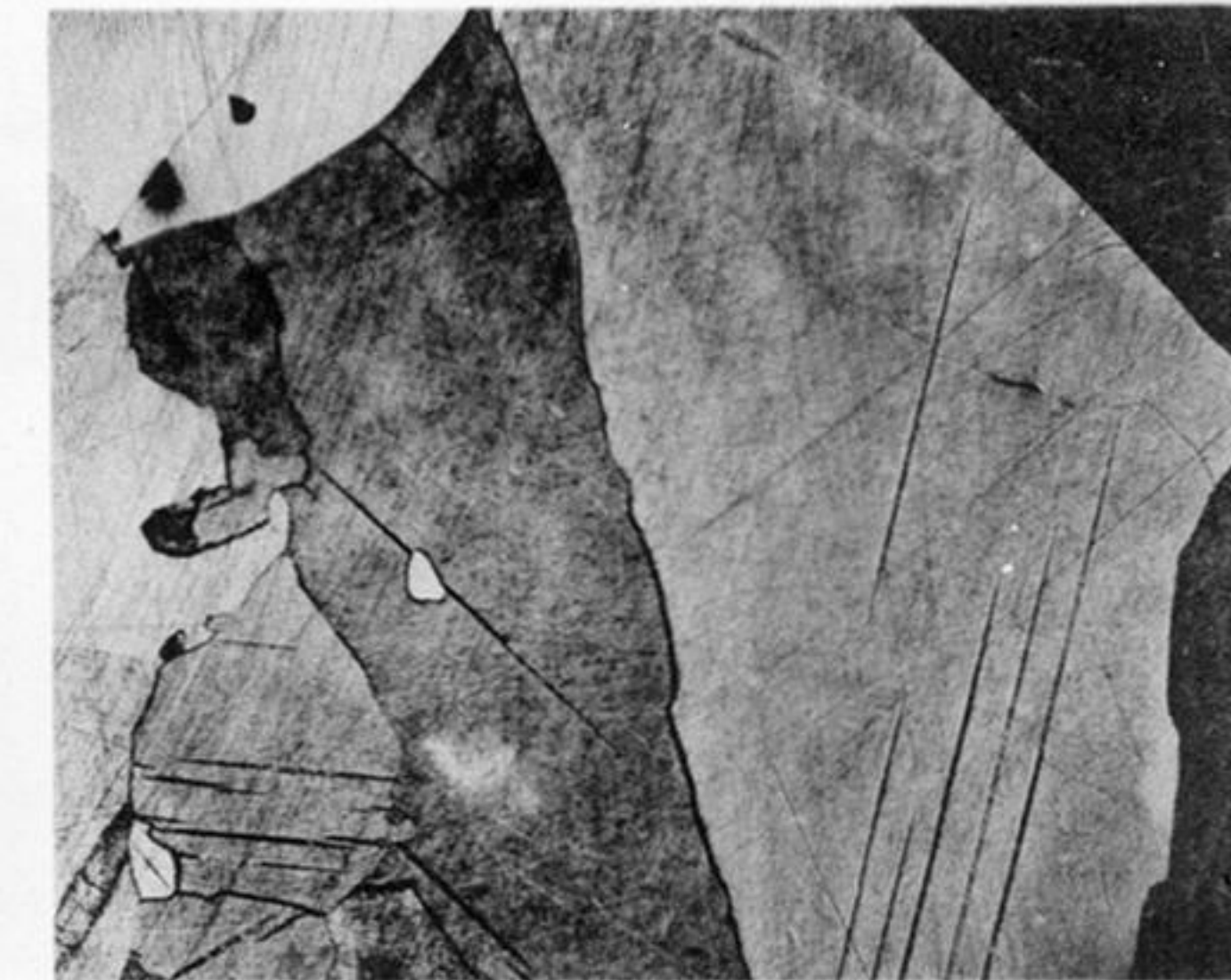
56



57



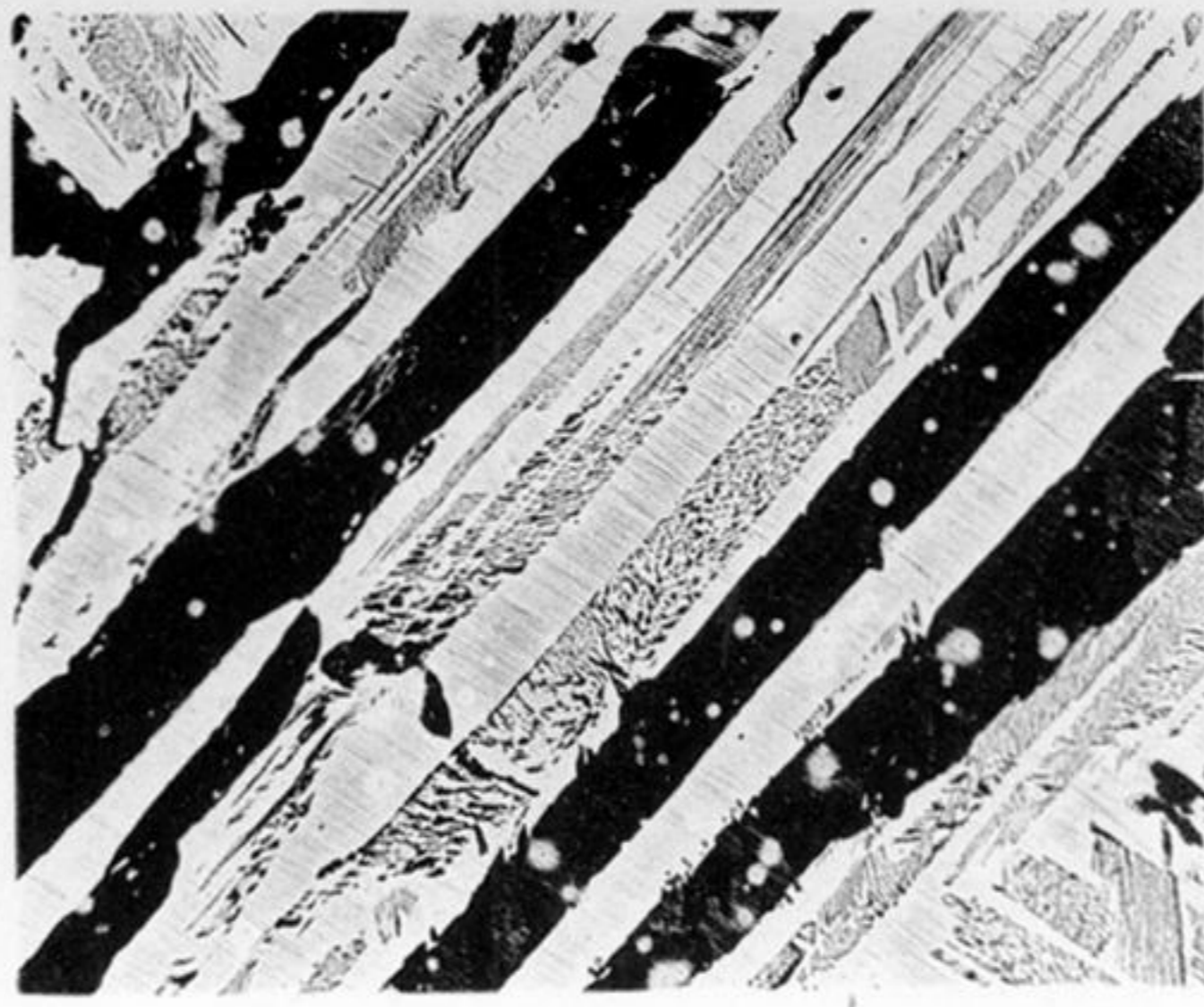
58



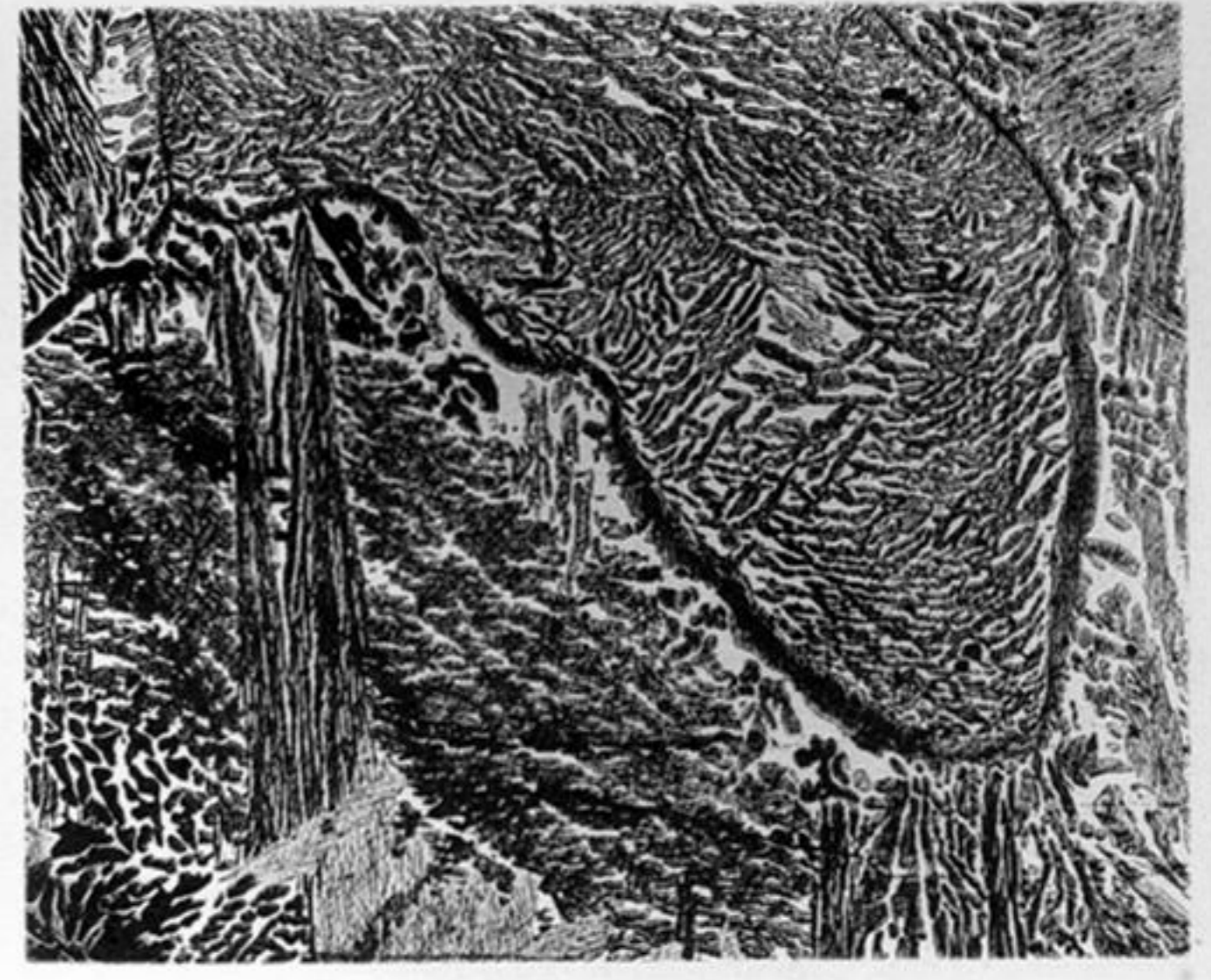
59



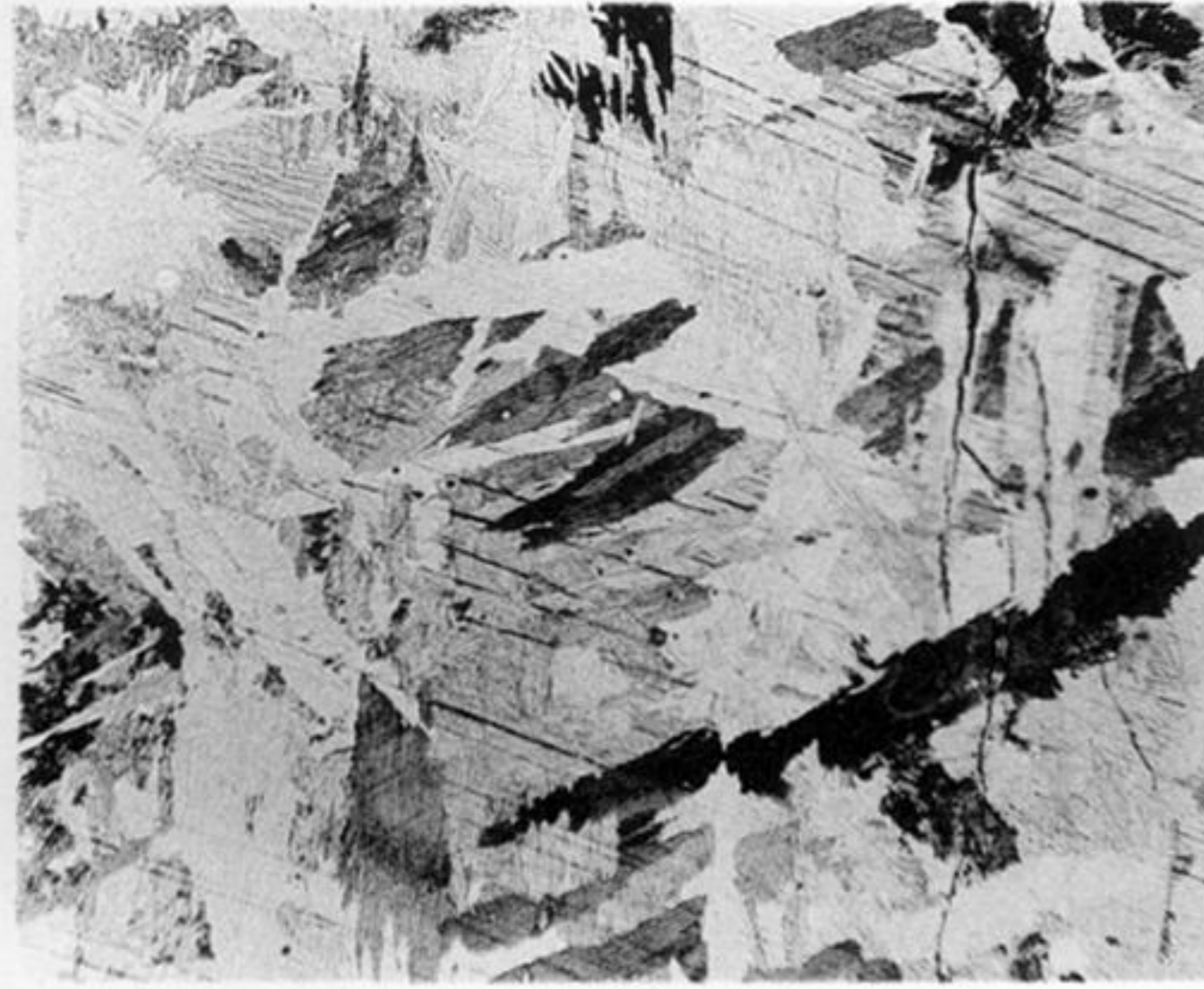
60



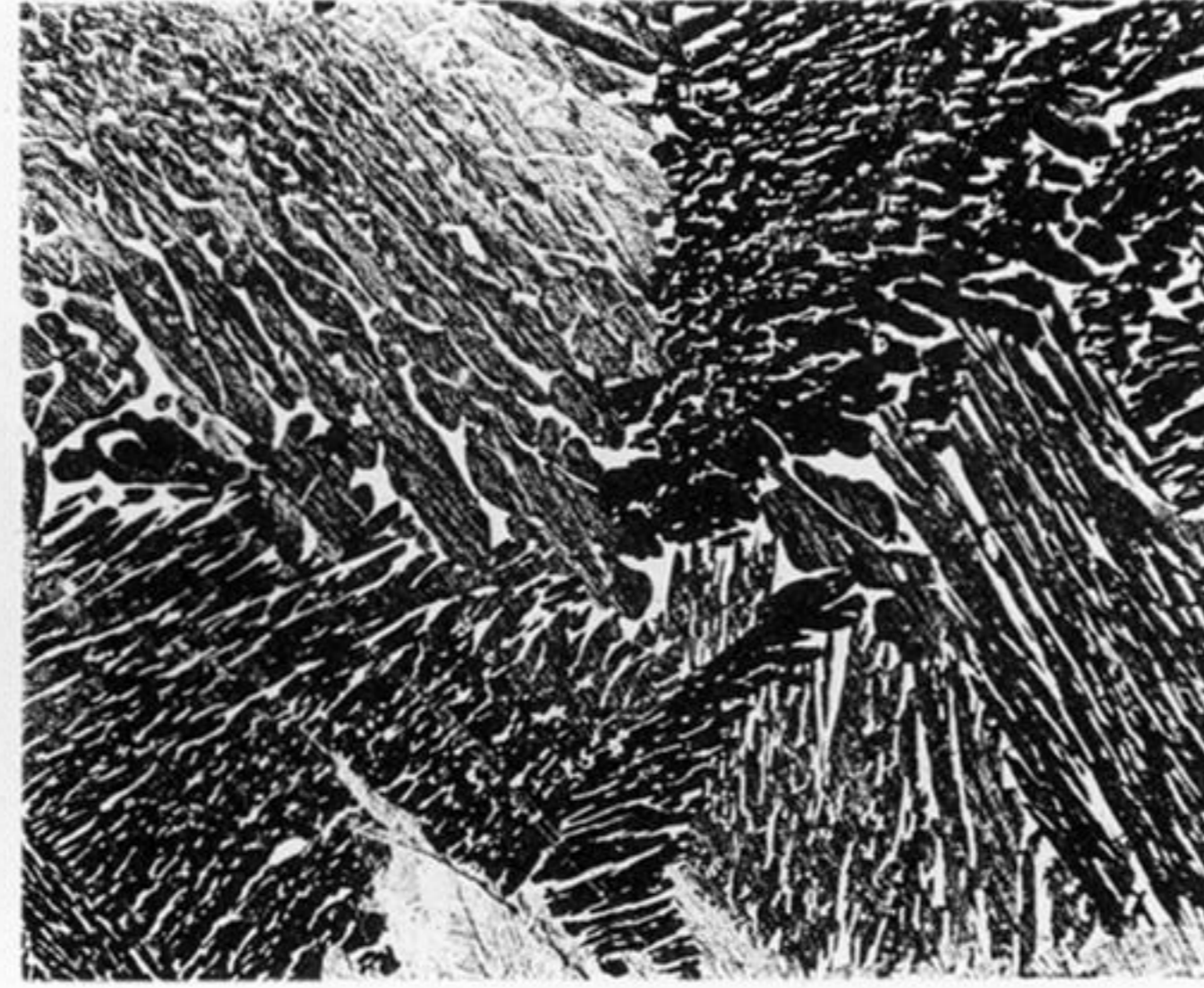
61



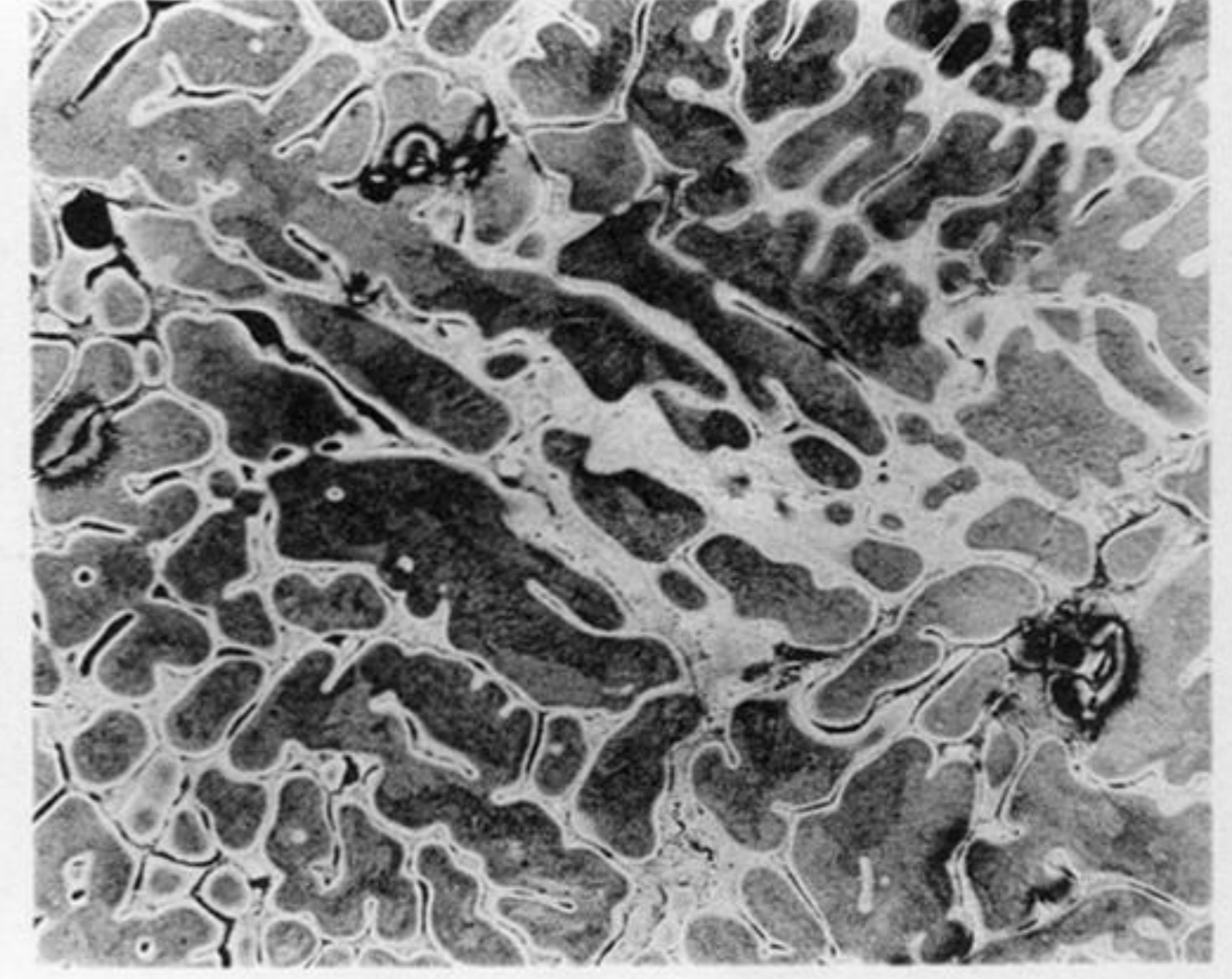
62



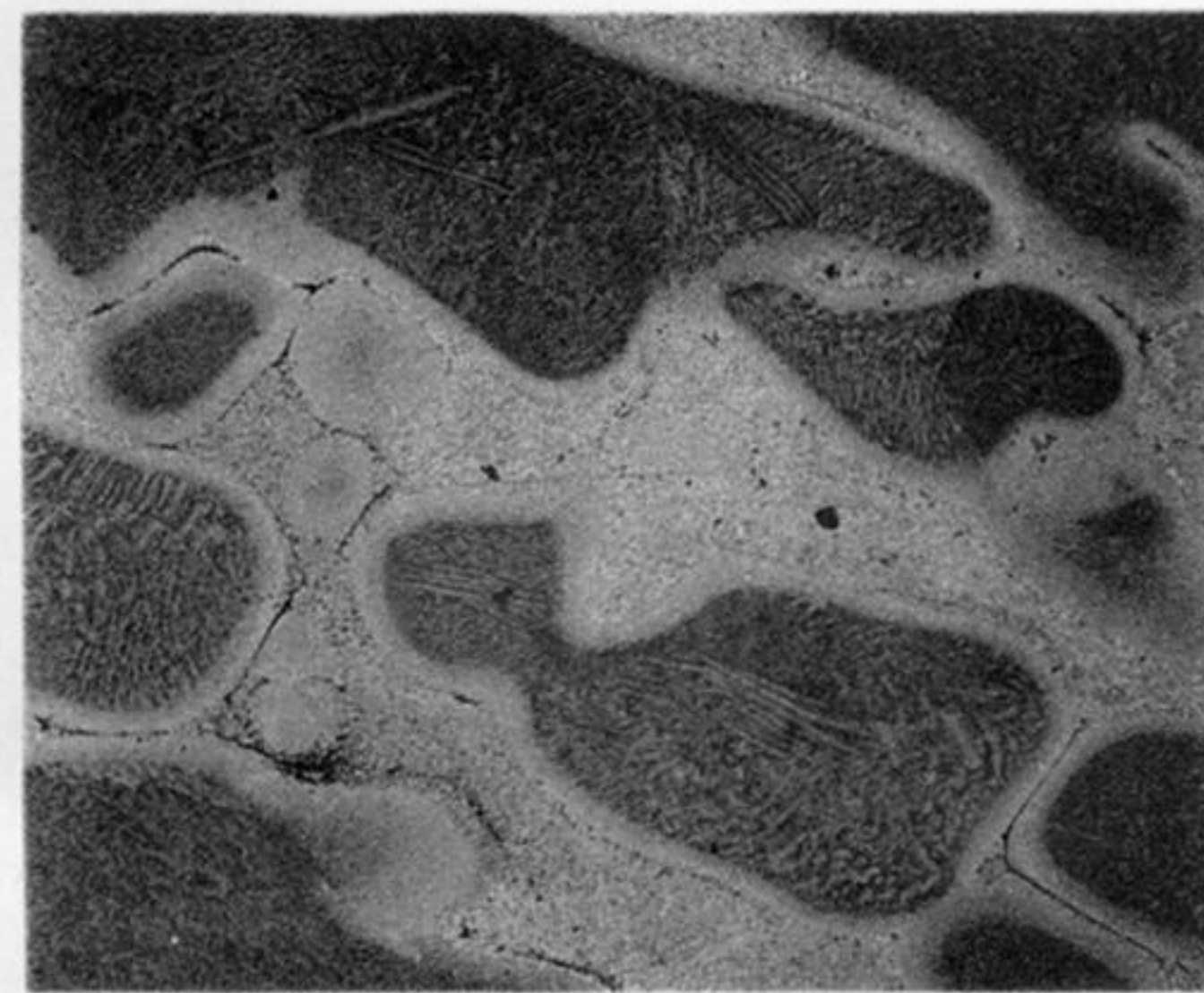
63



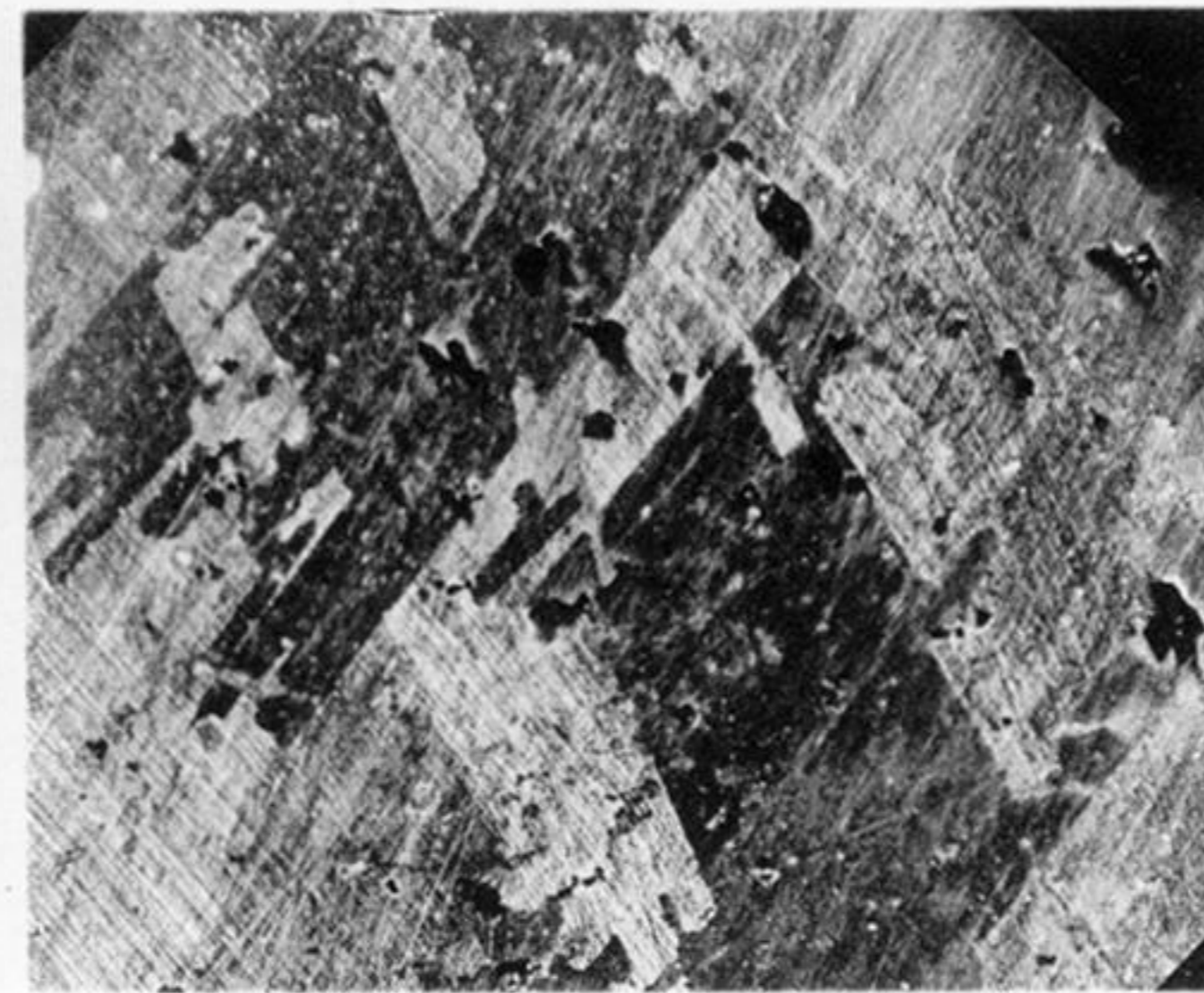
64



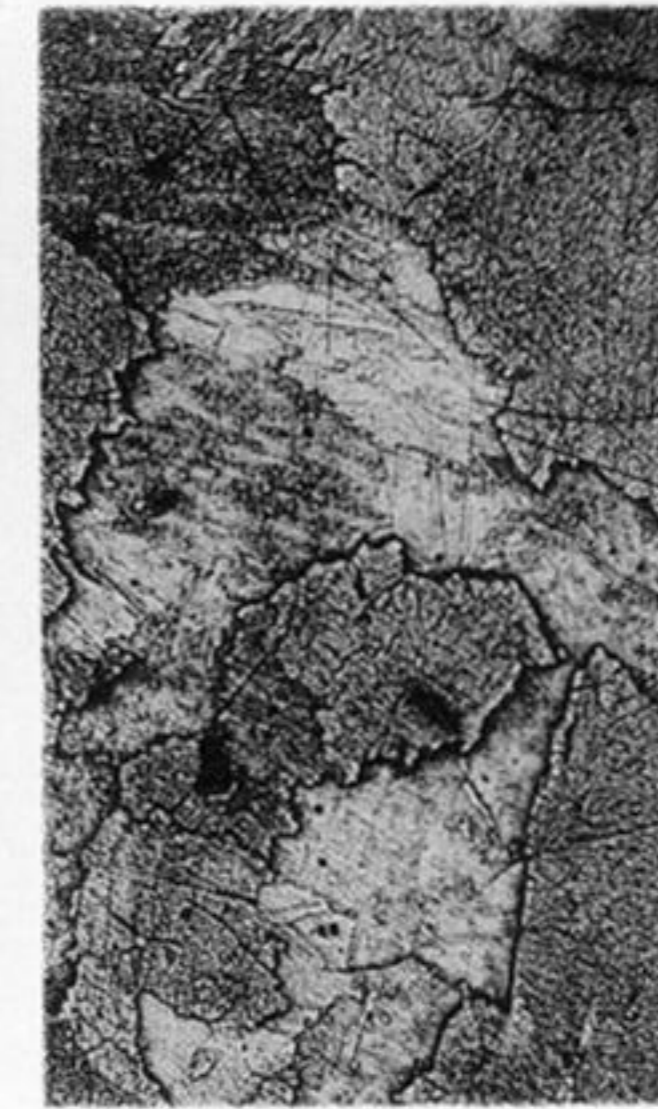
65



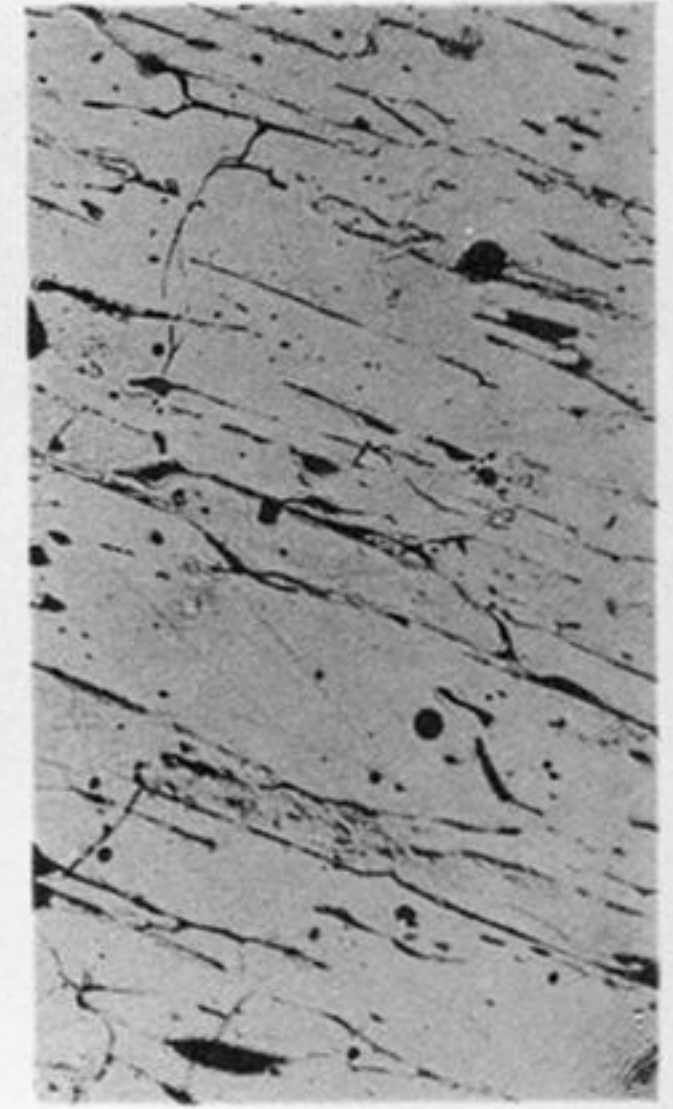
65A



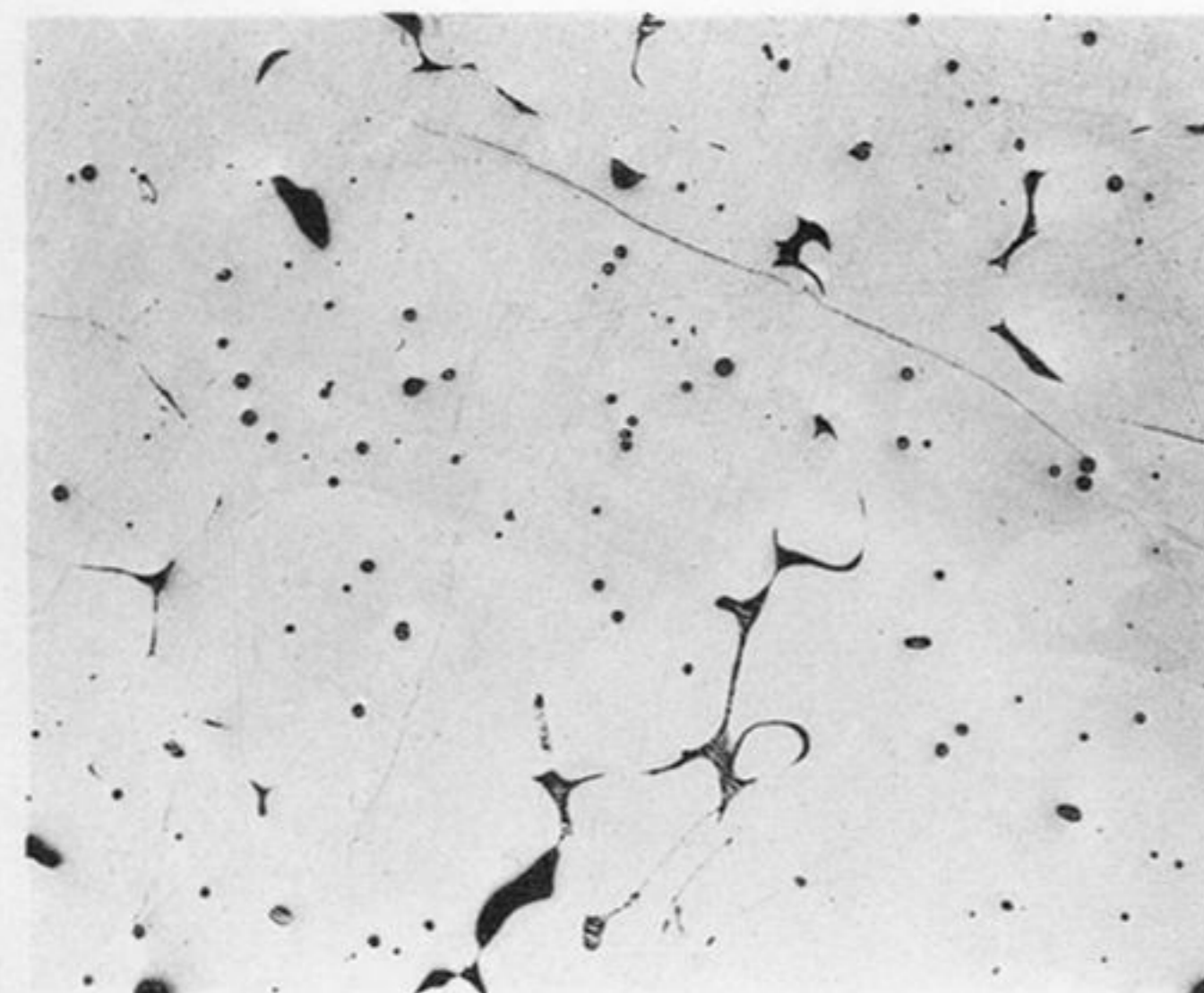
66



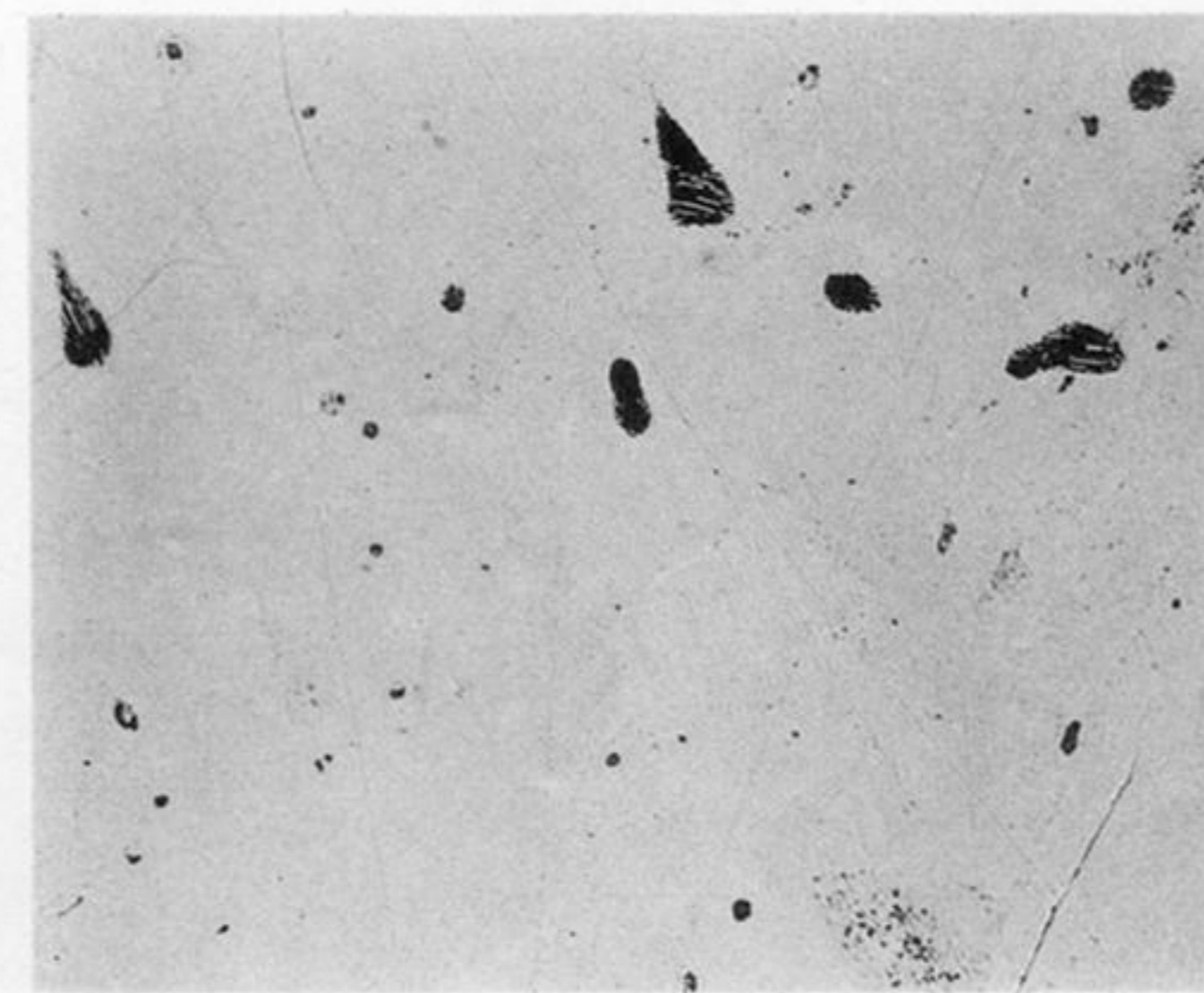
67



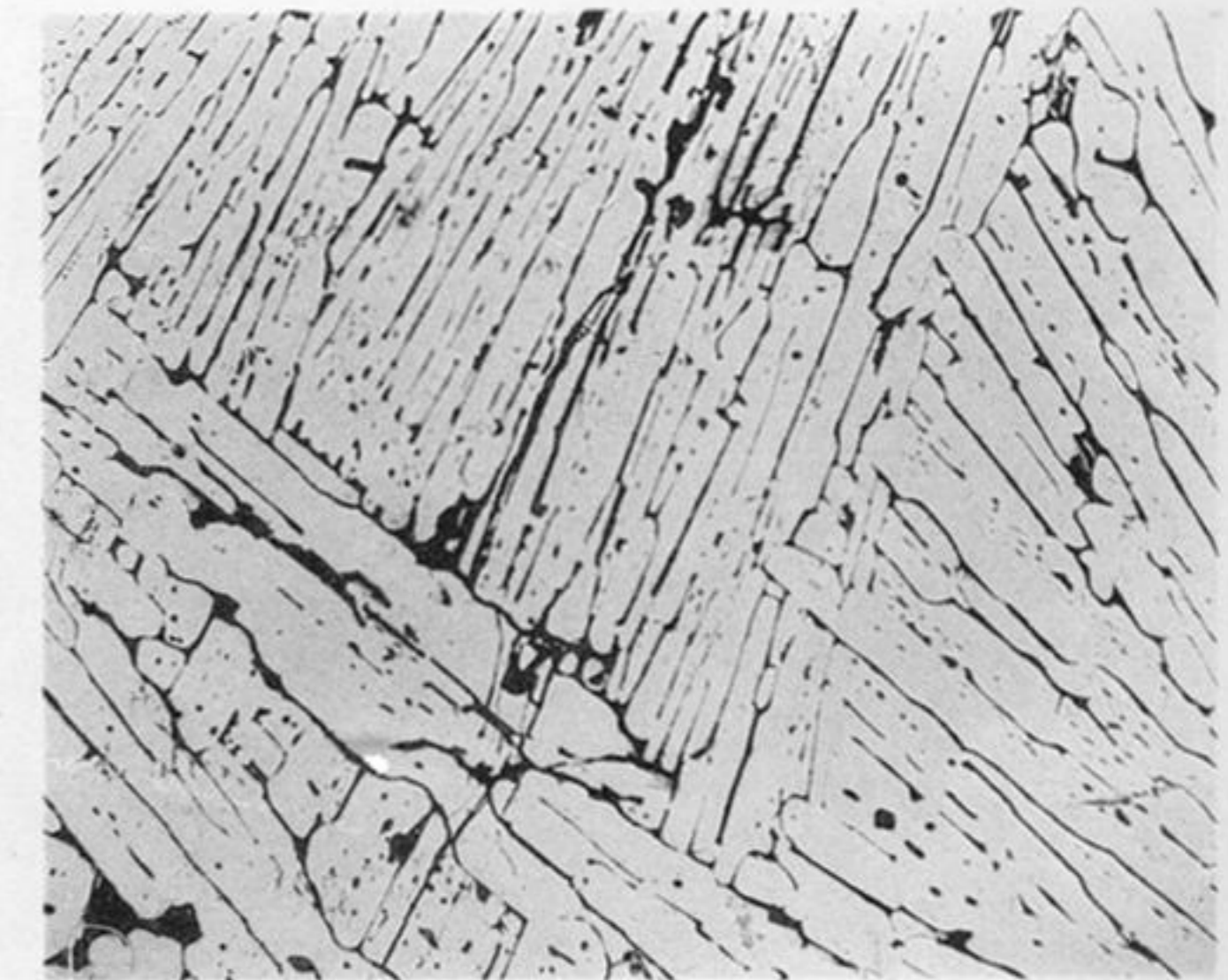
68



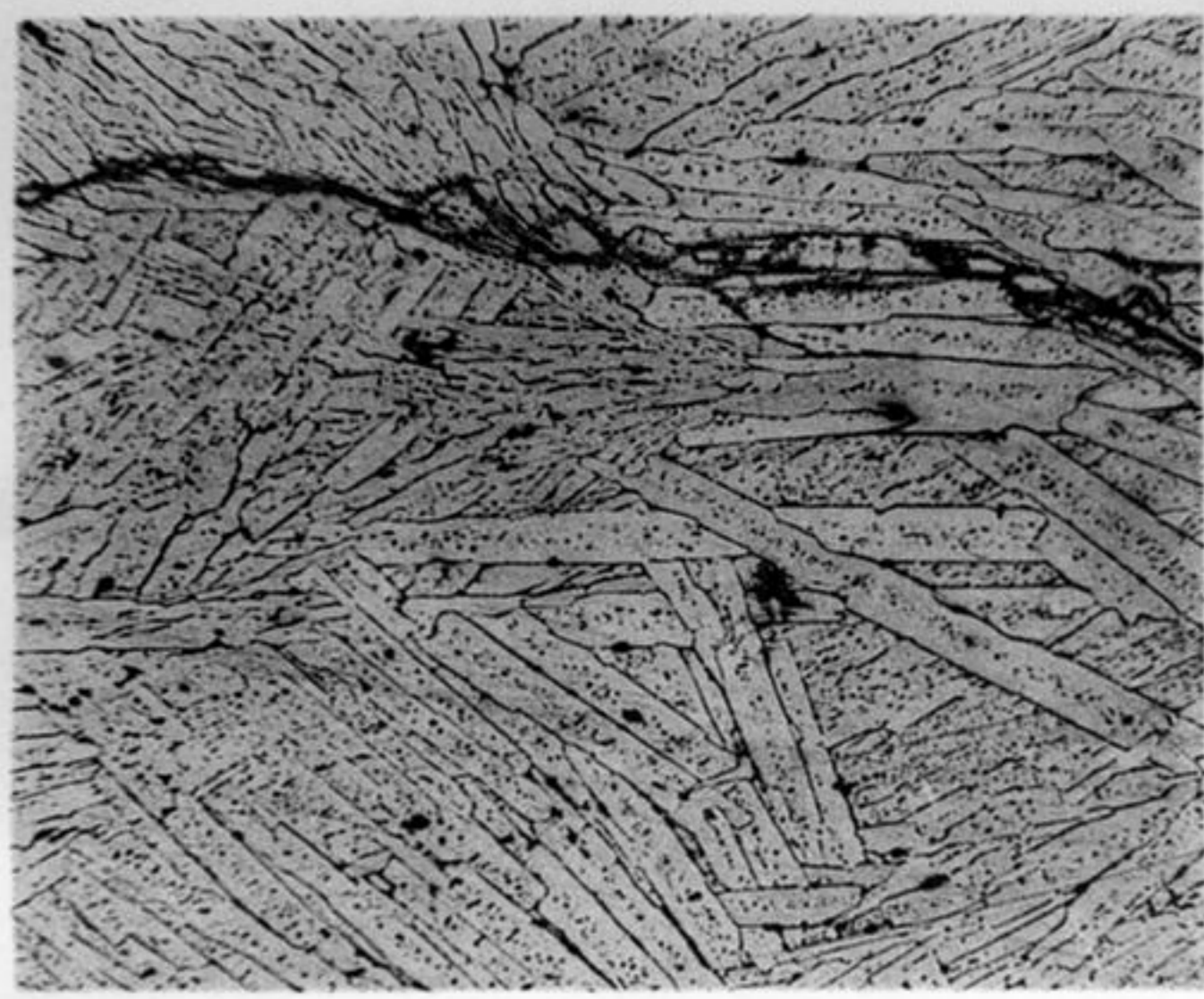
69



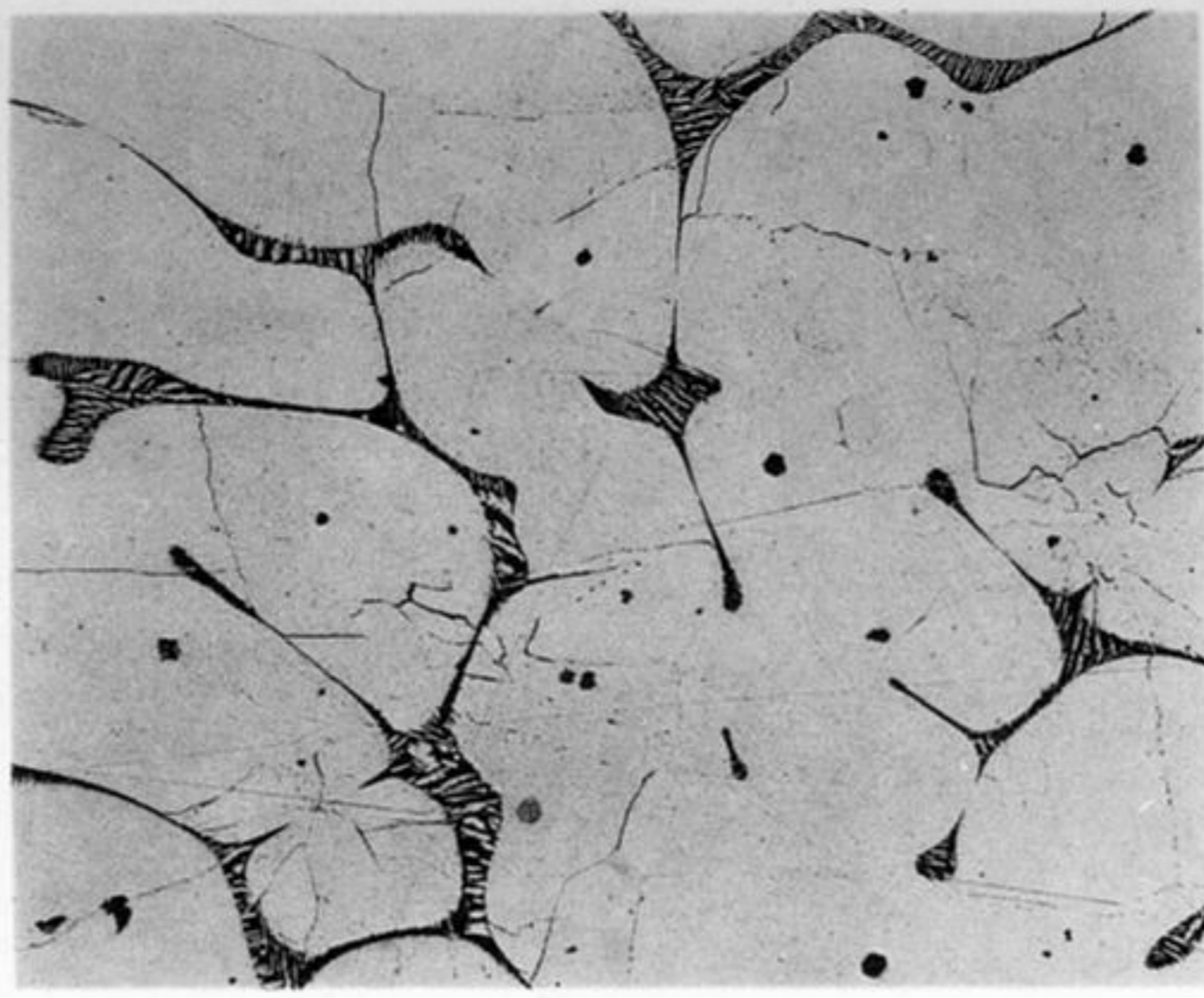
70



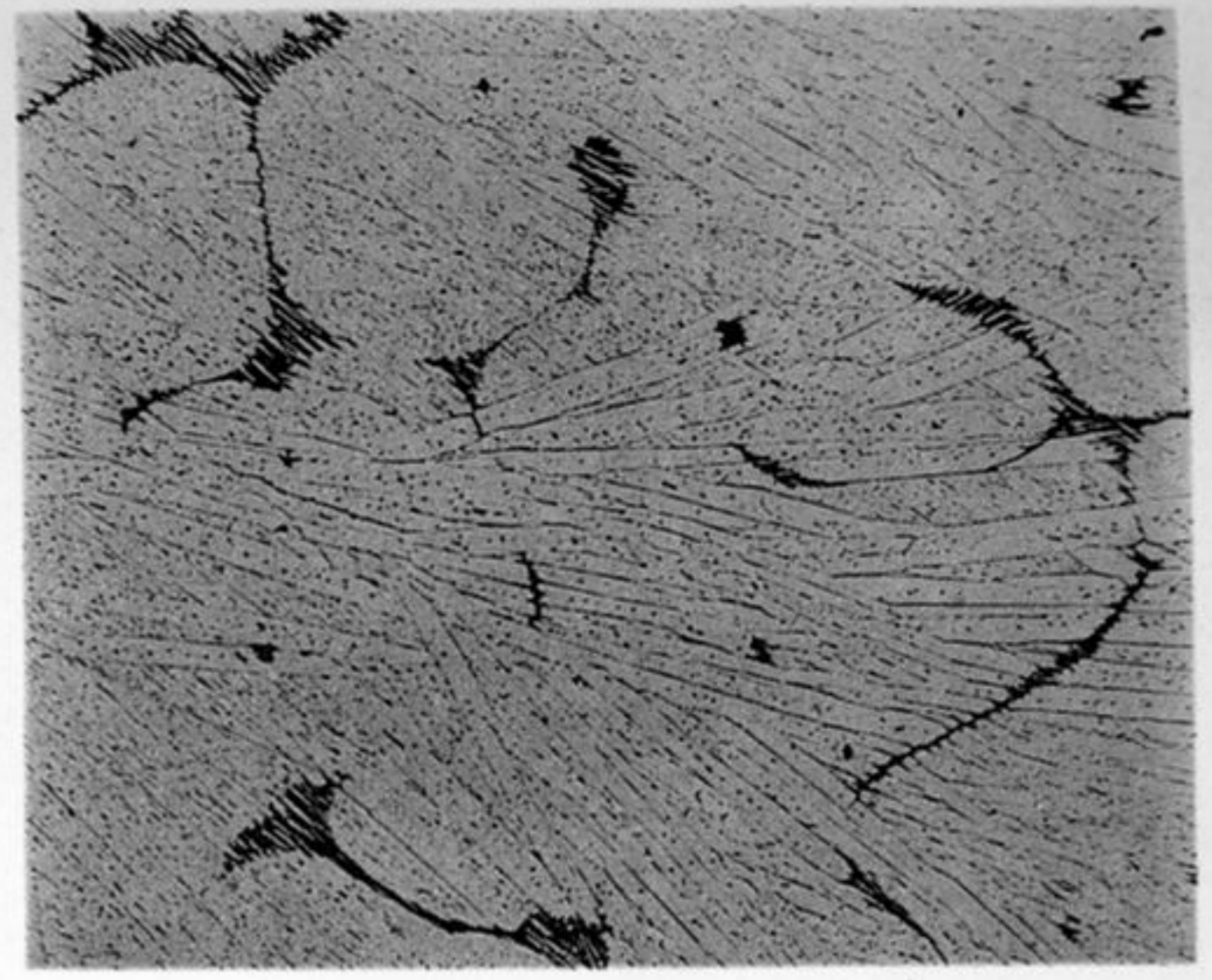
71



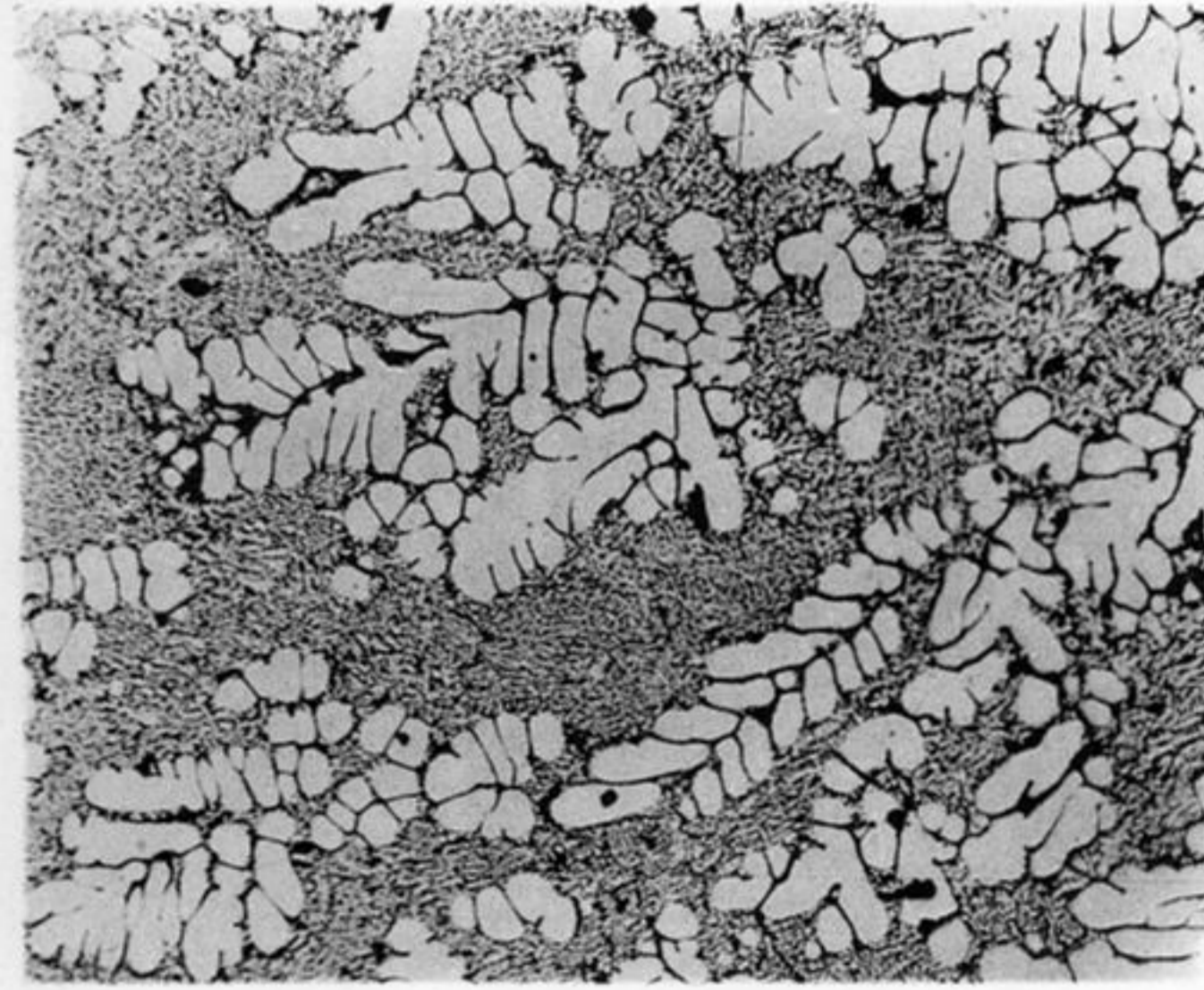
72



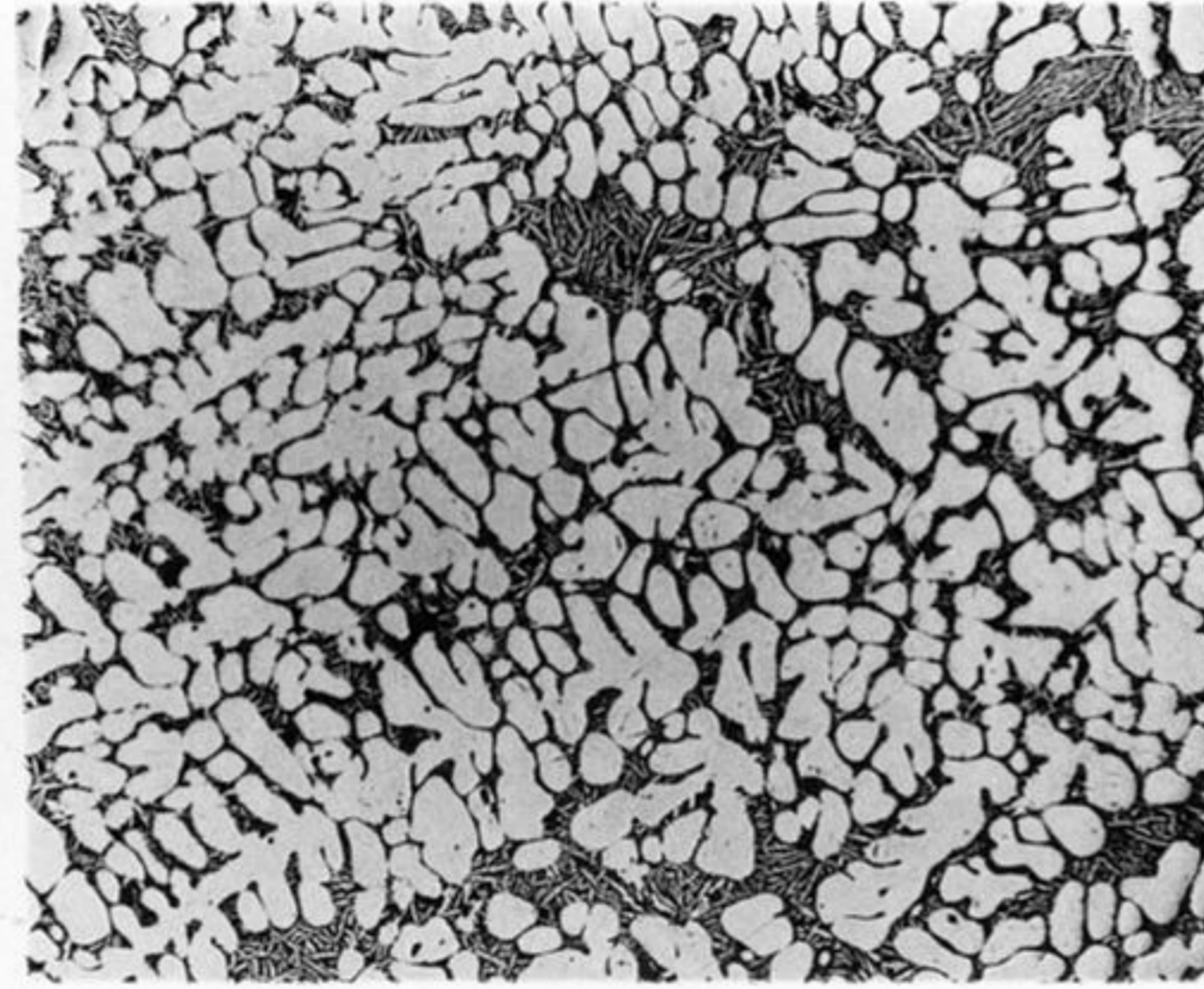
73



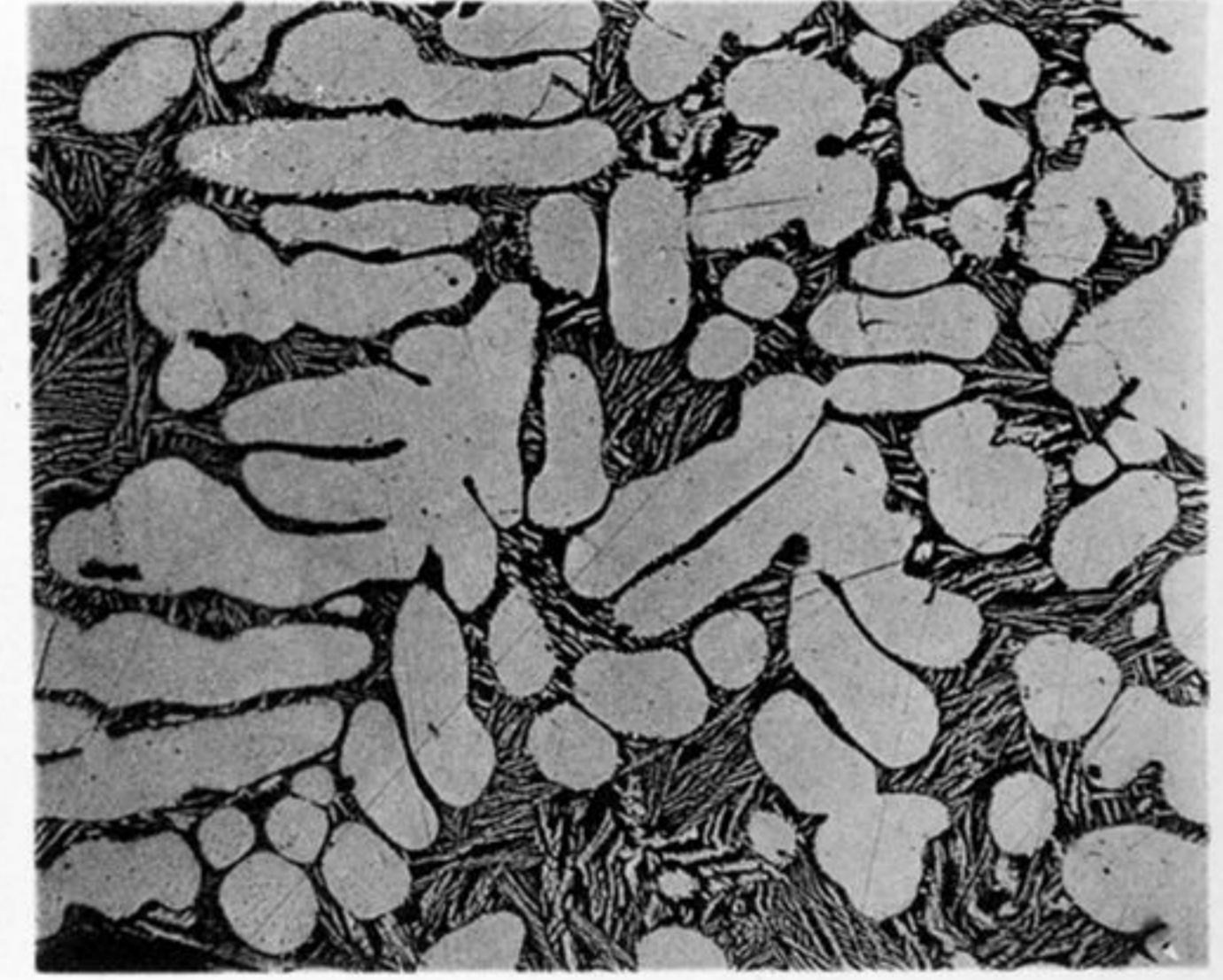
74



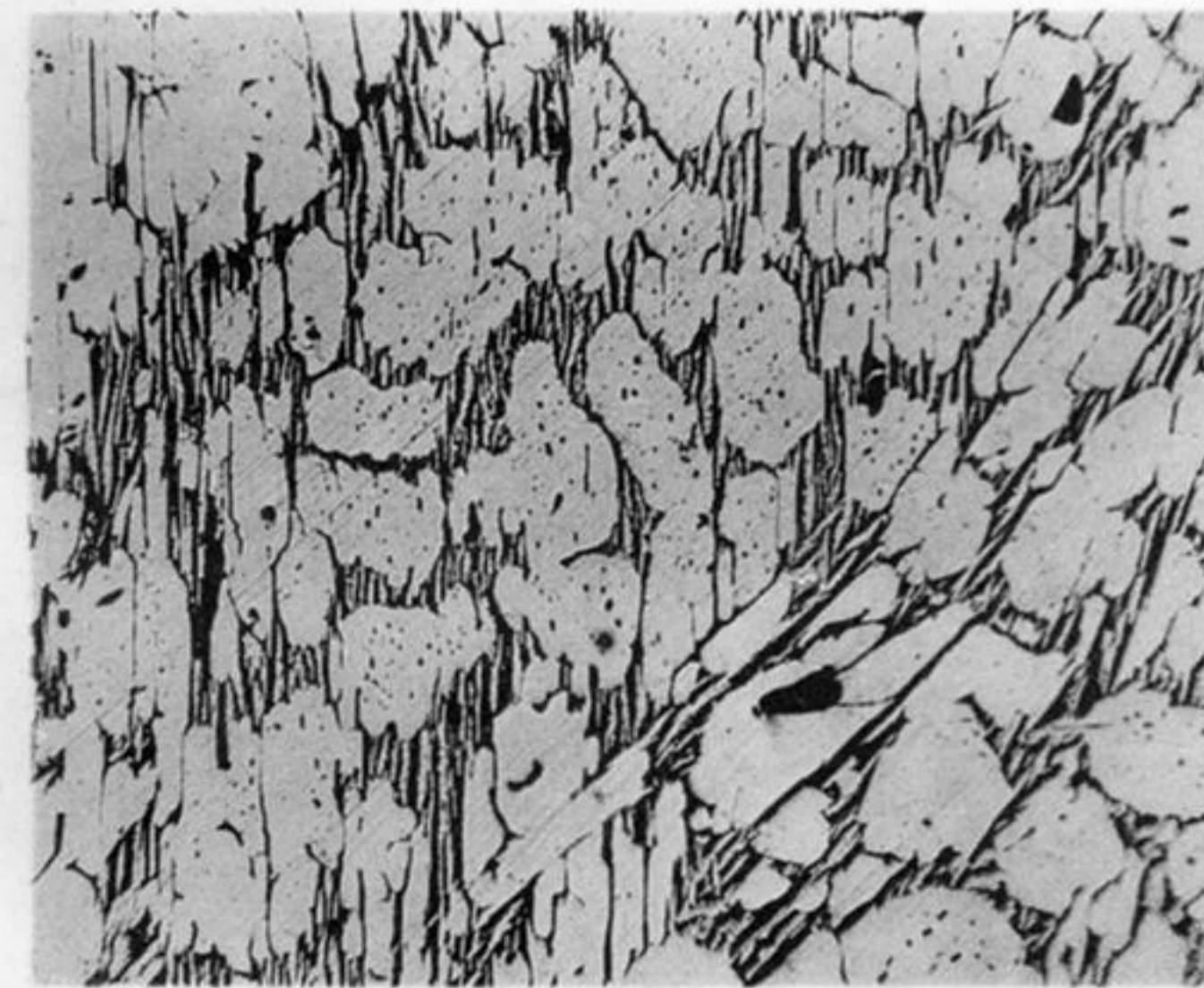
75



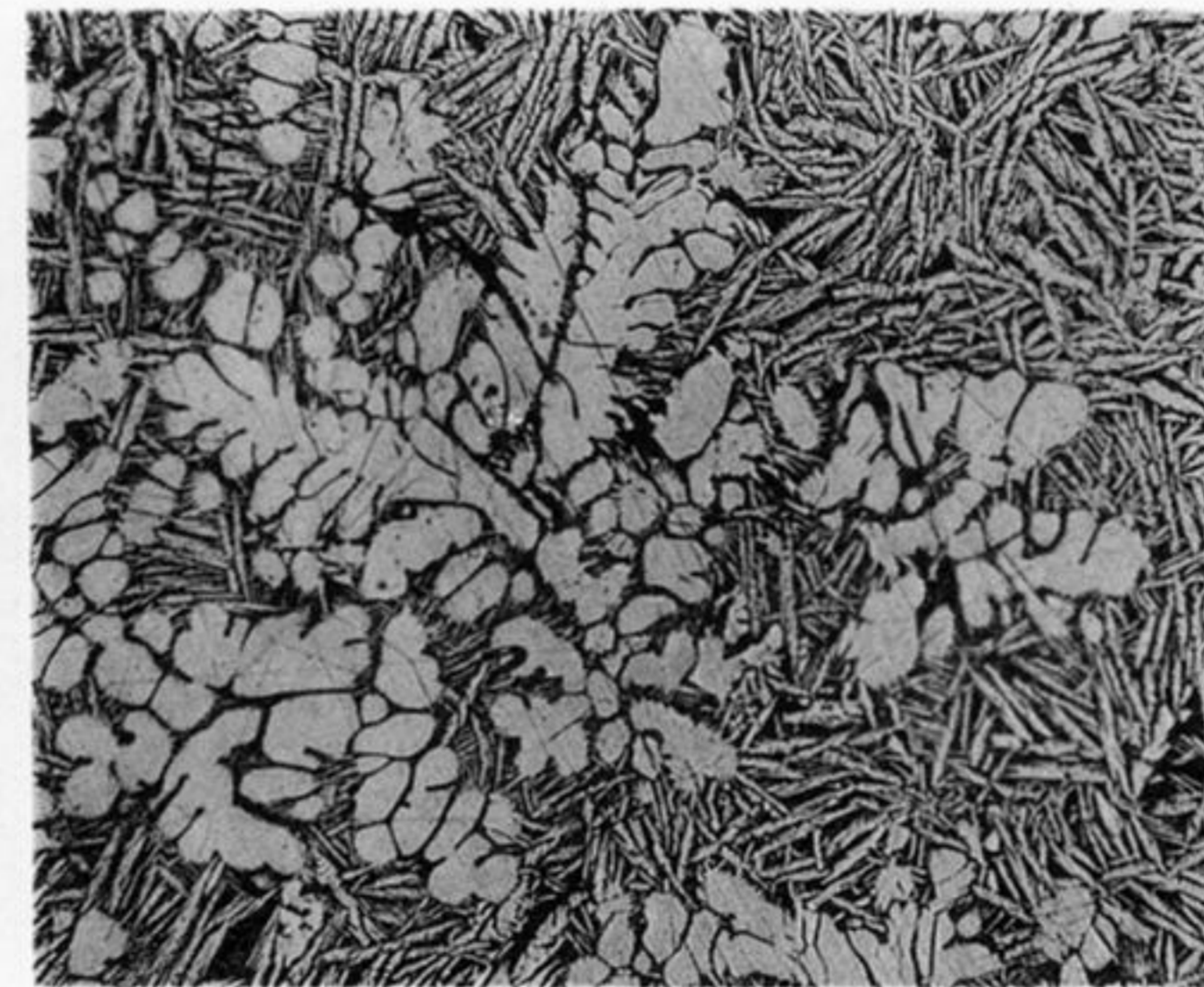
76



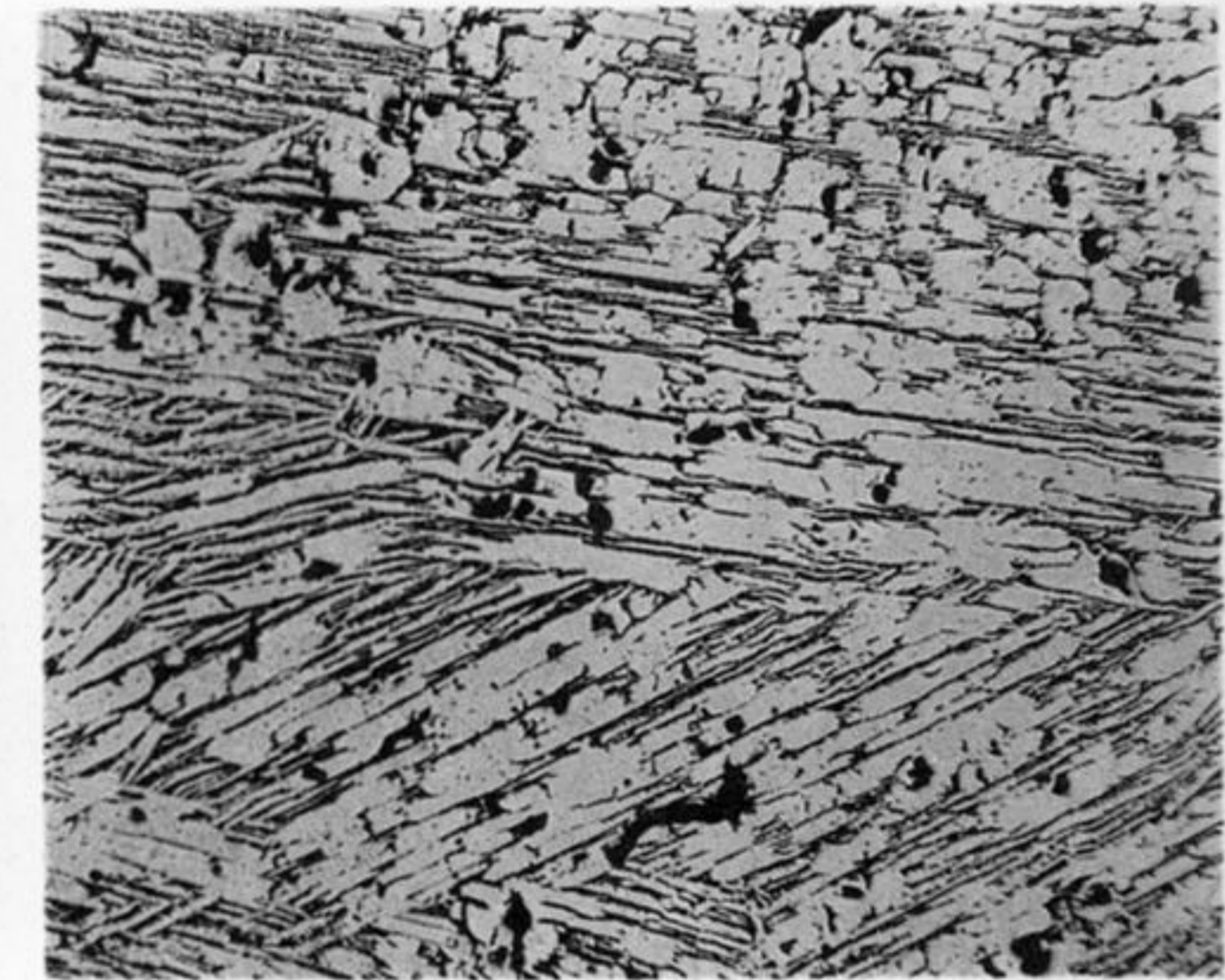
77



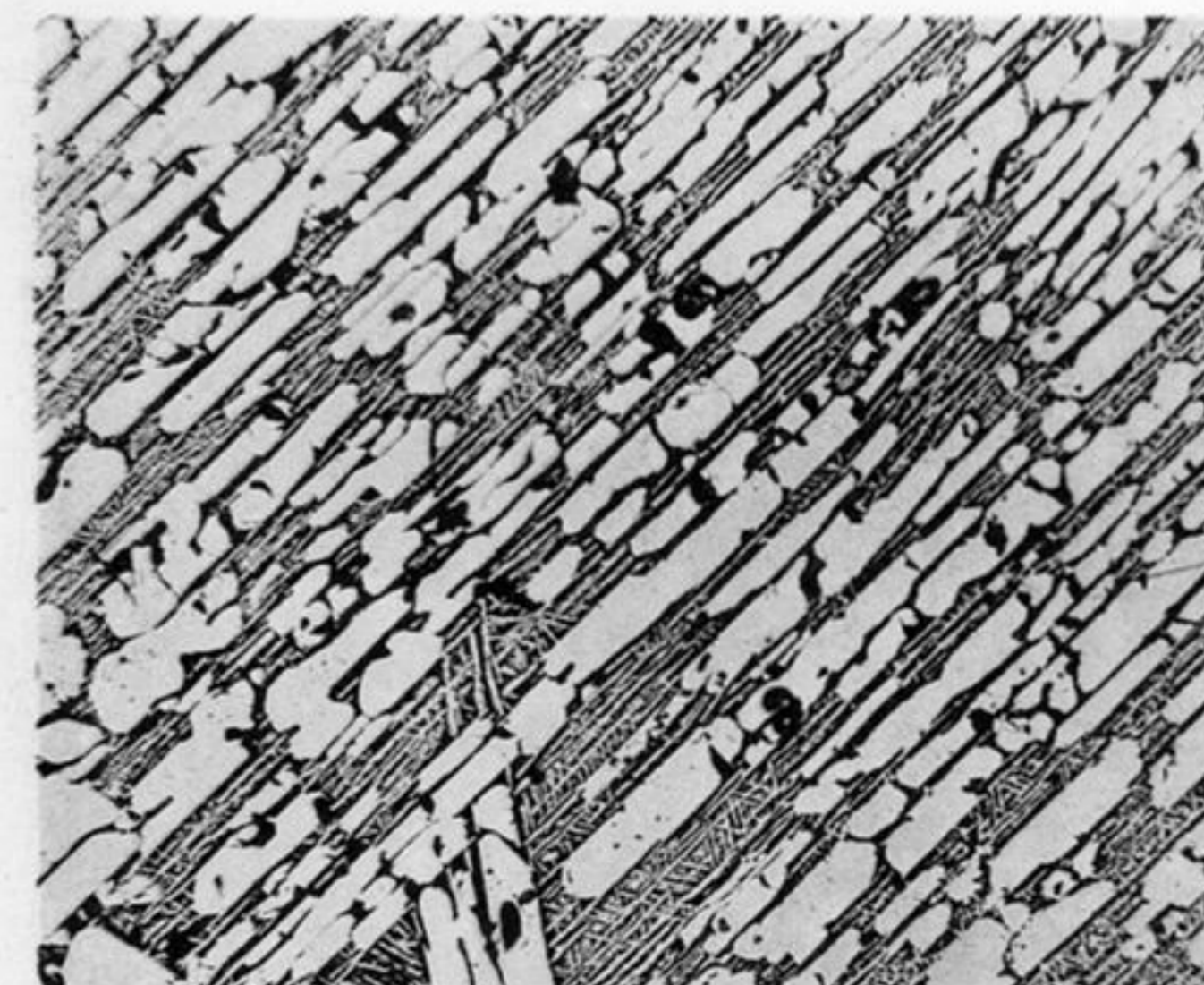
78



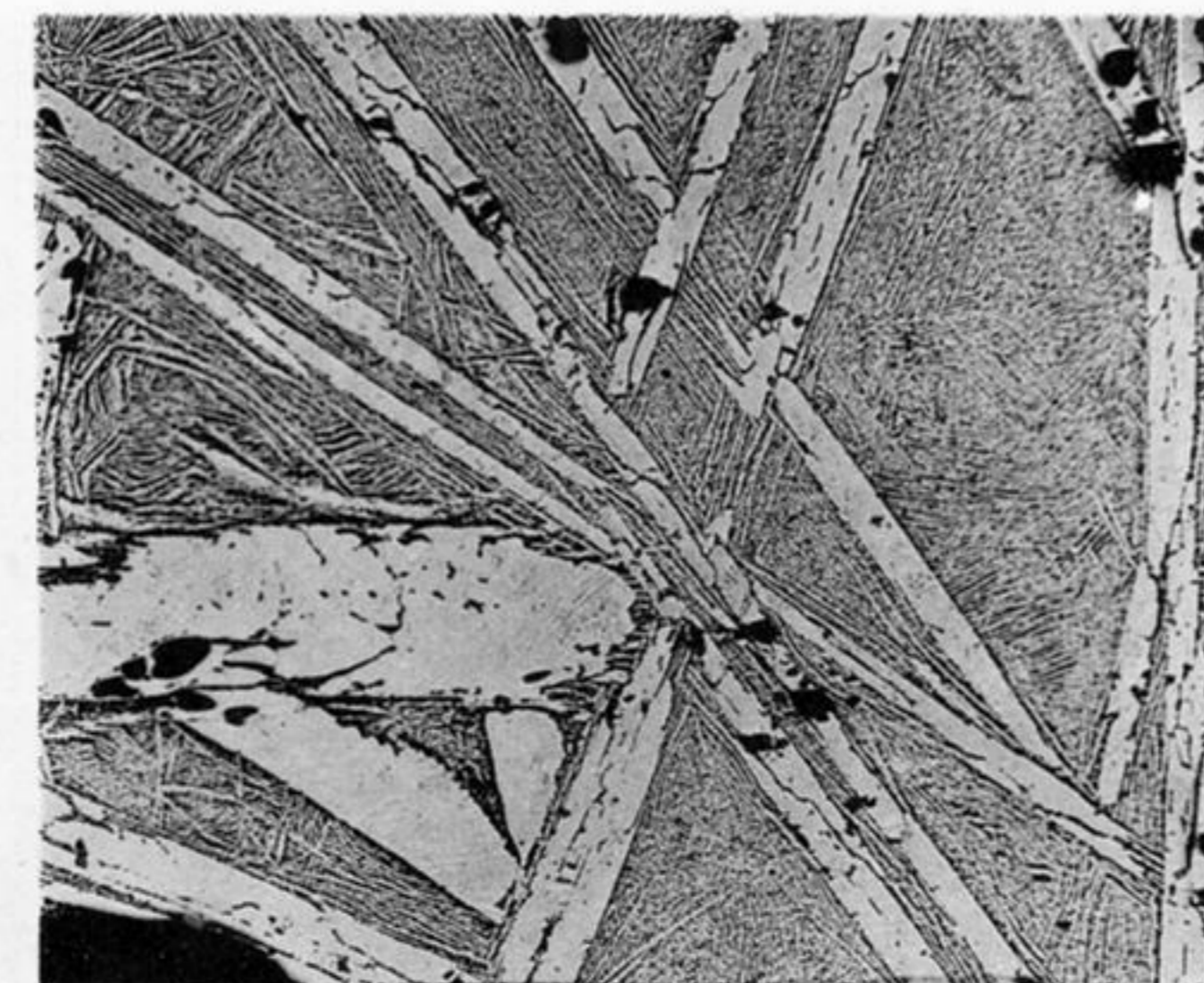
79



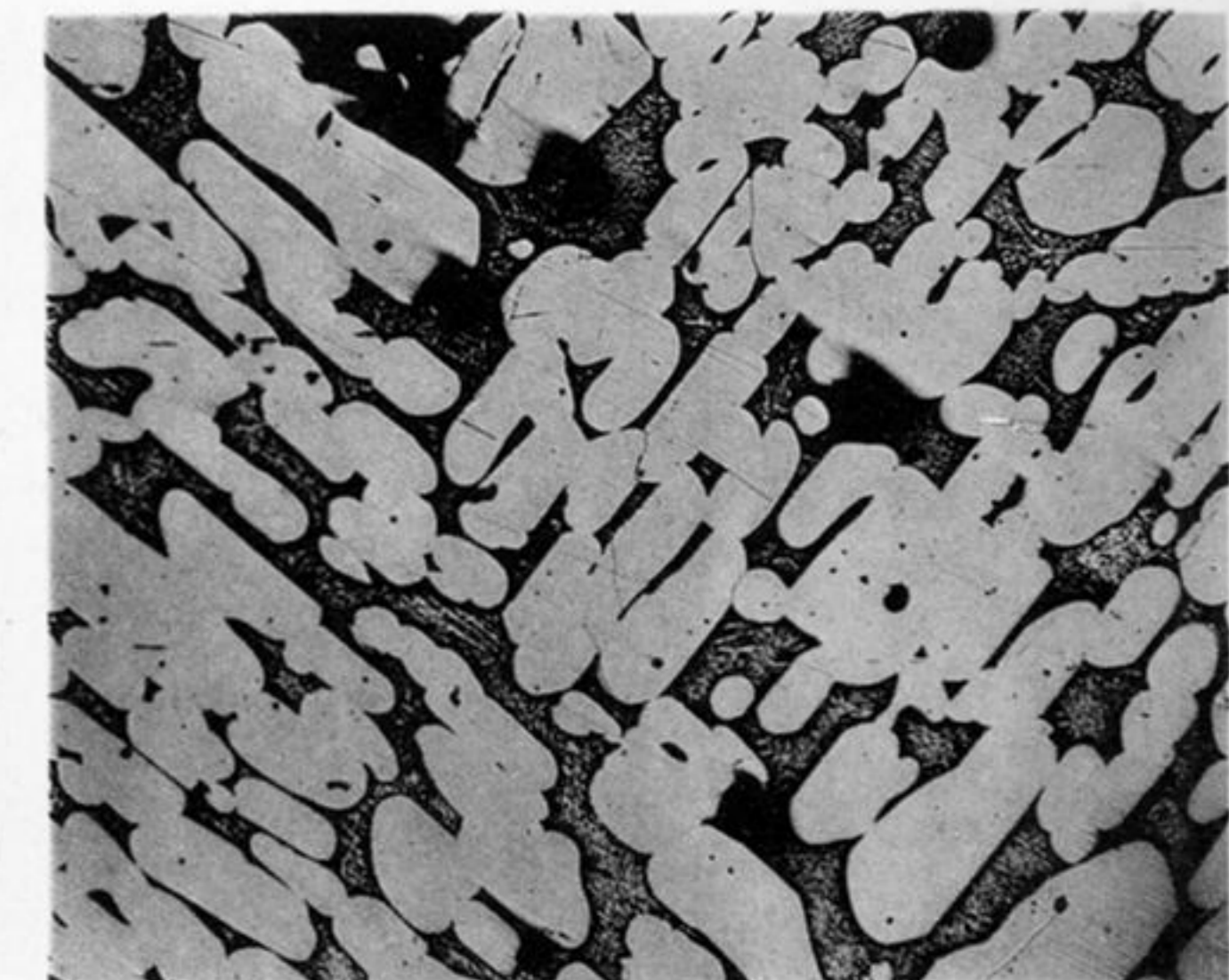
80



81



82



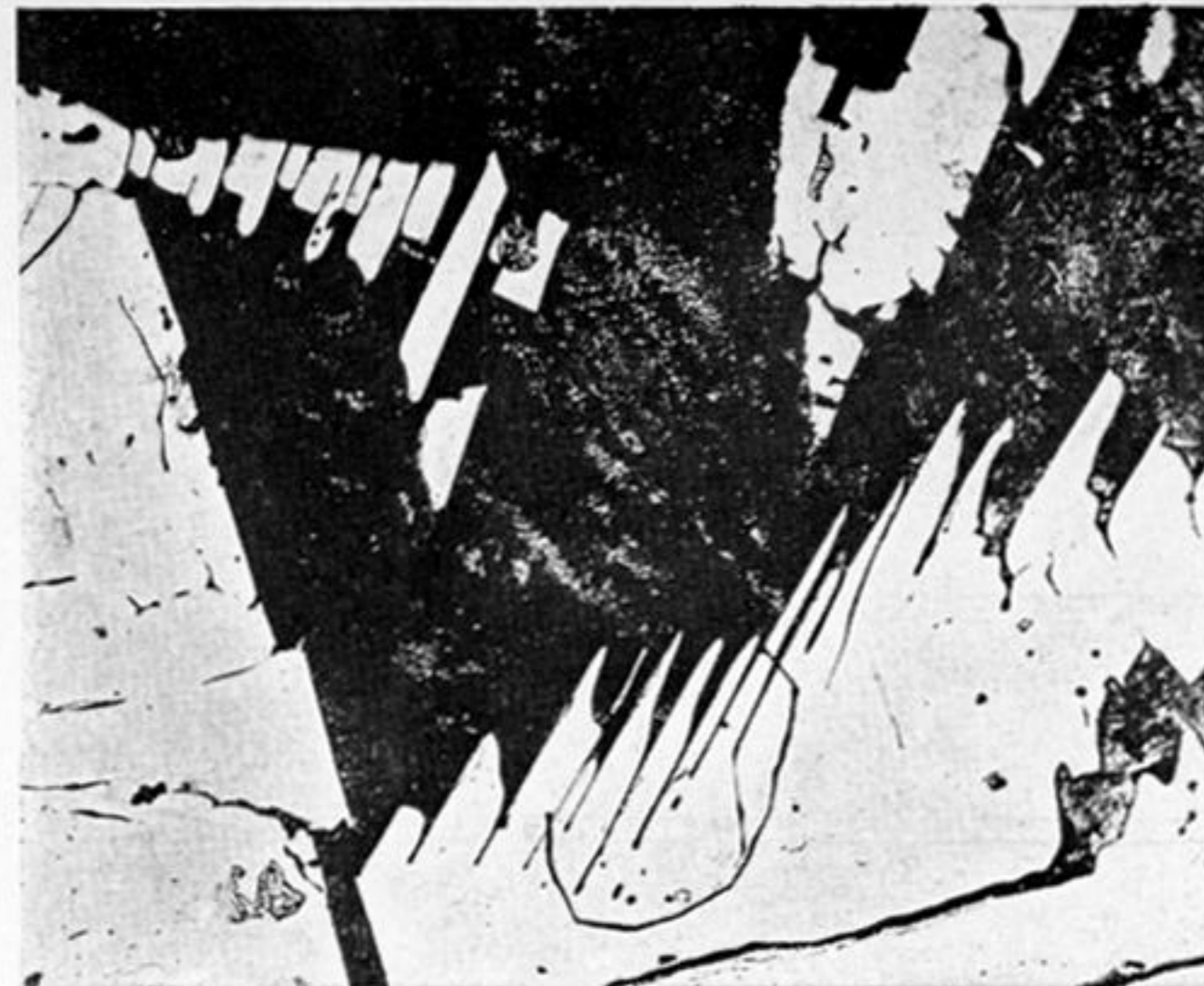
83



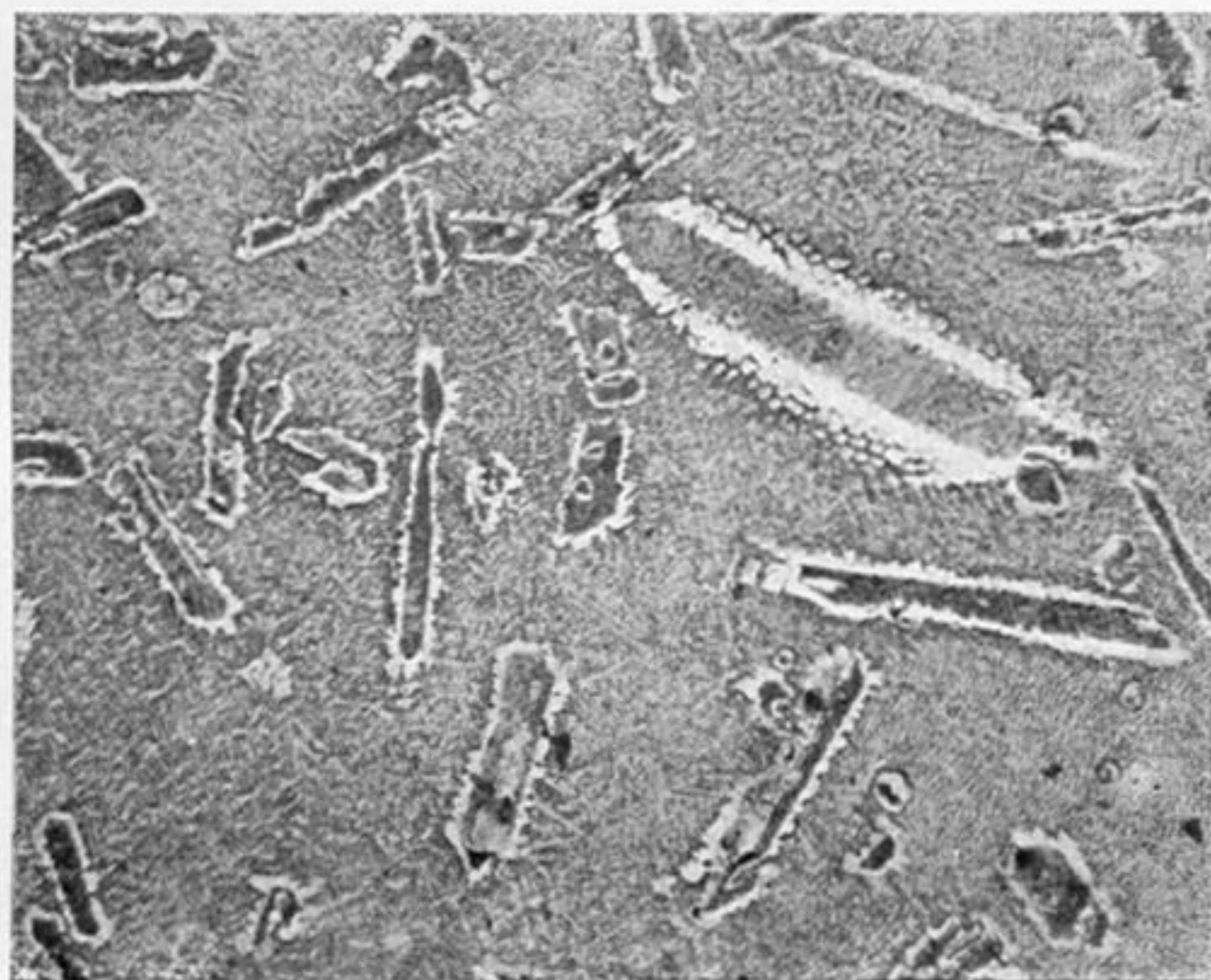
84



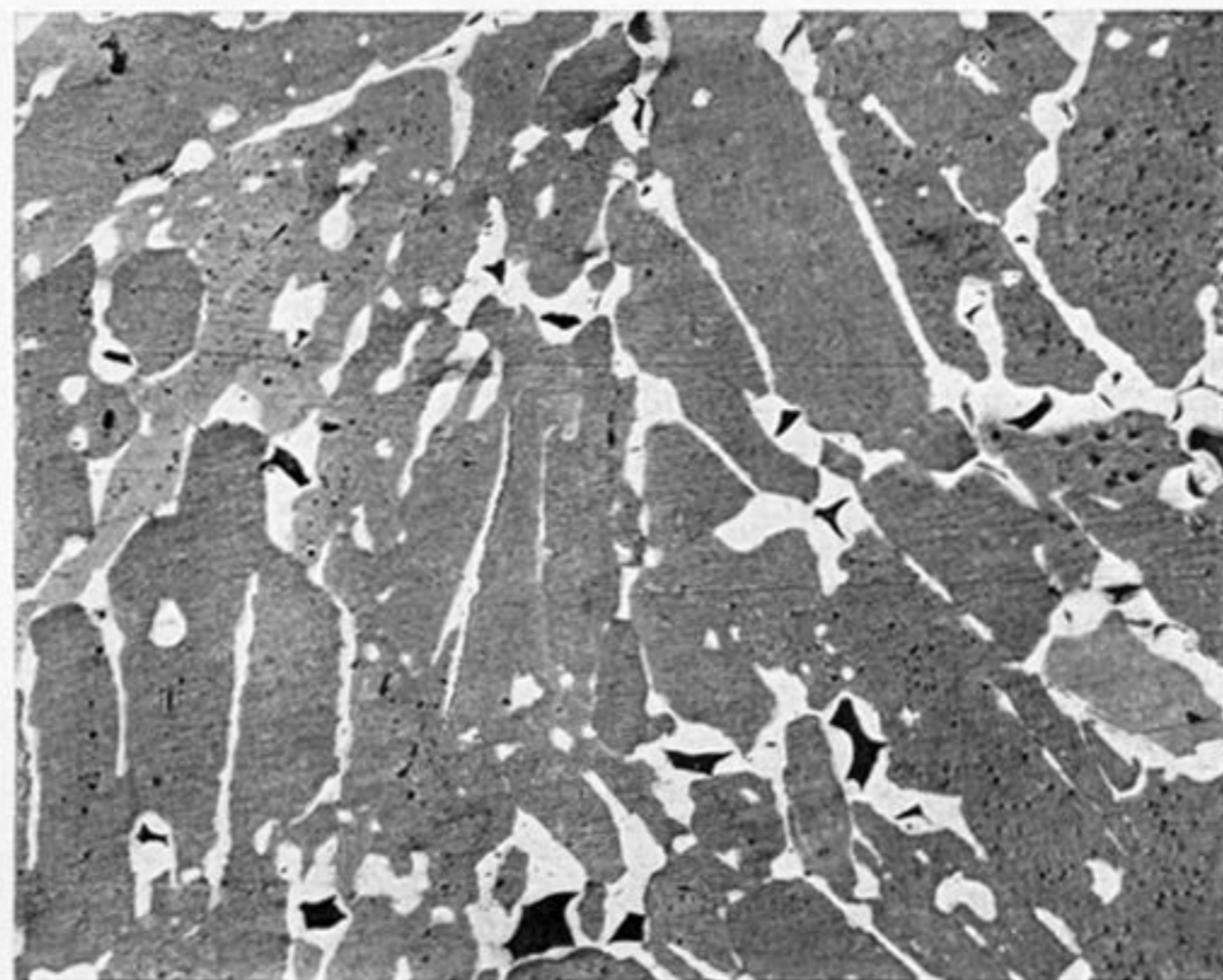
85



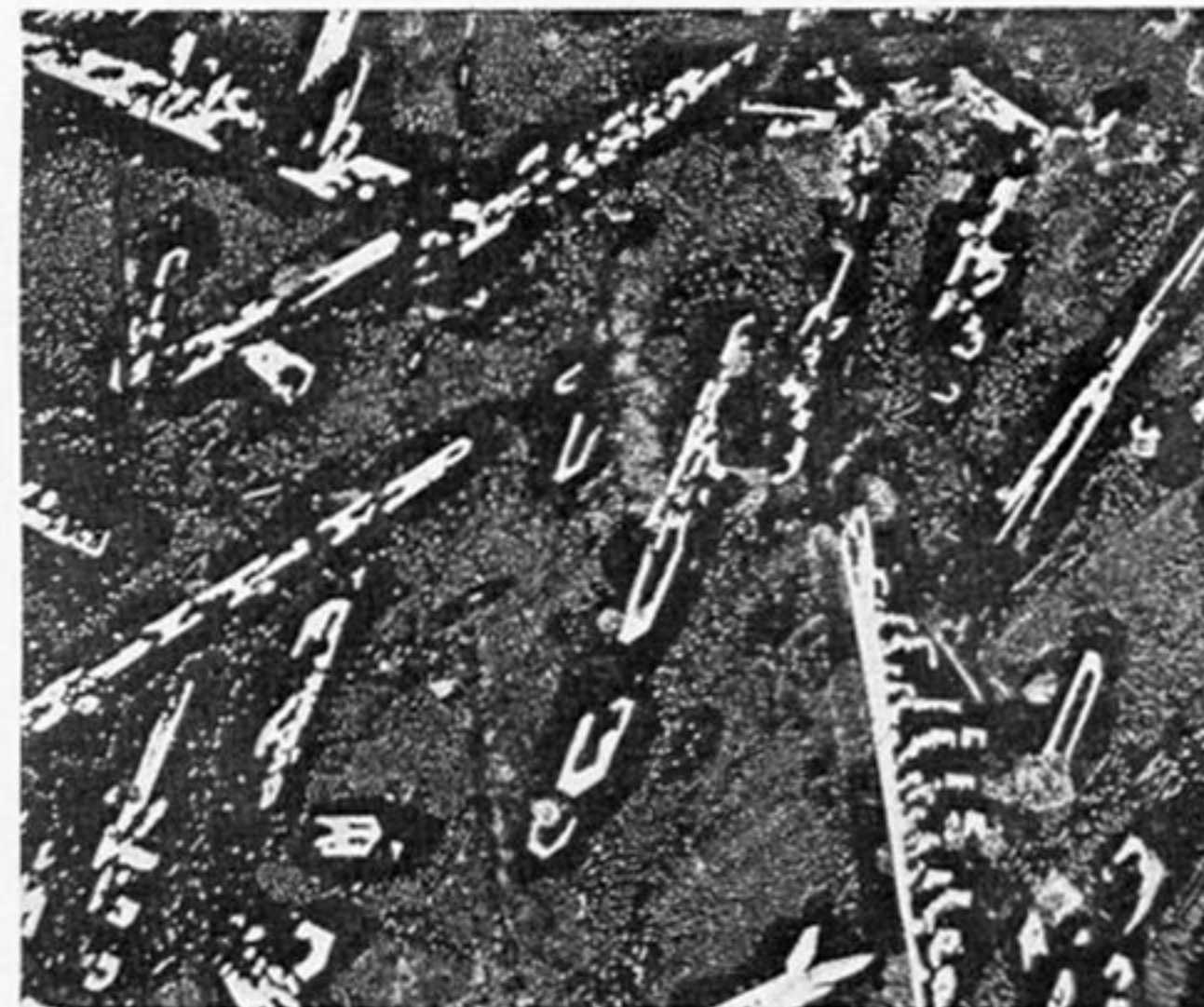
86



87



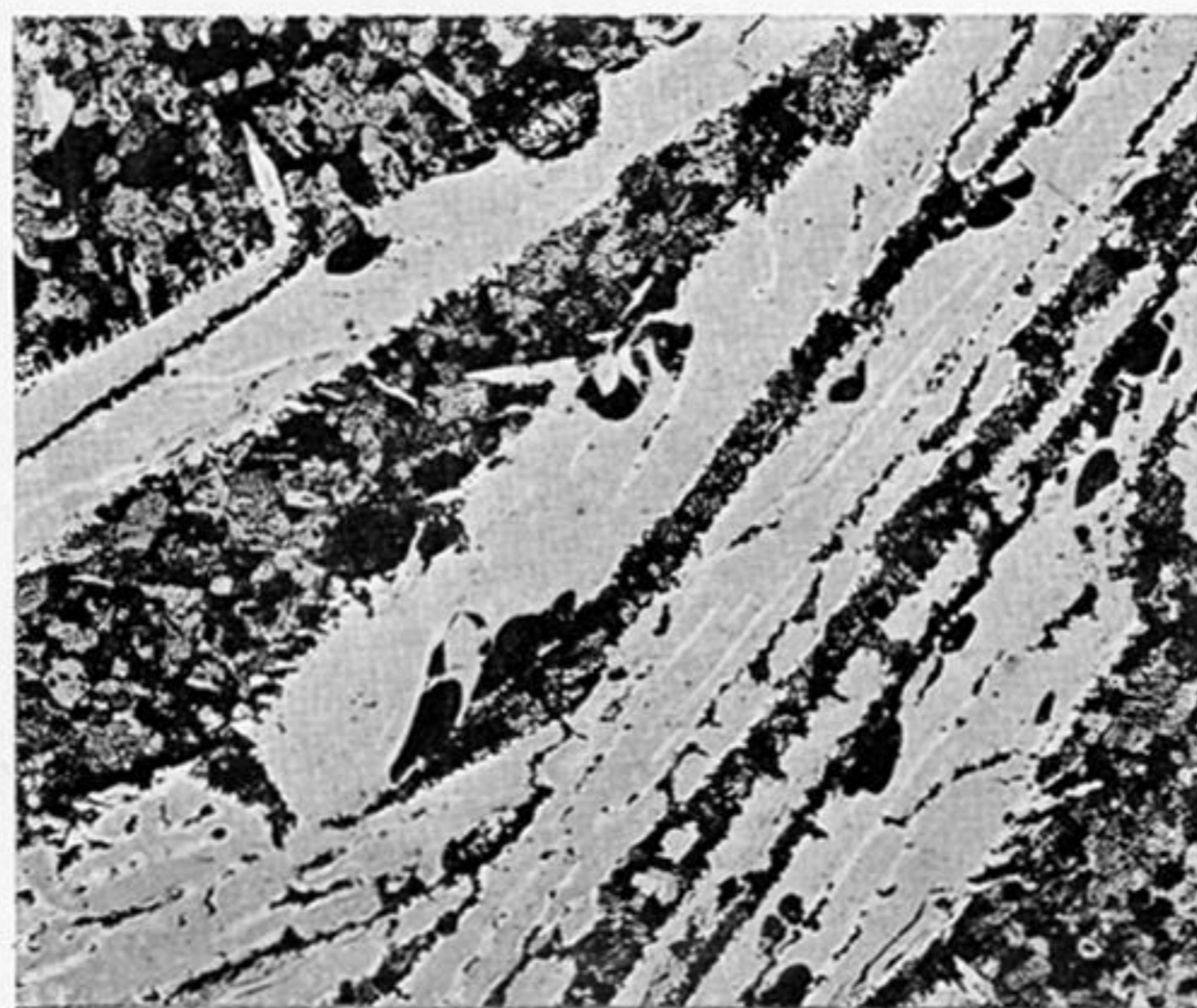
88



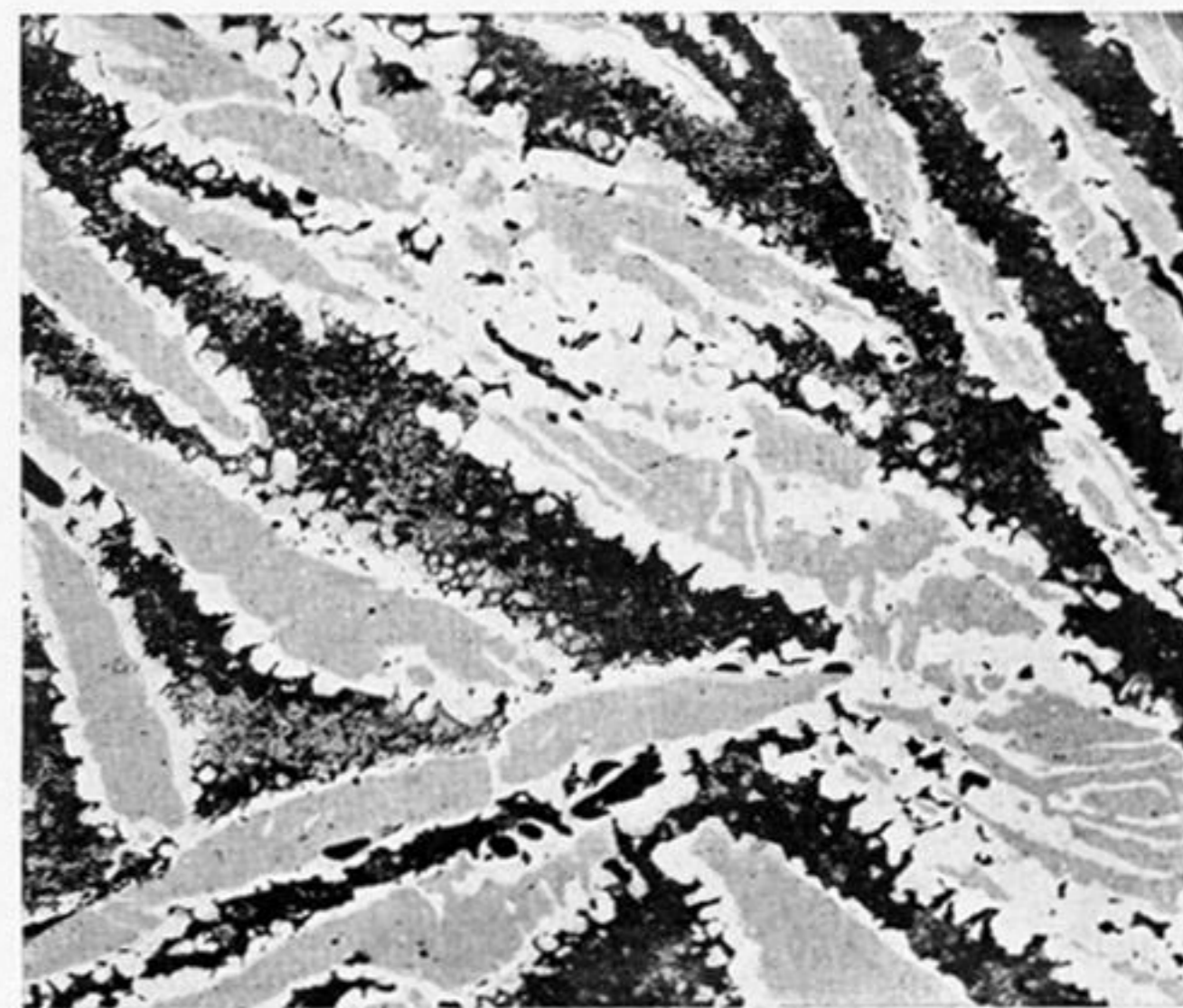
89



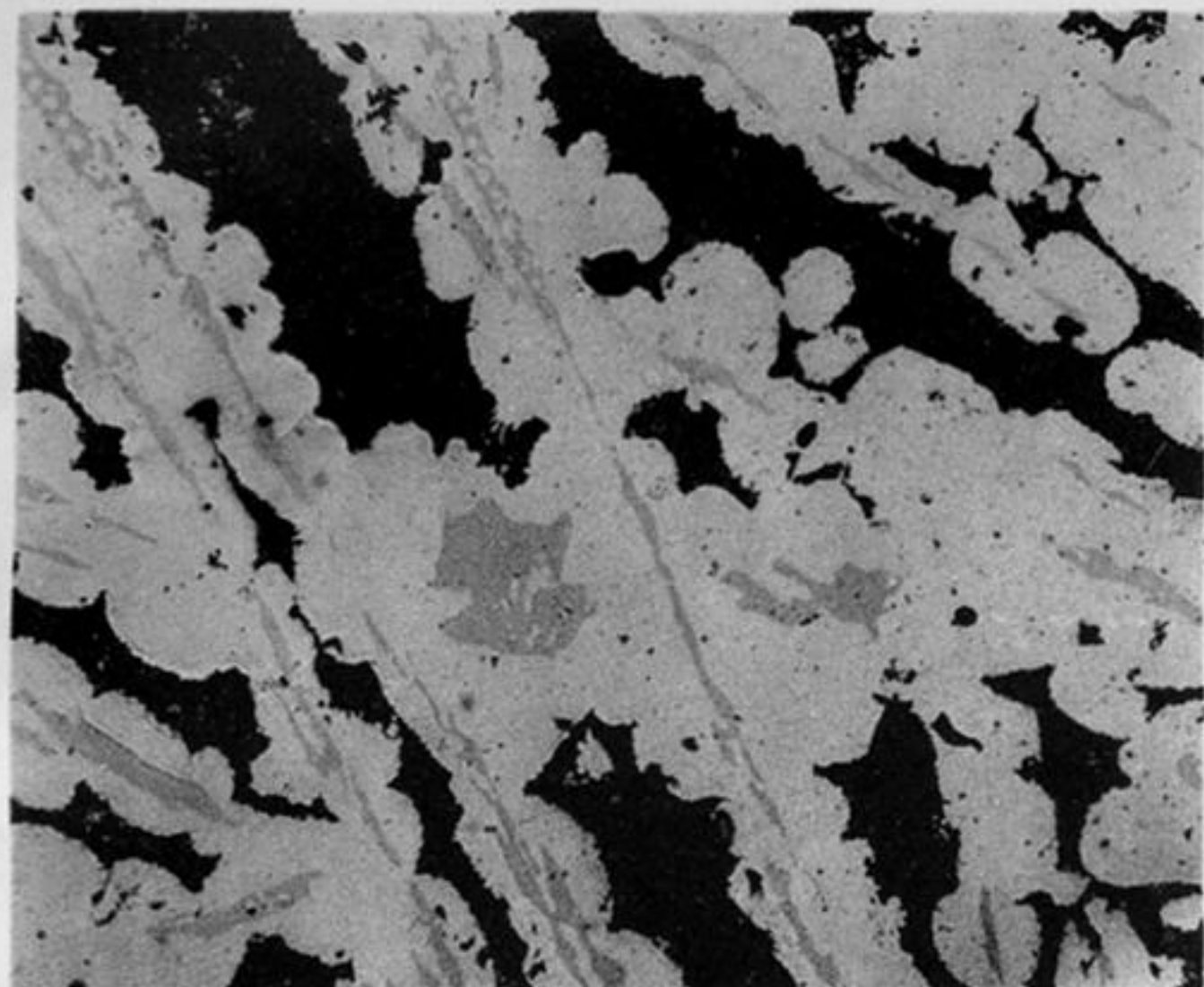
90



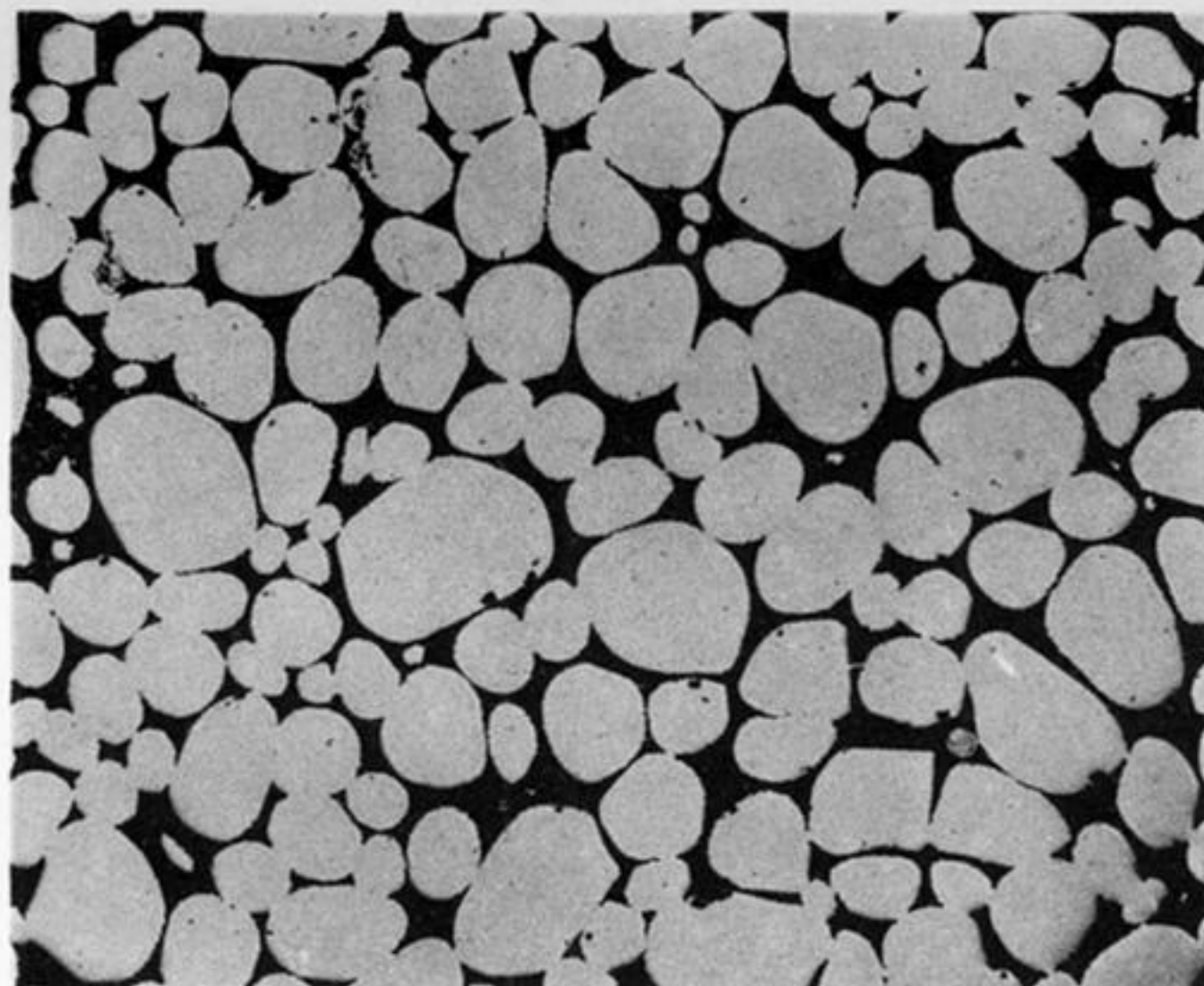
91



92



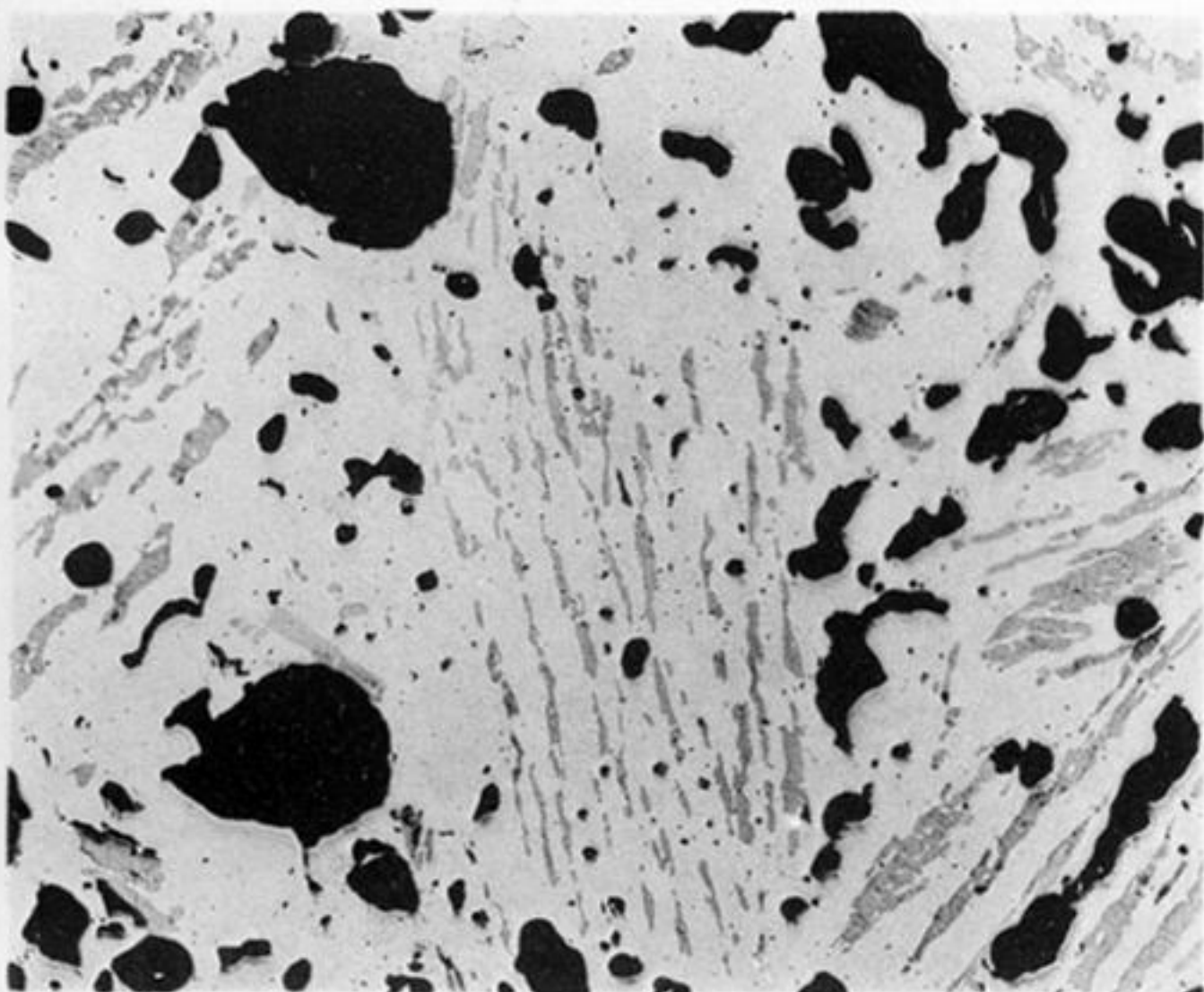
93



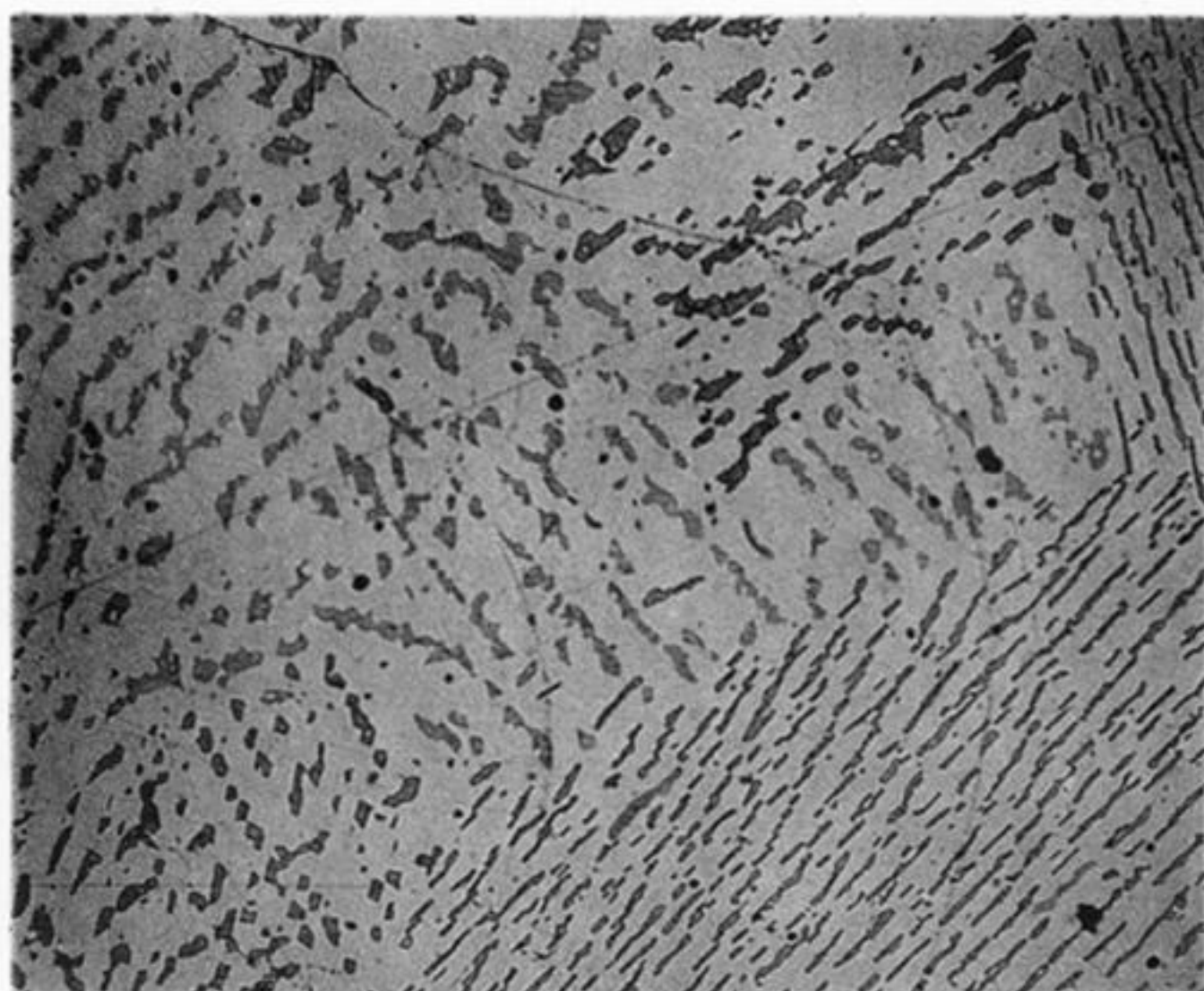
94



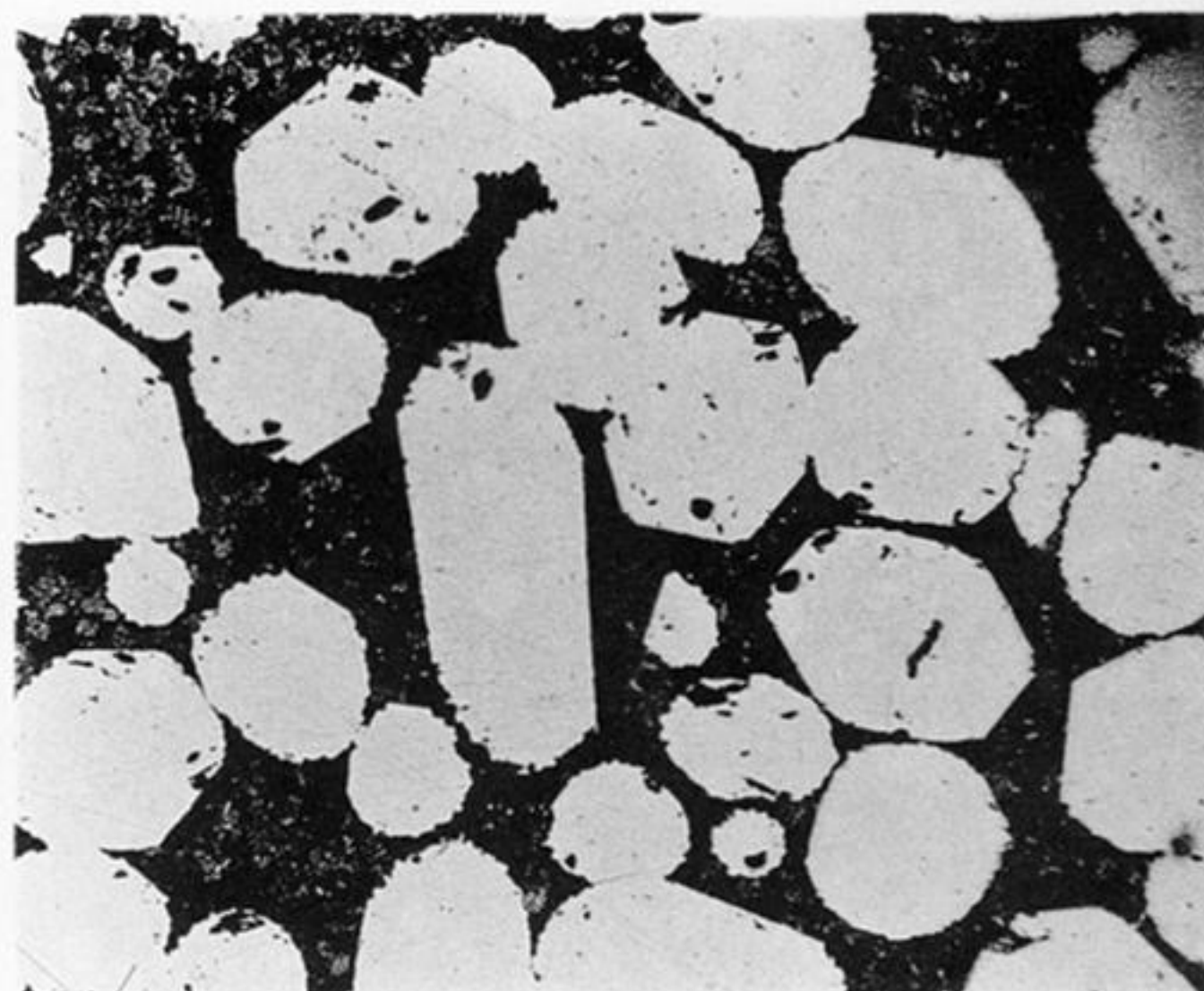
95



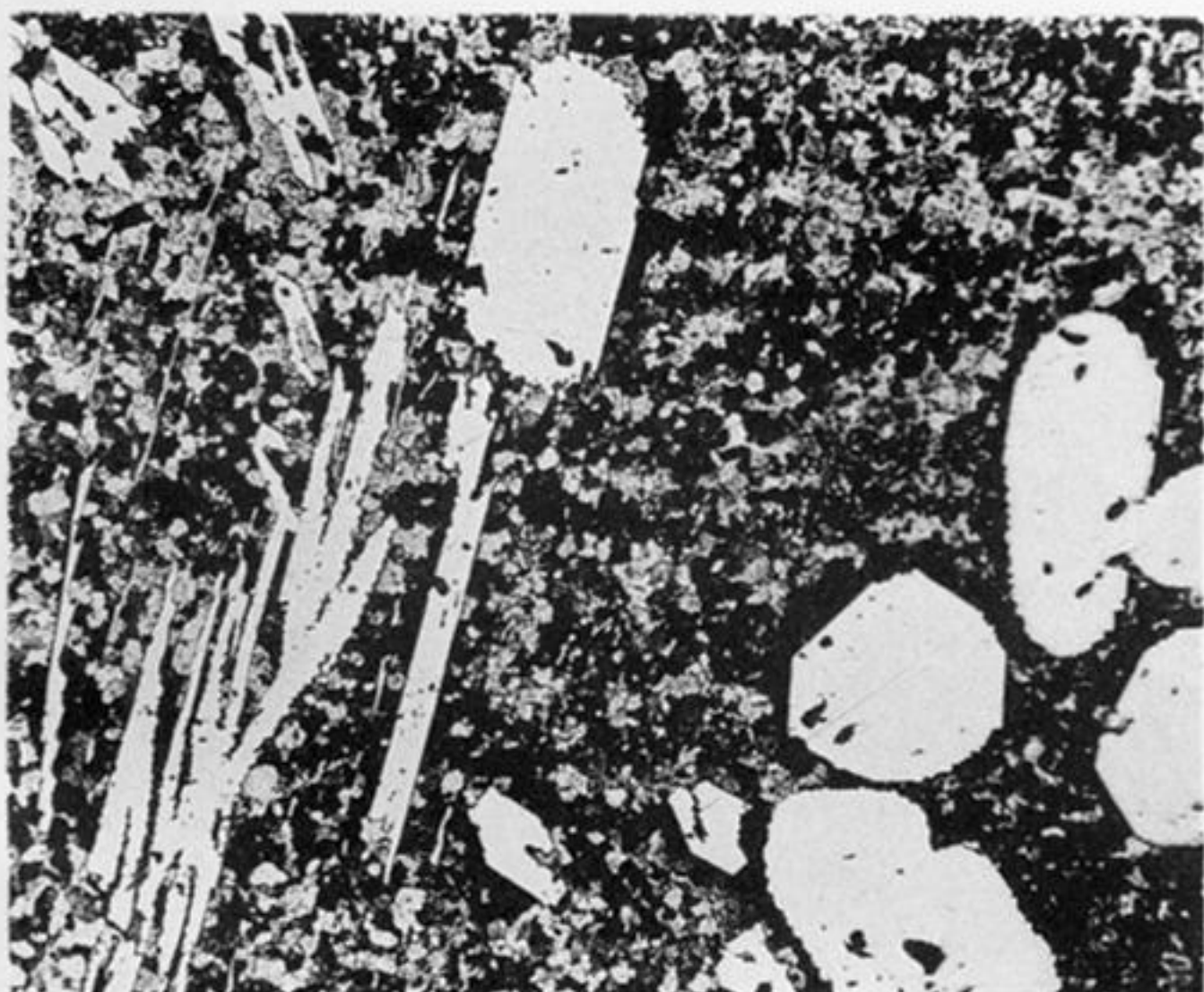
96



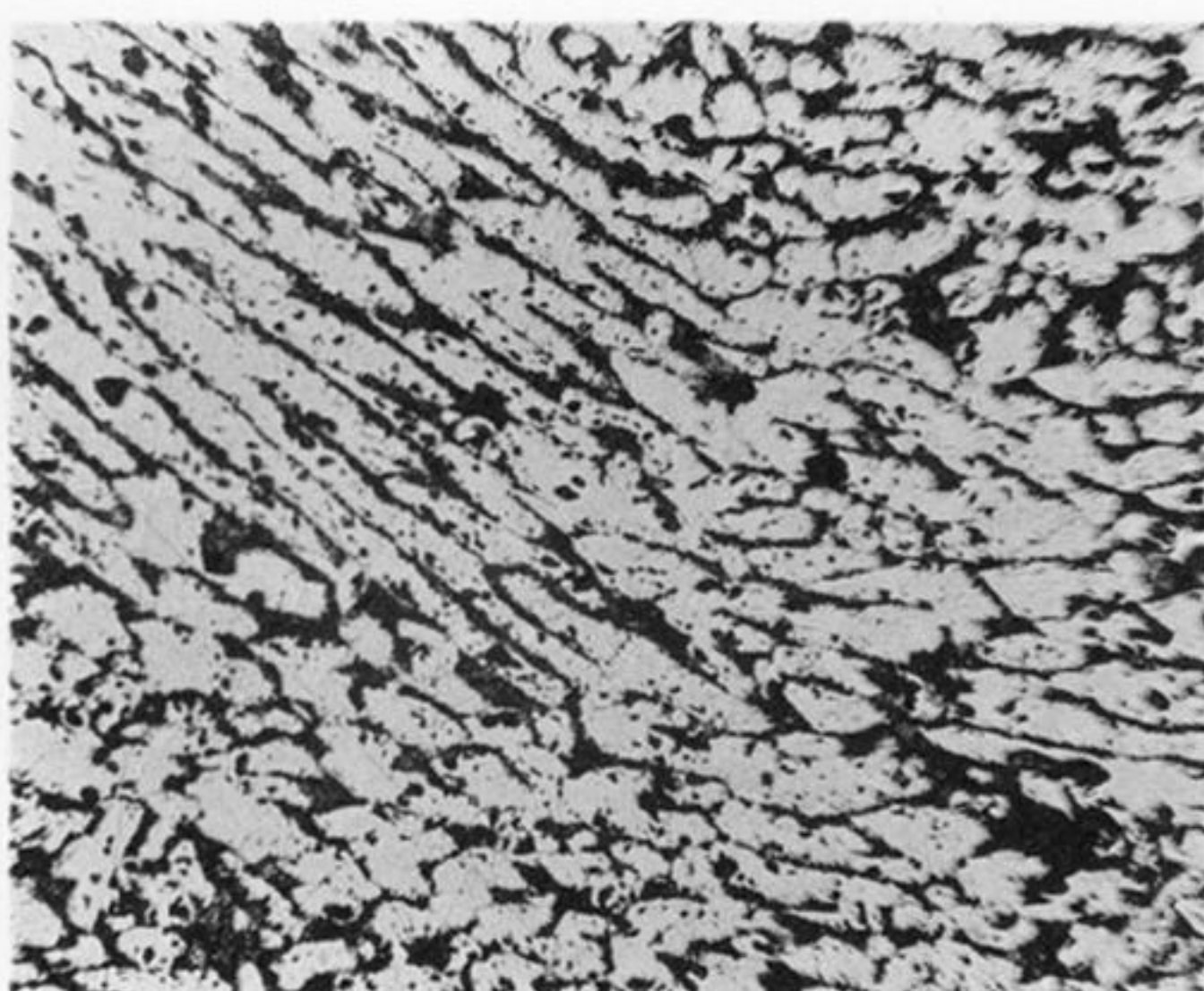
97



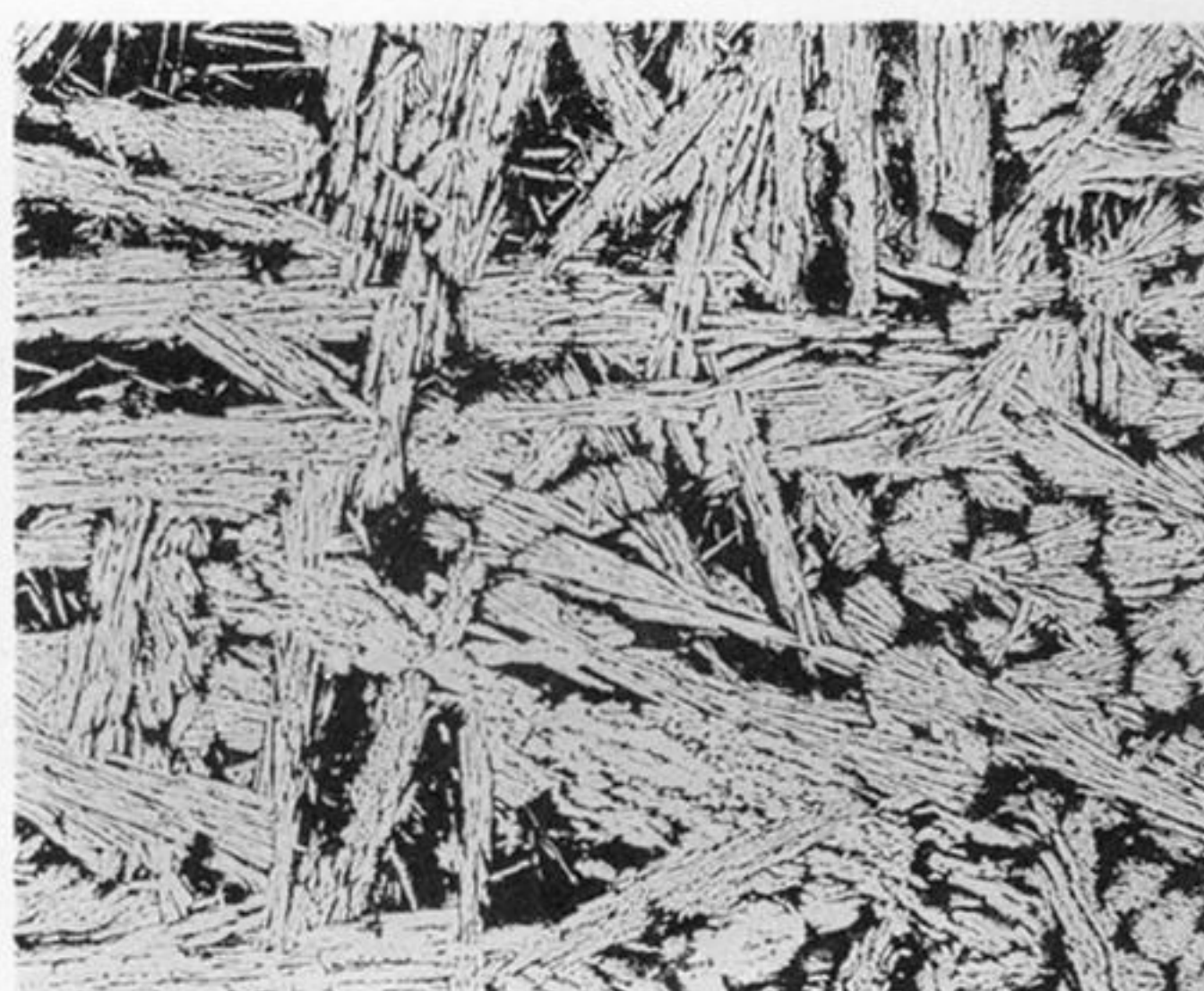
98



99

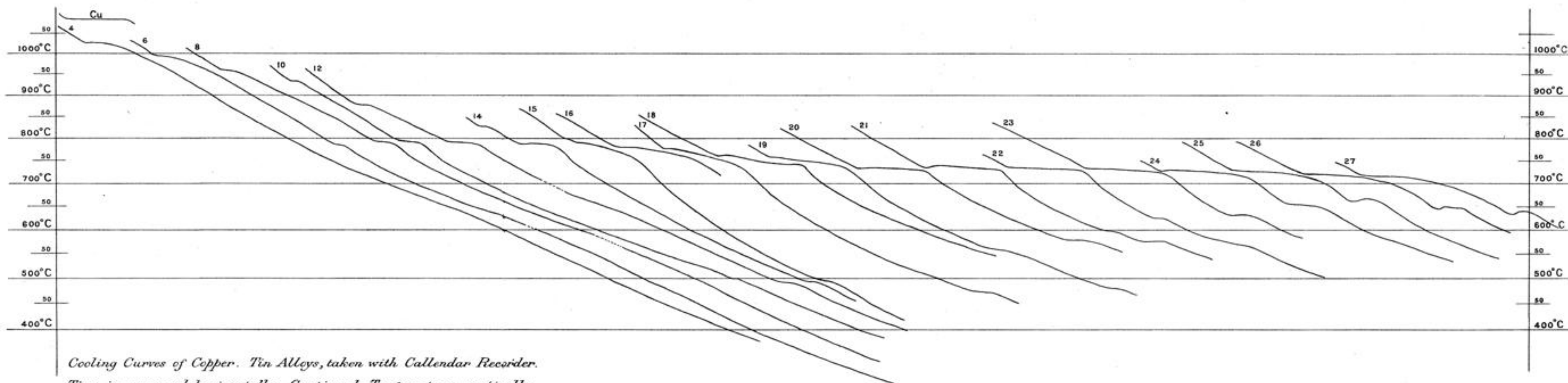


100



101

COOLING CURVES
OF
COPPER-TIN ALLOYS.



Cooling Curves of Copper. Tin Alloys, taken with Callendar Recorder.

Time is measured horizontally, Centigrade Temperature vertically.

The numerals near beginning of each Cooling Curve give Atomic Percentage of Tin in the Alloy of the Curve.

Curves are given for Alloys between Sn₄ and Sn₂₇.

Equal vertical distances correspond to equal differences of Temperature on the Platinum Scale.

