V. *Eutectic Research.—No.* 1. *The Alloys of Lead and Tin.*

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[Plates 5–9.]

The investigations described in the present paper were begun in pursuance of a scheme for the systematic investigation of the constitution and properties of eutectic alloys. The first steps in such an investigation naturally consist in the preparation of some samples of typical eutectic bodies in a state approaching purity, followed by the determination of their chemical composition and constitution. Since a large number of systems of binary alloys have been closely studied and diagrams claiming to set forth their equilibrium conditions have been published, it was thought at the outset that there would be no difficulty in finding a number of typical eutectic alloys whose chemical composition was accurately known and whose constitution could be deduced from the corresponding equilibrium diagrams. The eutectic of the lead-tin series was chosen as a suitable example for early study partly because the alloys of this series are very easily prepared and manipulated, but principally because this series has hitherto been regarded as the typical example of the simplest class of binary alloys, viz., those in which the two metals are mutually insoluble in the solid state.

In the preparation of the eutectic alloy of lead and tin on the basis of the data given by Roberts-Austen* it was found that the results of the present experiments did not agree well with the data given by that author. Thus, while Roberts-Austen gives the composition of the eutectic alloy as approximately 31 per cent. of lead and 69 per cent. of tin, the present investigation shows the composition of this alloy to be very nearly 37 per cent. of lead and 63 per cent. of tin. Further, the diagram given by Roberts-Austen indicates that solid lead and tin are nearly mutually insoluble in the solid state, or, in other words, that the eutectic alloy is present in alloys quite near the two ends of the series. As regards the lead end of the series, such serious

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[*] Roberts-Austen, 'Fourth Report to the Alloys Research Committee, Inst. Mech. Eng., 1897.'

discrepancies from these views were found when the attempt was made to verify them, that it became evident that the investigation of this point had not been pushed far enough. It has accordingly been thought desirable to undertake a complete redetermination of the equilibria of the lead-tin system with a view to placing our knowledge of the *constitution* of the eutectic on a surer footing. This task was rendered more difficult, as well as more interesting, by the discovery of a transformation which occurs in the alloys rich in lead at temperatures below that of complete solidification.

In the present paper the investigation of the equilibria of the lead-tin system will first be described, some observations on the structure and properties of the eutectic alloy of this series being subsequently given.

Constitution of the Alloys of Lead and Tin.

Preparation of the Alloys.—Chemically pure lead and tin were obtained from Messrs. Kahlbaum's London agents and on analysis proved to contain only slight traces of impurities. The alloys were prepared by weighing out, on an analytical balance, the requisite quantities of the two metals and melting them together in a suitable manner, the tin being usually melted first and the lead added to the molten tin. In all cases the temperature was kept as low as possible, except in some special experiments where the effect of exposure to high temperatures was studied with, however, only negative results. As a rule the alloys were melted in small fire-clay crucibles heated over gas burners, the metal being protected from oxidation by various means. In some cases a flux of borax and powdered charcoal was employed, while in other cases the metal was melted under oil, glass vessels being employed for the latter purpose. In some cases a very small amount of oxidation was found to occur in spite of these precautions, but the composition of the alloys has been found by analysis not to be materially affected thereby. This is shown in the tabulated results of analyses given in Table I.

TABLE I.—Calculated and Analytically Determined Composition of Alloys.

Calculated.	Determined.	Calculated.	Determined.
5 per cent. Sn.	5·30 per cent. Sn.	50 per cent. Sn.	50·13 per cent. Sn.
10 „ „	10·29 „ „	55 „ „	55·19 „ „
15 „ „	15·31 „ „	60 „ „	60·02 „ „
20 „ „	20·26 „ „	65 „ „	65·12 „ „
25 „ „	25·15 „ „	70 „ „	70·10 „ „
30 „ „	30·28 „ „	75 „ „	75·23 „ „
35 „ „	35·07 „ „	80 „ „	80·08 „ „
40 „ „	40·10 „ „	85 „ „	85·02 „ „
45 „ „	45·28 „ „	90 „ „	90·11 „ „
63 „ „	63·06 „ „	95 „ „	95·07 „ „

It will be seen that the largest difference between calculated and analytically determined composition never exceeds 0·3 per cent., and this degree of accuracy is adequate for the purposes of these experiments as a whole. Those alloys whose composition is required to be more accurately known have been analysed.

Experimental Methods.—The "thermal analysis" of the alloys was carried out by means of cooling-curves taken both by the "inverse-rate" and the differential methods. Thermocouples of platinum and platinum-iridium were used for the most part, although for some special purposes, notably the cooling- and heating-curves at very low temperatures, a Constantan-iron couple was used. The indications of the thermocouples were observed by means of the delicate potentiometer installed at the Laboratory. The time observations in the case of the inverse-rate curves were made with the aid of a chronograph indicating seconds by means of an electrical connexion with the standard clock of the Laboratory. The differential curves were obtained by observations of the deflection of the differential galvanometer on the same scale as that used for the galvanometer connected with the potentiometer already referred to. The details of this apparatus and of the method of using it have been published previously,* so that no further reference is required here. The thermocouples were all carefully calibrated at frequent intervals during the progress of the research, both by comparison with the standard couples of the Laboratory and by direct determination of well-known fixed points, viz., the boiling-point of water and the freezing-points of pure tin and pure lead, the former being taken as 232° C. and the latter as 328° C. Graphic interpolation on large-scale curves was used to obtain the values of intermediate points on the thermocouple scale. These repeated calibrations gave remarkably constant results, and the indications of the platinum couples may therefore be regarded as accurate to within 0·8 of a degree, although it must be admitted that a slightly greater error may be introduced by the small difference of temperature which is liable to exist between a thermocouple and the mass of metal in which it is immersed.

The microscopic examination of alloys containing more than 30 per cent. of tin presented no serious difficulty, as it was found possible to polish these alloys by the ordinary methods used for the preparation of soft metals. Alloys richer in lead, however, proved intractable until special means were employed for polishing them. These special means, adopted on the advice of M. F. OSMOND, consisted in the preparation of laevigated oxide of chromium in the manner described by LE CHATELIER.† When the finer grades of this material are used sparingly on "beaver-cloth" discs driven at moderate speeds, it is found possible to prepare polished surfaces of the alloys close to the lead end of the series for microscopic

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* CARPENTER and KEELING, "The Range of Solidification and Critical Ranges of Iron-Carbon Alloys," 'Journal of the Iron and Steel Institute,' vol. i.; also STANSFIELD, 'Phil. Mag.,' vol. xlvi., pp. 59–82.

† LE CHATELIER, 'Metallographist,' vol. 4, January, 1901.

examination. When these alloys are polished, the lead, or lead-rich constituent, assumes a dark tint, no doubt owing to slight surface oxidation, while any free tin present remains bright. When necessary, the contrast thus produced can be heightened by etching. These alloys are best etched by the aid of a weak electric current passed through a saturated solution of lead nitrate. Nitric acid can also be used as an etching agent, but it has the disadvantage that at times it is apt to darken the tin as well as the lead. The opening up of the alloys rich in lead to microscopic examination, which has thus become possible, has, it is believed, considerably increased the certainty of the results indicated by the pyrometric study of the alloys.

Experimental Results.

The Cooling-curves of the Alloys.—Five series of cooling-curves were taken, many of the individual curves being, however, repeated several times under varying conditions. Three of these series are inverse-rate curves, while two are differential. The inverse-rate curves of Series A were taken primarily for the determination of the "liquidus" curve, *i.e.*, for the determination of the points of initial freezing of the alloys; the observations were, however, carried to temperatures well below that of the final solidification of the metal, and on the majority of the curves, therefore, the arrest due to the freezing of the eutectic as well as that due to a transformation occurring in the solid alloys are shown. In taking these curves uniform quantities of 200 grammes of each alloy were used and the rates of cooling were kept as constant as possible. Typical examples of the curves of this series (A) representing the cooling of the alloys containing 10, 20, 30, 50, 63, 75, and 85 per cent. of tin respectively are shown in fig. 1. The points of initial freezing derived from these curves are shown by the small circles on the line AEB in the equilibrium diagram of fig. 30 (p. 117). The curve thus obtained is in good agreement with that given by ROBERTS-AUSTEN.* With regard to the eutectic, it will be seen that in the alloy containing 10 per cent. of tin the curve shows a very small eutectic peak, and this peak is much smaller than would be anticipated if the eutectic extended to within a fraction of one per cent. of the lead end of the series. The curves of this series (A), however, are not regarded as giving very reliable data for temperatures below the liquidus for alloys near the lead end of the series, and they have accordingly been used only for the determination of the liquidus for that range of alloys. In the proved absence of complications at the other end of the series, however, the points obtained from these curves have been utilised for both liquidus and solidus in the range of alloys containing more than 65 per cent. of tin.

Series B and C consist of differential curves, and typical examples of both series are

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* Paper referred to above.

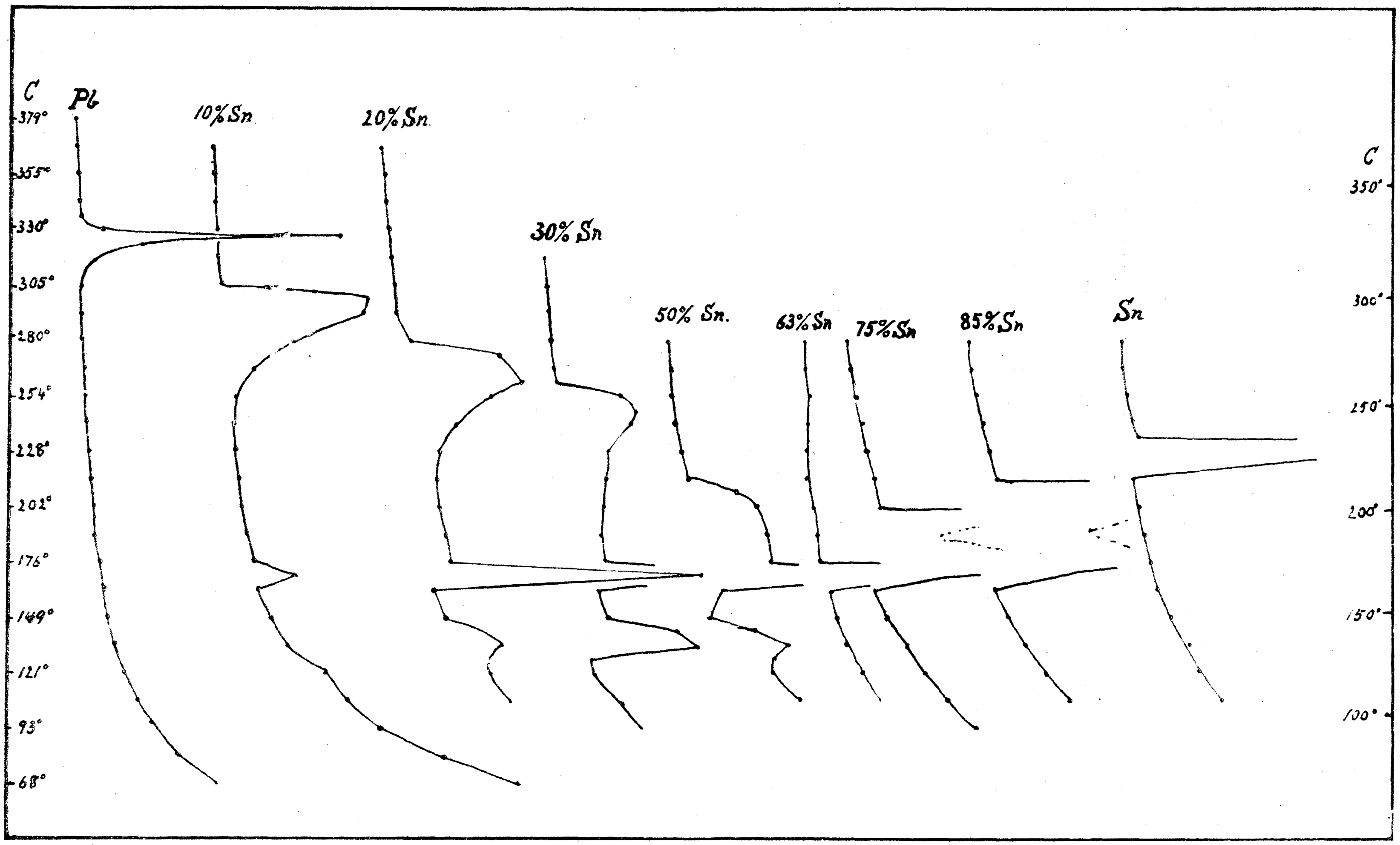

Fig. 1. "Inverse-rate" cooling-curves. Series A. Abscissæ represent intervals of time occupied by equal decrements of temperature.

shown in figs. 2 and 3 respectively in the form of "derived differential" curves.* The curves, as reproduced in the figures, are very much reduced from the original curves as plotted from the observations; in order to illustrate the smoothness of the curves, as originally obtained, the observed figures of the curves of Series B are given in Table II., p. 97, exactly as given in the Laboratory notebook. These figures apply to the ordinary, or "direct," differential curves; the abscissæ of the derived curves are obtained by subtracting successive readings of the differential galvanometer from one another.

The blank body used in taking these curves was a piece of pure lead of the same size as the cylinders of the alloys. In Series B these cylinders were of the size generally used in taking the recalescence curves of steel, viz., $\frac{5}{8}$ inch long by $\frac{5}{8}$ inch diameter, the cylinders weighing approximately 35 grammes. In Series C, with the object of obtaining greater sensitiveness, the weight of the cylinders was increased to 175 grammes. In both cases the rate of cooling was very slow, the fall of temperature from 180° C. to 100° C. taking from 30 to 40 minutes. It was at first expected that this rate of cooling would be sufficiently slow to allow of the attainment of complete equilibrium, but subsequent observations showed that this was not quite the case.

The curves of these two series (B and C) were not taken for alloys containing more than 40 per cent. of tin. With higher percentages of tin, the amount of eutectic present is so great that the entire cylinder "runs down" when heated above 180° C., the metal thus eluding observation by the ordinary differential method during the subsequent cooling. Even in the case of alloys containing above 25 per cent. of tin a certain amount of the liquid eutectic exudes and runs away from the cylinder, thus failing to impart its heat of solidification to the thermocouple on subsequent cooling. This fact must be borne in mind in connexion with the approximate quantitative interpretation of these curves.

On examining the curves of Series B it is found that the eutectic peak first appears

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* The well-known "differential cooling-curves" are obtained by means of the apparatus of ROBERTS-AUSTEN, in which a specimen of the alloy under observation is allowed to cool in the same furnace, and, therefore, at approximately the same average rate, as a standard neutral or comparison body. Similar thermojunctions are inserted in these two cooling bodies and are so connected to the "differential" galvanometer as to oppose one another; any evolution or absorption of heat in the experimental body then produces a deflection of the differential galvanometer, as it sets up a difference of temperature between the two cooling bodies. In the usual form of "differential cooling-curve" the position of the differential galvanometer is plotted (or recorded) as abscissa, with the actual temperature of the cooling body—indicated by a third thermocouple—as ordinate. The "derived differential curves" of the present paper simply represent the differential coefficient of the ordinary differential curve, *i.e.*, abscissæ represent the changes of position of the differential galvanometer which have occurred during successive equal decrements of temperature. The nature and use of these curves has been fully described by the author in a paper on "Observations on Recalescence Curves" read before the Physical Society of London, January 24, 1908. In accordance with the conclusions of that paper all differential observations in the present paper are plotted and interpreted in the form of derived differential curves, while the approximate quantitative interpretation of the cooling-curves has also been carried out on the lines laid down in that paper.

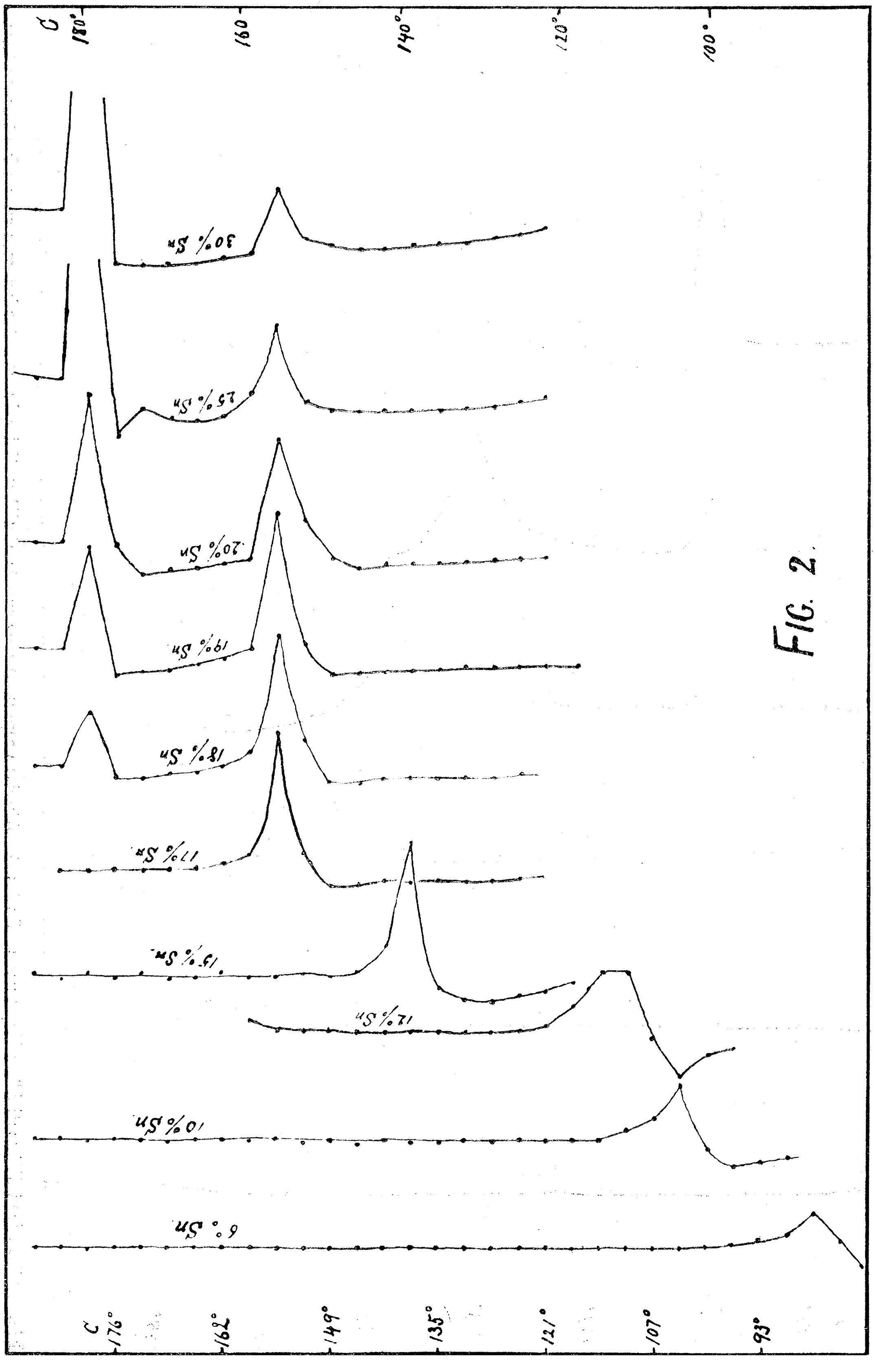

FIG. 2.

"Derived differential" cooling-curves. Series B. Abscissæ represent movements of differential galvanometer between successive temperatures.

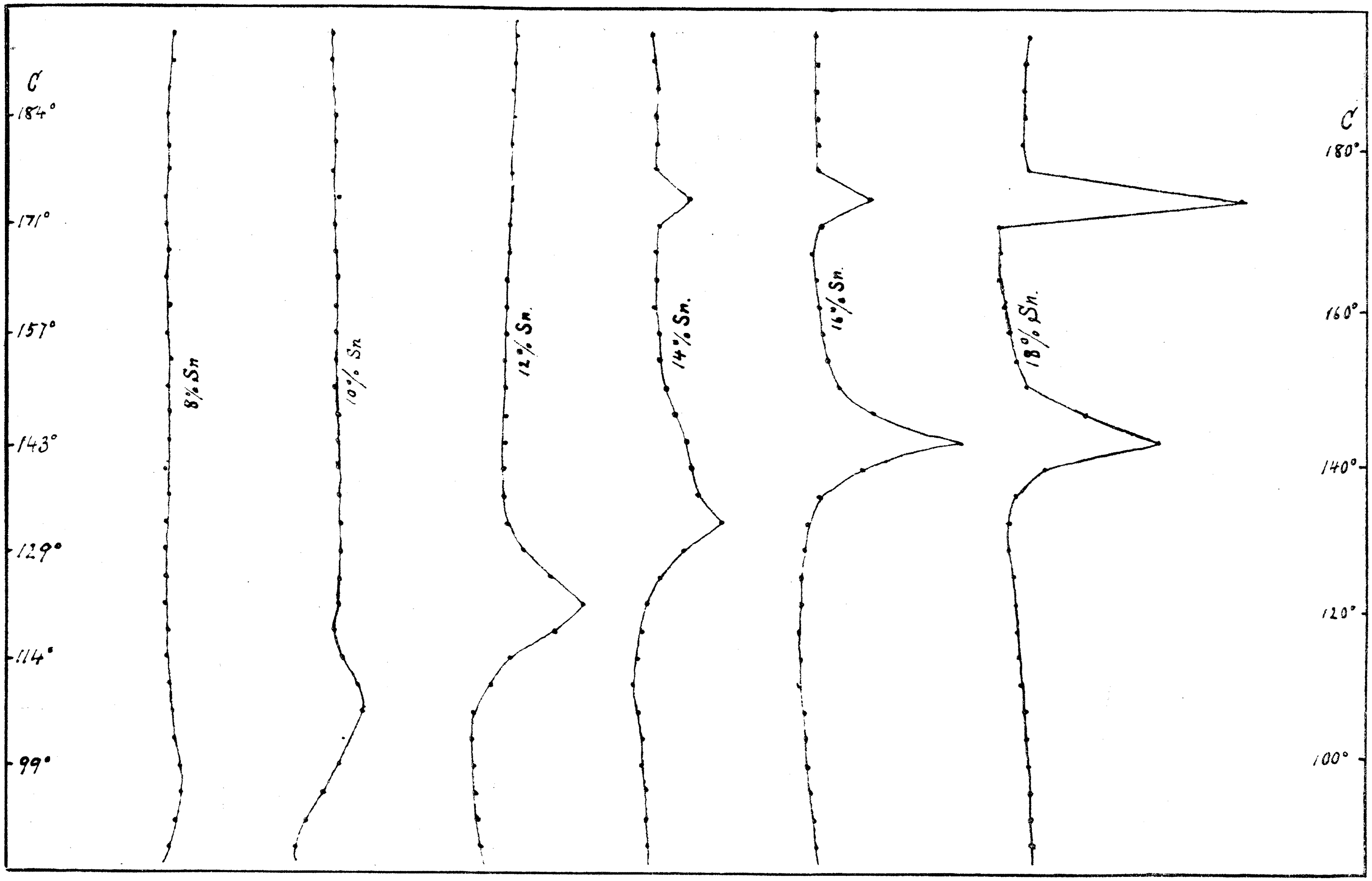

Fig. 3. "Derived differential" cooling-curves. Series C. Abscissæ represent movements of differential galvanometer between successive temperatures.

Table II.—Differential Cooling-curve Observations, Series B.

Absolute temperature in micro-volts. Couple M8.	Readings of differential galvanometer.									
Alloy with	8	10	12	15	17	18	19	20	25	30 per cent. Sn.
1275	15	12	—	-9	-9	11	1	2	-11	-13
1250	13	11	—	-8	-9	10	2	2	-10	-11
1225	12	11	—	-8	-9	9	21	2	-9	-9
1200	11	10	—	-7	-9	19	17	30	62	83
1175	10	9	—	-7	-9	16	14	30	52	75
1150	9	9	—	-6	-9	13	11	24	48	66
1125	8	8	—	-6	-8	11	8	20	40	57
1100	7	7	—	-6	-8	9	7	16	33	48
1075	6	6	-2	-5	-7	8	8	13	27	41
1050	5	6	0	-5	-4	10	34	11	25	35
1025	4	5	0	-5	21	34	35	31	37	41
1000	4	5	0	-4	24	37	31	36	34	38
975	3	4	0	-4	21	33	28	34	30	34
950	2	4	0	-3	18	29	24	30	26	29
925	1	3	0	3	16	26	21	27	22	24
900	1	3	0	29	14	23	18	23	18	20
875	0	2	0	27	11	20	16	20	15	16
850	-1	2	0	23	9	15	14	17	12	12
825	-1	1	0	19	7	14	11	15	9	9
800	-2	1	0	16	6	12	10	13	7	7
775	-2	1	1	13	5	10	8	—	5	5
750	-2	1	6	11	—	—	—	—	—	3
725	-3	1	17	9						
700	-3	3	28	8						
675	-3	7	28	7						
650	-4	17	20	5						
625	-3	15	16							
600	-3	10	13							
575	-1	6								
550	1	3								
525	6									
500	8									
475	4									
450	0									
425	-3									

in the alloy containing 18 per cent. of tin, while the alloys containing 17, 15, 12, 10 and 8 per cent. of tin pass through the corresponding temperature without any retardation of cooling. The curves of alloys containing less than 8 per cent. of tin are not reproduced, as they are entirely blank down to the ordinary temperature.

In Series C, on the other hand, there is a very small peak at the eutectic temperature in the alloy containing 14 per cent. of tin, from which it would seem that the greater sensitiveness attained with larger masses of alloy has rendered possible the detection of smaller quantities of eutectic. While this is probably the case, the microscopic evidence shows that even the most delicate pyrometric methods which have been applied in the present research are inadequate to detect the presence of the first small proportions of eutectic; in both series of cylinders (B and C) small traces of eutectic could be found in the sections of alloys containing as little as 10 per cent. of tin. These small traces of eutectic, however, can be ascribed to the fact that the cooling of the alloys had not been slow enough to allow complete equilibrium to be established. The effect can be readily explained from a consideration of the process of solidification of a solid solution as indicated in the diagram fig. 4. In this diagram

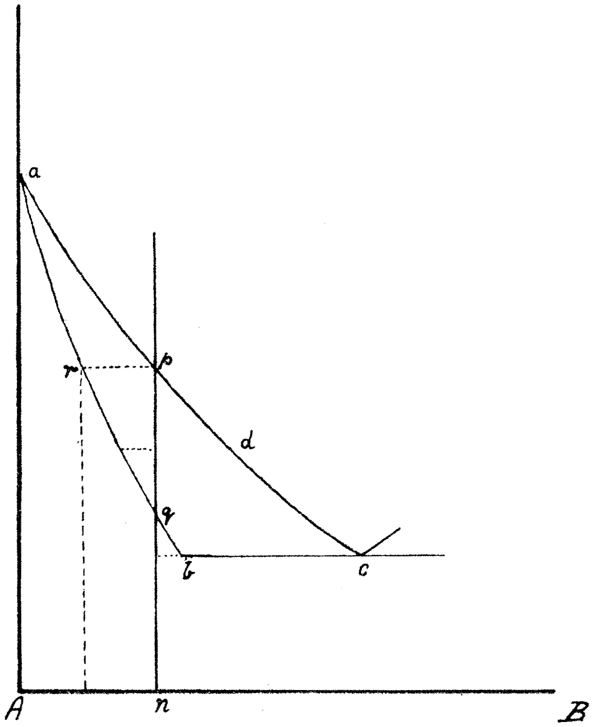

Fig. 4.

the line *adc* represents the liquidus curve of a series of binary alloys of metals A and B, while the line *abc* represents the solidus. The abscissa of the point *b* is thus the limiting solubility of B in solid A, while *bc* is the line of eutectic solidification Now, consider the process of solidification of an alloy containing *n* per cent. of B, where *n* is a little less than *b*. The cooling of the alloy will be represented on the diagram by the line *pqn*. As the line reaches the point *p* solidification will begin and a solid solution of B in A will be formed having a concentration represented by the abscissa of the point *r*, where a horizontal line through *p* cuts the solidus curve *ab*. Similarly, as has been indicated by ROOZEBOOM and others, the composition of the solid formed at successively lower temperatures will correspond in composition to the abscissæ of successively lower points on the solidus *ab*. If sufficient time be allowed, the composition of the whole of the solid present at any given temperature will become equalised to that which is formed at that temperature; this equalisation can, however, only occur by the slow process of solid diffusion, and therefore in most cases the solid formed will consist of layers of solid solution whose concentration varies more or less continuously, increasing from the centre outwards. If the formation of such layers has taken place, and time has not been allowed for diffusion to obliterate them, the whole of the alloy will not be solid when the point q is reached, since the average composition of the solid formed up to that time will be lower in its content of B than the alloy as a whole; the remaining liquid portion will therefore contain more than n per cent. of B, and as the alloy cools further, fresh layers of solid solution will be formed containing more than n per cent. of B. This will continue until the remaining liquid attains the concentration represented by b, but as soon as this concentration is exceeded, the remaining liquid will solidify as eutectic. This will only happen if the rate of cooling is rapid, or if the rate of diffusion is very slow, and the concentration (n) of the alloy not far below the saturation point of the solid solution. Once, however, that a small proportion of eutectic is formed in this way, the meta-stable equilibrium thus established can only be abolished by the process of diffusion through successive solid layers, and it is reasonable to suppose that this diffusion would be still further retarded by the fact that in the formation of the eutectic some of the B constituent has been mechanically separated; diffusion thus has a larger task to perform in overcoming this separation as well as in obliterating the concentration gradient existing in the mass of the solid solution itself.

On the basis of this consideration it is possible to account for the divergence between the results of ROBERTS-AUSTEN and those given here. In the experiments of ROBERTS-AUSTEN the rate of cooling was probably such as to allow of the formation of layers of solid solution differing widely in concentration, with the result that alloys lying in reality well within the limits of solid solubility showed the presence of small quantities of eutectic. This view is confirmed by the authors' observations on the effect of different rates of cooling on the indications of the cooling-curves. With moderately rapid cooling the results of ROBERTS-AUSTEN as to the presence of eutectic in alloys very near the lead end of the series have been confirmed. With more moderate rates of cooling, such as that employed in taking the curves of Series A and B, the appearance of the eutectic is postponed to concentrations near 10 per cent. of tin, while in the still more slowly cooled series B and C no eutectic becomes apparent until much higher concentrations are attained.

In consequence of these observations it appears necessary, in order to ascertain the limit of solubility with accuracy, to expose the alloys to such thermal treatment as will facilitate the attainment of complete equilibrium at a temperature just below the "solidus." Prolonged exposure to a temperature of 175° C. was chosen for this purpose, since this temperature lies safely below the "solidus," even in alloys containing eutectic, while it lies well above the temperature of the transformation already referred to. The exposure to this temperature was carried out in electrically heated ovens whose temperature could be accurately regulated, and in some cases the alloys were maintained at 175° C. for a period of six weeks, specimens being removed and experimented upon in various ways at intervals. The most important evidence derived from these heated specimens is that obtained from a study of their micro-structure, but this will be better understood when the complications arising from the transformations which occur at lower temperatures in the solid alloys have been discussed; the account of the micro-structure of these specimens will therefore be given later. The heat-treated specimens were, however, also used for obtaining cooling-curves of these alloys in a state closely approaching complete equilibrium. In some cases the cooling-curve was taken without allowing the specimen to undergo any intermediate cooling and re-heating, while in other cases specimens were allowed either to cool slowly in the ordinary way, or were cooled rapidly (quenched) and subsequently re-heated for the observation of the cooling-curve. The initial temperature for all these curves was taken slightly above the freezing-point of the eutectic, so that the eutectic arrest—if any—should appear on the curves. The inverse-rate curves derived from specimens which had been heated at 175° C. for four and six weeks respectively are given in figs. 5, 6, and 7. It will be seen that the eutectic arrest appears for the first time in these curves in the alloy containing 18 per cent. of tin. Microscopic evidence, however, leads to the view that the first appearance of eutectic occurs in alloys slightly richer in lead, viz., at a concentration of about 16 per cent. of tin.

The cooling-curves of all five series referred to above, in so far as they relate to the alloys rich in lead, show a further recalescence occurring in the solid alloys. In one direction this recalescence has been traced down to the alloy containing 8 per cent. of tin, while in the other it can just be detected by delicate means in the alloy containing 60 per cent. of tin (just below the eutectic concentration). The temperature at which this arrest-point occurs in the cooling of these alloys is lowest in the 8 per cent. alloy, and attains a maximum temperature at a concentration of about 18 per cent. of tin, occurring at this highest temperature in all alloys richer in tin up to, or nearly up to, the eutectic alloy, where the arrest ceases to be observable. As will be seen from the diagram of fig. 30, this maximum temperature is 149° C., while the lowest temperature found in the 8 per cent. alloy is 72° C. As the temperature at which this recalescence occurs falls to this low point at a tin content of 8 per cent., it was at first supposed that the non-observation of the arrest in alloys of lower tin content might be due to the fact that the temperature at which the recalescence occurs had fallen down to or even below the ordinary temperature. To decide this question, both heating- and cooling-curves of alloys containing 2 per cent. and 4 per cent. of tin and also of pure lead were taken down to very low temperatures by means of liquid air and a thermo-couple of Iron-Constantan.

For the purpose of obtaining a cooling-curve over this low range of temperatures the specimen of metal into which the thermojunction had first been inserted was wrapped in thick asbestos cloth and first gently warmed to a temperature just above

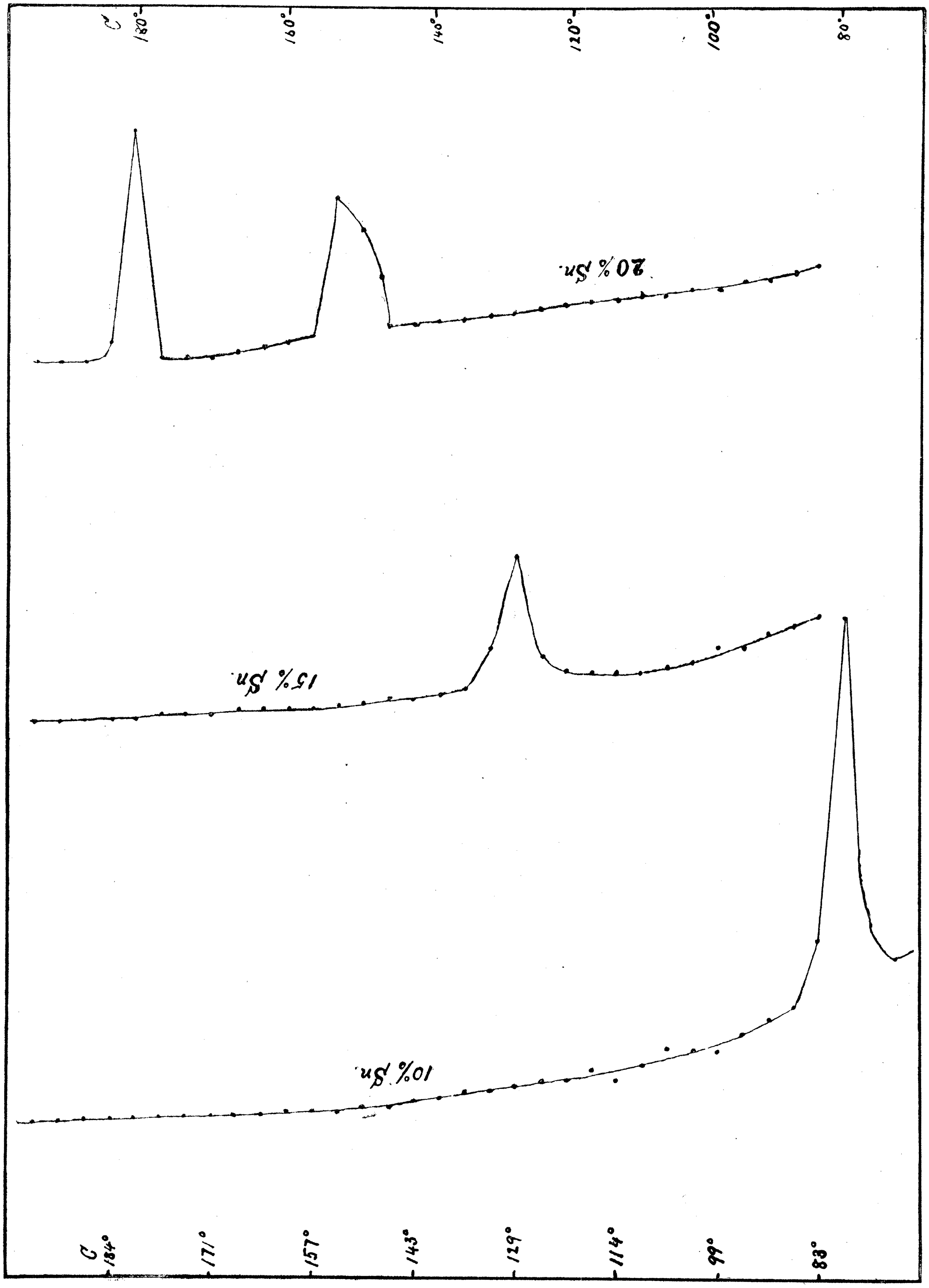

Fig. 5. "Derived differential" cooling-curves. Abscissæ represent movements of differential galvanometer between successive temperatures.

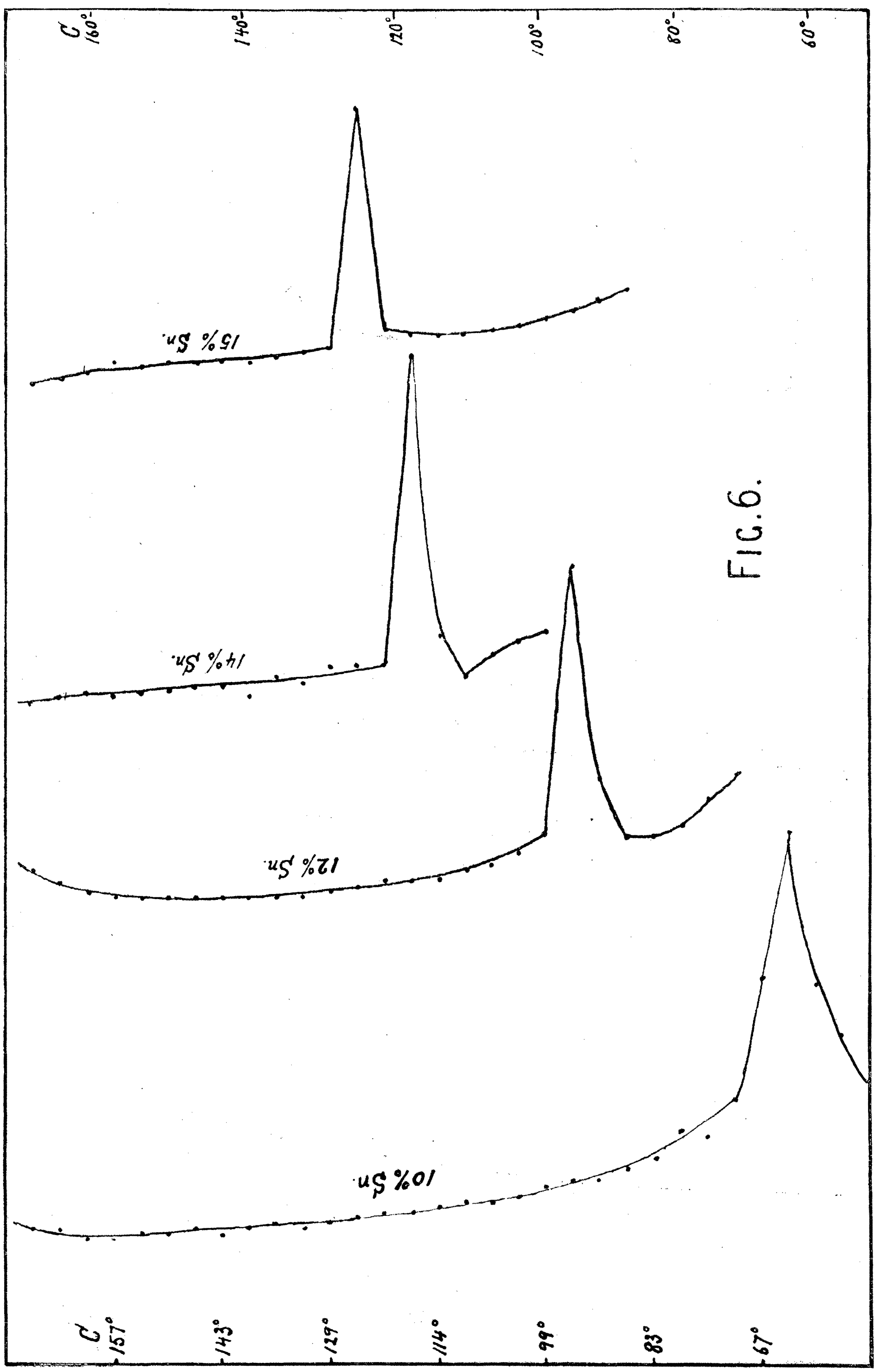

FIG. 6.

"Derived differential" cooling-curves. Abscissæ represent movements of differential galvanometer between successive temperatures.

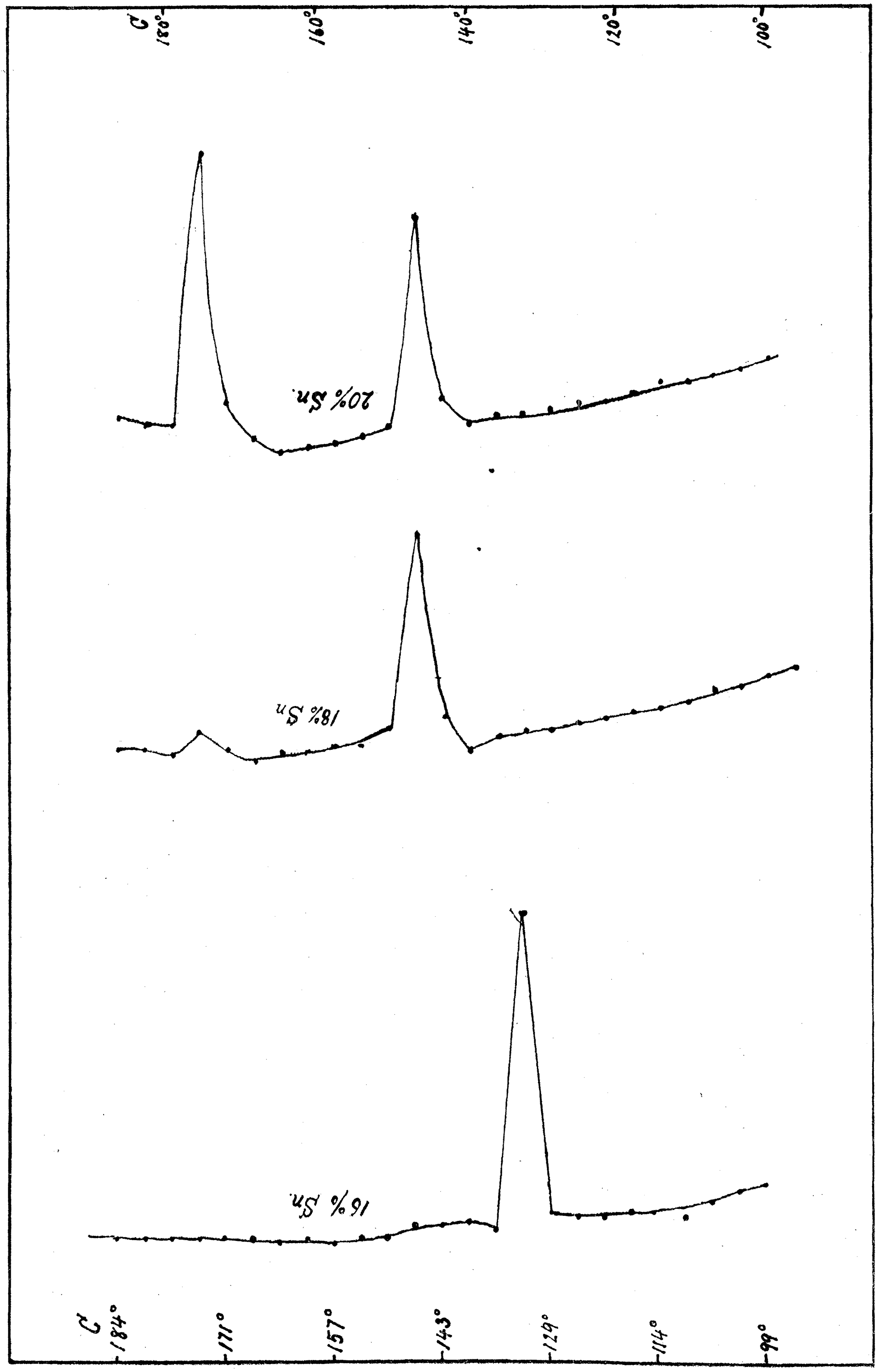

Fig. 7. "Derived differential" cooling-curves. Abscissæ represent movements of differential galvanometer between successive temperatures.

100° C. By means of a thin wire attached to the specimen, this was then lowered into a large Dewar vessel containing a moderate quantity of liquid air; the specimen hung just above the surface of the liquid air, the mouth of the vessel being loosely stuffed with cotton-wool in the usual manner. Thus arranged, the specimens, weighing about 200 grammes, were found to cool at a convenient rate, and inverse-rate observations could readily be taken. Heating-curves were obtained by removing the specimen from the Dewar vessel, having first immersed it in the liquid air so as to ensure the attainment of the temperature of boiling liquid air (−189° C.). If the specimens were simply allowed to warm in the air of the room the process was found to be inconveniently slow, while the heating-curve could not be carried up to the ordinary temperature; the specimens were therefore hung up in a vertical metal cylinder placed above a previously warmed crucible; this arrangement gave a convenient rate of heating, and allowed the observations to be carried well above the ordinary temperature. One inconvenience arose, however, from the formation of rime (ice) on the surfaces of the specimens as soon as they were removed from the liquid-air vessel; when the temperature 0° C. was reached, the melting of this ice caused an arrest in the rate of heating which might have masked an arrest due to the alloys themselves, but the observation of the corresponding cooling-curve serves to remove this doubt. Typical examples of the curves obtained in this way are given in fig. 8, and it will be seen at once that they contain no indication of any evolution (or absorption) of heat at low temperatures in these alloys. It follows, therefore, that the transformation to which these evolutions of heat are due does not occur in alloys containing less than 8 per cent. of tin.

The above conclusion is further borne out by a consideration of the approximate quantitative interpretation of the curves already described. TAMMANN* has pointed out that the determination of the quantity of heat generated in a recalescence, whether it arises from the solidification of a eutectic or from transformations in the solid, may yield valuable information as to the constitution of a series of alloys. On the other hand, the present author has recently discussed† the theory and interpretation of cooling-curves, and has shown that any strictly accurate quantitative interpretation of the areas of the peaks on inverse-rate or derived differential cooling-curves in terms of quantities of heat is not possible, at the same time indicating the manner in which rough approximations may be obtained. The results now to be quoted must therefore be read with all the limitations which apply to such approximations, but even with these limitations they appear to yield some interesting results.

Apart from errors introduced by variations in the mass of the cooling body and in its specific heat, and by variations in the rate of cooling, it has been shown in the paper cited above that the areas of the peaks of inverse-rate and of derived differential curves represent the quantities of heat generated by the recalescences in

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[*] 'Zeitschr. Anorg. Chem.,' 37 (1903), p. 303; 45 (1905), p. 24; 47 (1905), p. 299.

[†] Paper cited above.

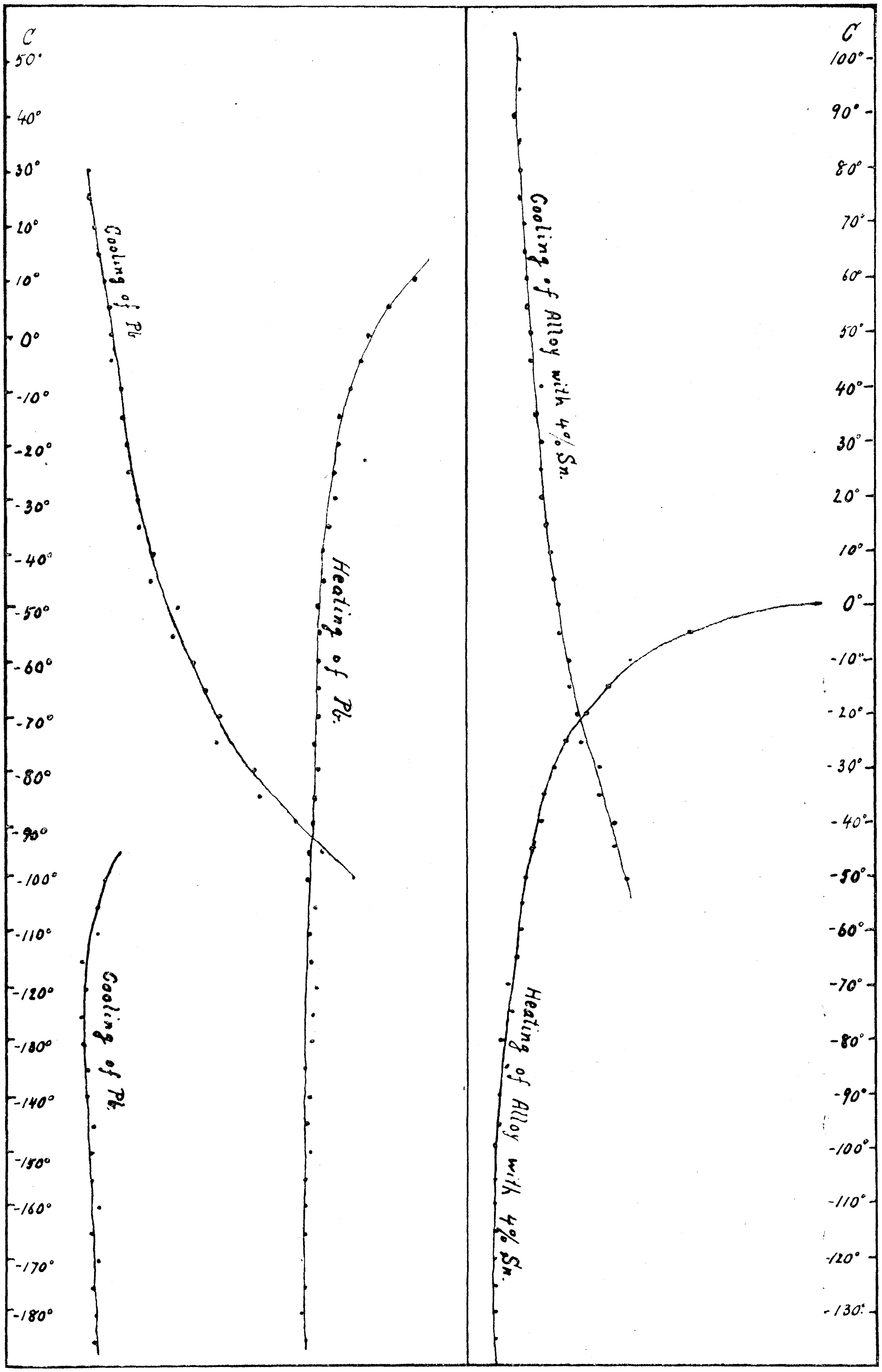

Fig. 8. "Inverse-rate" cooling-curves.

question. A practical difficulty lies in determining the proper boundaries of these areas on the side not bounded by the observed curve. In the present instance the areas have been closed by lines drawn in free-hand in such a way as to coincide as nearly as possible with the limits of the recalescence, these limits being graphically estimated on the general lines laid down in the paper cited above. While this is obviously only a rough approximation, the errors involved are probably much smaller than those which are unavoidably introduced by variations in the rate of cooling as from one curve to another of the same series. These variations in the rates of cooling have been approximately allowed for in each estimation, but the rates of cooling from which this was done are the average rates during that particular experiment, and probably differ considerably from the rate at which cooling actually took place during the course of the recalescence. The weights of the specimens of metal were accurately known in each case, and these have been allowed for in making the estimations of the heat equivalents of the recalescence peaks. The actual areas of these peaks were obtained by plotting the cooling-observations on a large scale, and measuring the areas of the peaks by means of a planimeter. The area so found was divided by the weight of the cooling body and multiplied by the inverse of the rate of cooling. The resulting approximate values of the quantities of heat evolved have been plotted for the three most complete series of curves, and are shown in figs. 9, 10, and 11. Fig. 9 refers to the eutectic arrest-points in the derived differential curves of Series A, and for the alloys lying between 18 and 25 per cent. of tin the points fall on a straight line, *i.e.*, the heat evolved by the solidification of a gramme of eutectic appears to be constant for these alloys. The good agreement of this result with theoretical expectations serves to show that under favourable conditions the method of approximation yields reasonably satisfactory results. If TAMMANN'S method of extrapolation be applied to this curve, we find that the zero of the eutectic falls at about 17 per cent. of tin, a result which agrees well with other lines of evidence, except that in the present set of curves the limit is shifted slightly towards the tin side of the series, because—as has already been pointed out—the rates of cooling used in the experiments were not sufficiently slow to allow of the attainment of complete equilibrium.

When the same process of approximation is applied to the study of the recalescences which occur in the solid alloys at a lower temperature, the conditions are not so favourable and the results consequently much less concordant. In the alloys containing the larger proportions of lead the temperature at which the heat-evolution occurs varies considerably from one alloy to another, and this introduces large corrections derived from widely differing rates of cooling. It is therefore not surprising to find the points in the curves of figs. 10 and 11, which refer to the cooling-curves shown in figs. 2 and 6 and 7 respectively, lie somewhat irregularly. In fig. 11 the points relating to alloys with 14, 16, and 18 per cent. of tin, which are marked with a small circle, refer to cooling-curves taken from specimens which had previously been quenched. Their erratic position is probably due to this difference in treatment, and

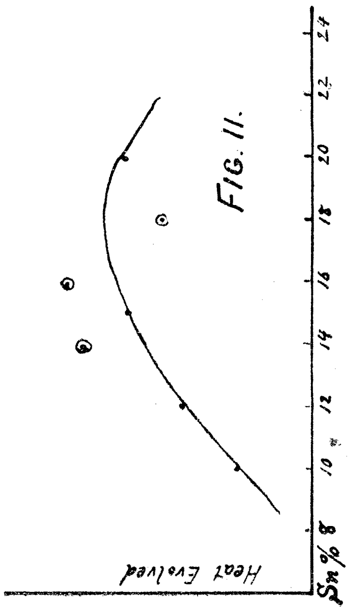

FIG. 11.

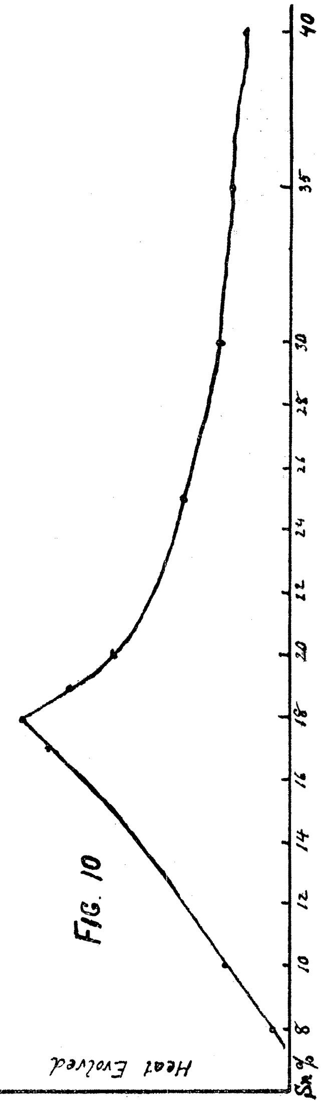

FIG. 10

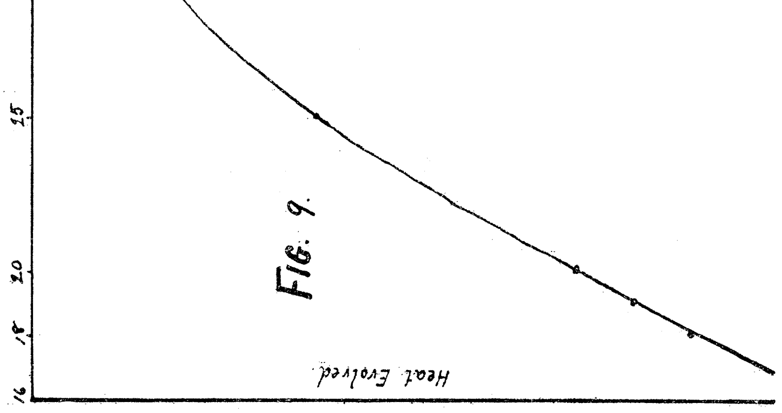

FIG. 9.

they have been ignored in drawing the curve of fig. 11. These curves, however, still bear out the conclusion that the evolution of heat reaches a maximum at or near a concentration of 18 per cent. of tin, and falls away on either side at such a rate as to reach a zero value at or about concentrations of 6 and 60 per cent. of tin respectively.

Other peculiarities connected with this evolution of heat are shown by cooling-curves taken under various circumstances. Thus alloys which have undergone prolonged heating at 175° C. show this evolution of heat much more markedly, and over a shorter range of temperature than alloys which are cooled in the ordinary way from the molten state. This indicates that the change which produces this evolution of heat is the inversion of a change which is itself gradual, and thus liable to be incomplete unless ample time be allowed. This question was tested by taking two successive cooling-curves of the same alloy, the first when the alloy had been rapidly heated to about 180° C. and allowed to cool at once, the second when the alloy had been kept hot for an hour and a half before the cooling was allowed to begin. The two curves are shown in fig. 12, and it will be seen that while the recalescence is observed in both cases, it is very feeble in the first case and quite well-marked in the second. The resulting conclusion that the change on heating is gradual is further borne out by the appearance of the heating-curves of these alloys. These are not reproduced, since they show nothing well defined ; apparently the change on heating is very gradual and is therefore spread out over a wide range of temperature, merely producing slight slopes in the various curves.

Another fact which appears to be connected with the same properties of the substances involved is found in the alloys lying between 8 and 16 per cent. of tin. In these alloys the temperature at which the evolution of heat occurs on cooling depends upon the time for which they have been exposed to a temperature of 175° C., *i.e.*, the alloys which have been kept at that temperature for six weeks show the arrest-point at a lower temperature than those which have only been kept hot for four weeks, while these in turn show the arrest-points at lower temperatures than those which have been simply slowly cooled from the molten state ; still more rapidly-cooled alloys show the point at still higher temperatures. The results of a number of experiments on this point are plotted in the diagram of fig. 13. The explanation for these observations is probably to be found in the formation of concentric layers of solid solutions of different concentrations in more rapidly-cooled alloys. The temperature at which the recalescence occurs depends upon the concentration of tin in the alloy (in alloys with less than 18 per cent. of tin), and consequently the layers richest in tin will undergo the change as soon as the temperature appropriate to their concentration is reached—and in the absence of homogeneity this will be higher than the temperature of reaction corresponding to the average composition of the whole of the alloy. It is this beginning of the reaction which is sharply indicated on the curves. The shape of these curves, however, strongly suggests that in these cases the change which has commenced in the layers of highest tin content is transmitted to the other layers, although these had not reached the temperature at which they would have spontaneously undergone the change in question. Other observations

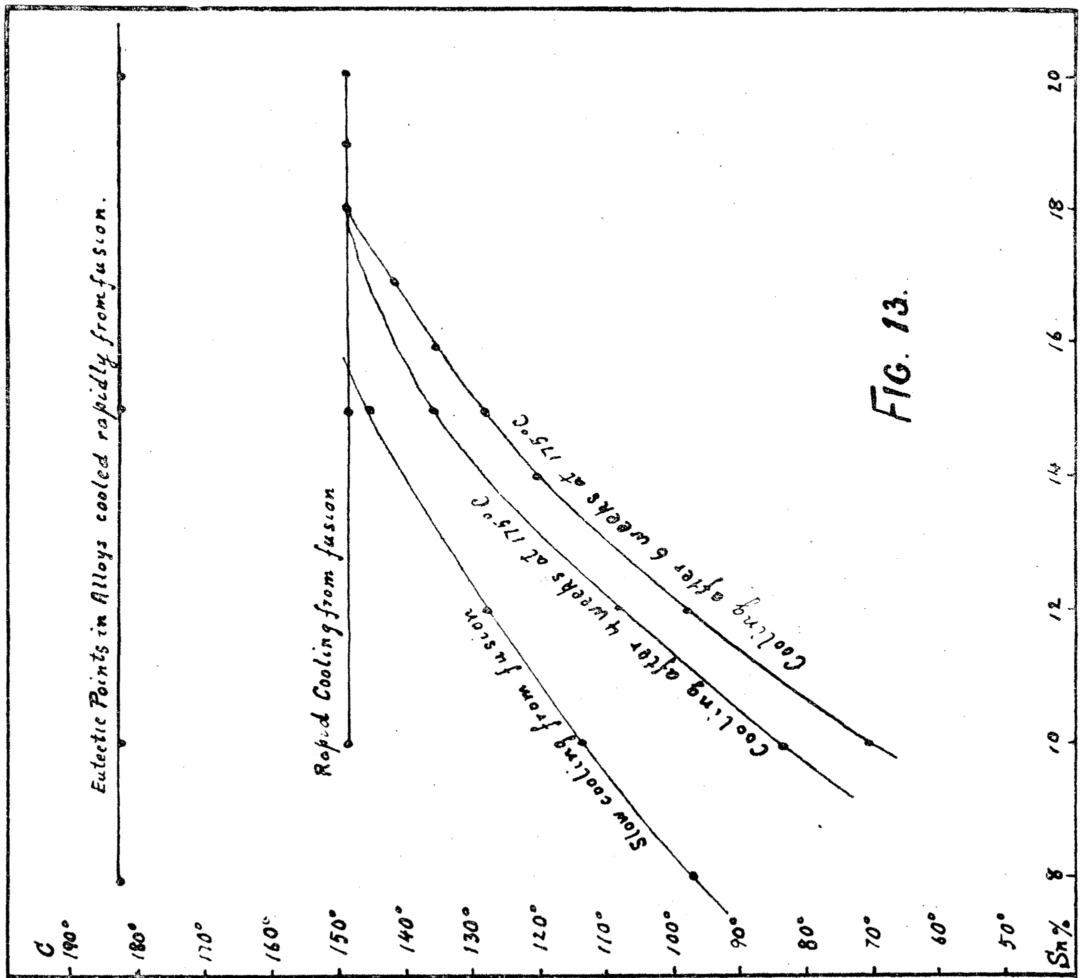
Eutectic Points in Alloys cooled rapidly from fusion.
Rapid Cooling from fusion
Slow cooling from fusion
Cooling after 4 weeks at 175°C
Cooling after 6 weeks at 175°C
C
190°
180°
170°
160°
150°
140°
130°
120°
110°
100°
90°
80°
70°
60°
50°
Sn%
8
10
12
14
16
18
20

FIG. 13.

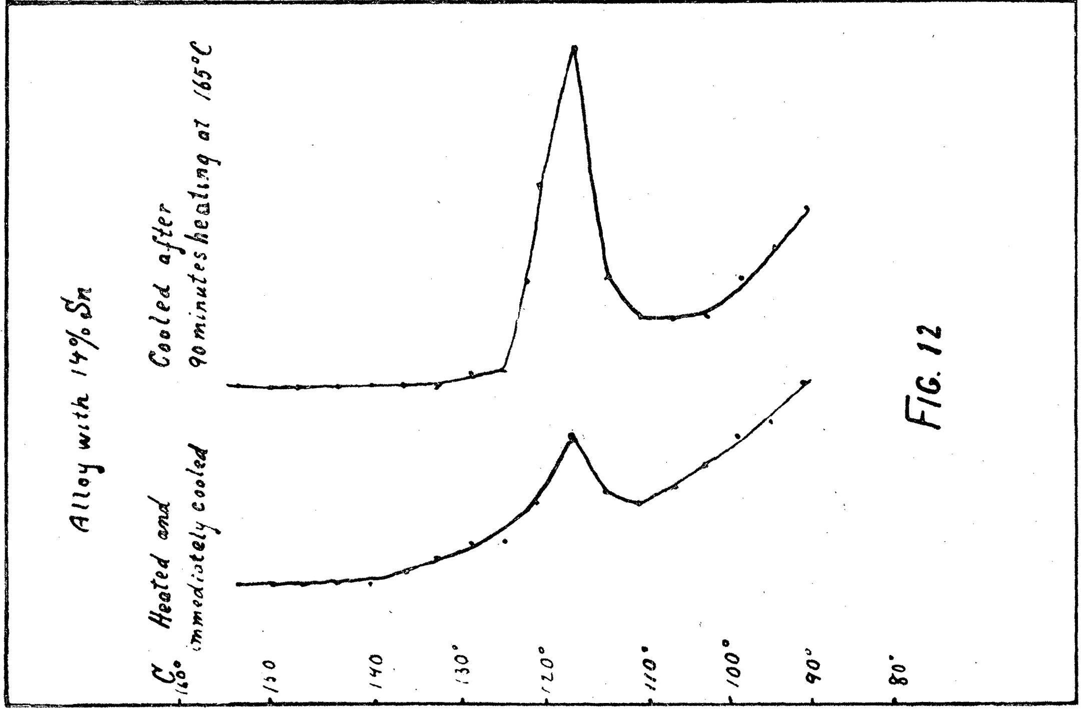
Alloy with 14% Sn
Heated and immediately cooled
Cooled after 90 minutes heating at 165°C
C
150°
150
140
130°
120°
110°
100°
90°
80°

FIG. 12

tend to confirm the view that the transformation connected with this heat-evolution is liable to be suppressed, or at all events to be retarded to a much lower temperature, in the absence of an initiating cause.

The data derived from the cooling-curves as just described appear to admit of a variety of interpretations, but their comprehension is so much assisted by the microscopic data that it will be preferable to deal with their interpretation in that connection.

The Micro-Structure of the Alloys.

The general micro-structure of the alloys is represented in figs. 14 to 22 inclusive (Plates 5–6*). The alloys near the lead end of the series will be discussed below. Fig. 14 shows the structure of the alloy with 15 per cent. of tin when rendered approximately homogeneous by four weeks' exposure to 175° C. (magnification × 100 vertical illumination). The dark ground-mass represents the solid solution of tin in lead; the bright dots correspond to the residue of free tin remaining unabsorbed from the eutectic which was formed during the initial relatively rapid solidification of the alloy. On more prolonged heating to 175° C., followed by rapid cooling, this alloy becomes entirely homogeneous. The next figure (No. 15) shows the alloy with 20 per cent. of tin, in which no amount of prolonged heating appears to be capable of entirely removing the free or eutectic tin. This photo-micrograph has been taken under a higher magnification in order to show the remains of the eutectic structure in the light areas which represent the free tin. Owing to the prolonged heating which this specimen has undergone, the lead constituent of the eutectic has almost entirely coalesced with the ground-mass, leaving the residual free tin in segregated masses containing only a few small globules of lead. The appearance of these segregated masses of eutectic tin is very characteristic, and can be readily used for the identification of free tin which is derived from eutectic as compared with free tin subsequently separated from the solid solution; apart from the difference in size of the masses, the secondary tin separated from the solid solution never shows the black dots and patches found in the primary or eutectic tin.

Fig. 16 shows the alloy with 45 per cent. of tin (magnification 200 diameters). This example is given as typical of the structure of the alloys lying between the eutectic alloy and a tin content of 20 per cent. In all these alloys the primary crystals of lead appear as dendritic crystallites of the type shown in this figure, appearing embedded in typically laminated eutectic. A special feature of these alloys is the fact that the lead crystallites are surrounded by zones of pure tin, *i.e.*, of eutectic whose lead constituent has coalesced with the lead of the crystallite. This feature is of considerable importance, because it explains the manner in which the sheaths of pure tin isolate the free lead of the crystallites from the lead constituent of the eutectic.

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* See Description of Plates, p. 122.

Fig. 17 shows one of the typical forms of the eutectic alloy (magnification 300 diameters) containing 62·97 per cent. of tin. The various forms taken by this alloy will be discussed in detail in the special section at the end of this paper.

Fig. 18 represents the alloy containing 65 per cent. of tin. As the micro-structure shows, this alloy is just above the eutectic composition, white crystallites of free tin appearing embedded in the eutectic. (Magnification 200 diameters.)

Fig. 19 represents the alloy containing 74 per cent. of tin, under a magnification of 200 diameters. The crystallites of free tin are seen in larger quantity and are surrounded, or nearly surrounded, by regions of the lead constituent.

Fig. 20 shows the alloy containing 85 per cent. of tin. Here the white crystals of tin occupy the greater part of the area of the section, the eutectic merely forming a meshwork between the crystals. In the 95 per cent. alloy shown in the next figure (No. 21, magnification 200 diameters) the meshwork of eutectic, or, rather, of the lead constituent of the eutectic, is very thin and no longer continuous. Finally, in fig. 22, the alloy containing only 1 per cent. of lead (99 per cent. of tin) is shown. The eutectic can be definitely traced in this micrograph, and the structure of this alloy is not affected in this respect by prolonged heating at 175° C. This fact, together with the cooling-curves already described, leads to the conclusion that the eutectic extends very nearly to the tin end of the series, and that the solubility of lead in tin is zero or very nearly zero.

For the purpose of determining the limiting solubility of tin in lead, the alloys in the neighbourhood of a tin content of 15 per cent. were carefully examined after six weeks' exposure to heat at a temperature of 175° C. Examined under moderate magnifications, by whose aid the presence of "primary" tin could not fail to be recognised, the 15 per cent. alloy was found to be entirely homogeneous, the few white spots seen after four weeks' heating (as seen in fig. 14) having entirely disappeared. In the 16 per cent. alloy small specks of primary tin could generally be observed, the appearance of this alloy after six weeks' heating being similar to that shown in fig. 14. By powdering this alloy, compressing the powder so as to form a solid, and then further heating at 175° C., the 16 per cent. alloy can, however, be rendered quite homogeneous under moderate magnifications. In alloys with 17 and 18 per cent. of tin the specks of primary tin are always clearly present, and in increasing quantity with increasing tin content. The conclusion drawn from these observations, taken together with the data derived from the cooling-curves described above, is that the limiting solubility of tin in lead at a temperature of about 180° C. (which is near the temperature of the freezing of the eutectic, and therefore very close to the solidus in alloys containing nearly 16 per cent. of tin) is very little more than 16 per cent. On this view an alloy containing a little less than 16 per cent. of tin, if cooled so slowly that complete equilibrium is attained, would solidify as a homogeneous mass, no eutectic being separated. It will be seen, however, that there is good reason to suppose that some "secondary" tin is separated from this solid solution at lower temperatures if the alloy is slowly cooled, and this fact has considerably complicated the determination of the limiting solubility. The fact that very gradual cooling would be required to produce this complete equilibrium is borne out by microscopic evidence, as well as by the cooling-curves described above. Figs. 23 and 24 (Plate 6) are photo-micrographs, at a magnification of 150 diameters, of alloys containing 10 and 15 per cent. of tin respectively, cooled from fusion in an ordinary laboratory furnace. Considerable quantities of eutectic appear in both, but, as has already been indicated, these alloys gradually become homogeneous on exposure to a temperature of 175° C.

In the alloys lying between 8 and approximately 60 per cent. of tin the cooling-curves show the existence of changes involving an evolution of heat at a temperature which lies at 149° C. for alloys above 18 per cent. of tin, and at lower temperatures for alloys of lower tin content. In order to correlate these evolutions of heat with changes in the micro-structure of the alloys it was necessary to cool specimens of the alloys from a temperature just above the recalescence point at so rapid a rate as to more or less suppress the change in question. It was evident that from a temperature so low as 149° C. mere quenching in cold water would not be sufficient for this purpose, and quenching in liquid air was therefore employed.

For this purpose a Dewar vessel containing a considerable quantity of liquid air was brought to the door of a small electric oven in which the specimens had been heated; the quenching operation was carried out by removing from the oven a small slab of uralite on which the specimens had been placed for this purpose and allowing the specimens to slide quickly and directly into the liquid air. The specimens were made of small dimensions, and the violent ebullition of the liquid air which they at first produced subsided very rapidly. As soon as the specimens had become quiescent in the bath they were removed from the liquid air and allowed to lie on the table until they had regained the ordinary temperature, when they were prepared for microscopic examination, as previously described. The object of using liquid air in this instance, it should be noted, was simply to ensure the most rapid possible rate of cooling, and not in any way to test the effect of liquid-air temperatures upon the alloys. It was, however, necessary to ascertain whether the mere fact of exposure to such a low temperature produced any change in the micro-structure of the alloys, and to test this point duplicate specimens of the alloys were immersed in liquid air for a similar length of time, but the immersion in this case only took place after the temperature of transformation had been passed; specimens of pure lead and of pure tin were included in this experiment. A third set of similar specimens was then allowed to cool very slowly in the electric oven itself, and the micro-structure of the three sets was subsequently compared. In the case of pure tin, the experiment was tried in view of the fact that tin is known to exist at low temperatures in the allotropic form of a grey powder, and it was supposed that some sign of this phase might be detected in the specimen cooled in liquid air; this was not the case, however, and the conclusion is justified that the duration of the exposure to liquid air was not long enough to allow this transformation to occur.

The comparison of the micro-structure of the specimens quenched from a temperature just below the recalescence in question with that of very slowly-cooled specimens also shows only very slight differences, so that the conclusion is justified that the differences observed between the structure of specimens quenched above the recalescence temperature and those which have been allowed to undergo the change unhindered are due entirely to the partial suppression of the transformation associated with these evolutions of heat.

The alloys chosen for close study in this respect were those containing 16 to 18 per cent. of tin, since in this range the heat-evolution reaches its maximum intensity. A high degree of magnification is required to bring out clearly the difference in micro-structure between the alloys which have been quenched above the transformation point and those which have been allowed to undergo the change. (See Plate 7.)

Fig. 25 is a photo-micrograph (magnification 1000 diameters) of a specimen of an alloy containing 16 per cent. of tin which has been kept at 175° C. for six weeks, and has then been quenched in liquid air from a temperature of 160° C. Seen under a low magnification this specimen appears practically homogeneous, but the high power used in the photograph reveals the presence of a large number of very fine white patches; from their behaviour and appearance these undoubtedly consist of free tin, but their minute size and their distribution over the specimen, as well as the entire absence of any spots or markings within the white patches, indicate that this tin is of "secondary" origin, having been separated from the solid solution during cooling. To some extent the presence of this tin in the quenched specimen is probably to be ascribed to the fact that the rate of cooling employed was not great enough to entirely suppress the change occurring at the recalescence. Figs. 26 and 27 are photo-micrographs of a piece of the same ingot as that represented in the previous figure, but in this case the specimen has not been quenched, but has undergone very gradual cooling from 150° C. to the ordinary temperature. The mottling of secondary tin is much more pronounced in these specimens, the quantity of tin being much larger, while it is also aggregated into larger masses. Since the appearance of a specimen quenched from a temperature just below the recalescence is very similar* to that of this specimen, it follows that the transformation in question has involved the rejection of a considerable quantity of tin from the solid solution.

Figs. 28 and 29 respectively represent typical sections, under a magnification of 1000 diameters, of quenched and slowly-cooled alloys containing 18 per cent. of tin. In the quenched specimen (fig. 28) we have two large masses of primary tin (remnants of eutectic) surrounded by the ground-mass of dark solid solution mottled with minute patches of secondary tin; in the slowly-cooled specimen (fig. 29) the quantity of

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* The laminæ of secondary tin, seen in fig. 27, are, however, only found in very slowly-cooled specimens—they evidently result from aggregation during this process.

secondary tin is much larger, while it has segregated into masses which compare in size with the primary tin in the same section; it would seem, in fact, that in this case a considerable proportion of the secondary tin had formed around the primary tin present, or had coalesced with it. In this alloy, as in the 16 per cent. alloy, it thus appears that the transformation which takes place at 149° C. involves the rejection of tin from the solid solution.

In view of these facts, and of the data supplied by the cooling-curves, the nature of the transformation in question may be considered. Three alternative explanations suggest themselves, viz. :—

(*a*) That the recalescence is due to the formation—on cooling—of a compound which only gradually dissociates on heating;

(*b*) That the recalescence arises from the decomposition of a compound which exists at higher temperatures, but which is only slowly formed on heating; and

(*c*) That the transformation is a change in the solid solution from a β to an α modification, the latter possessing a smaller solubility for tin than the former.

Hypothesis (*a*) may be rejected at once on the grounds that the maximum heat effect of the transformation does not occur at a concentration of tin which corresponds to any simple atomic formula, while the formation of a compound at the critical point in these alloys would lead us to anticipate that the slowly-cooled alloys—in which the reaction had been permitted to take place—would be more homogeneous than the quenched alloys in which the reaction had been inhibited, whereas the reverse is the case.

Hypothesis (*b*) would agree with the microscopic evidence, but the difficulty still remains that the maximum does not coincide with any simple atomic ratio. The nearest simple formula would be Pb_3Sn, and this would place the maximum at a concentration close to 16 per cent. of tin. This hypothesis has, however, to face the difficulty that there is no change of shape in the liquidus curve to correspond to the existence of such a compound; the liquidus, as determined in the present experiments and in those of ROBERTS-AUSTEN already cited, shows no signs of either a maximum or a break of continuity, while there is also no sign of any absorption of heat at any temperature between the liquidus and the solidus which might account for the formation of such a compound in that range of temperature. On this ground, hypothesis (*b*) must also be rejected.

The remaining explanation is the one which appears best to fit the facts. On this view the solid solution of tin in lead, when it contains more than 8 per cent. of tin, is capable of existing in two forms which may be called α and β respectively. The saturated (β) form of this solution, containing 16 per cent. of tin (approximately), passes into the α form on cooling to 149° C., and at that point rejects a certain amount of the dissolved tin in a finely divided "secondary" state. It is probable that the solubility of tin in the α body decreases still further as the temperature falls, but this decrease is certainly slight—its possible existence, however, makes it difficult to give any estimate of the solubility of tin in the α body at its transition temperature. On heating, the reverse change (from α to β) only takes place gradually, a fact which is partly accounted for by the slowness with which the β body takes up its full amount of tin. When the concentration of tin in the β body is lower than 16 per cent., the transformation on cooling is retarded until a lower temperature is reached; at the same time the intensity of the reaction falls off until, with a tin content less than 8 per cent., the β form appears to remain stable down to the temperature of liquid air. The fact that the intensity of the reaction falls off so markedly as the concentration of tin falls below 16 per cent. suggests that the actual separation of the tin itself is to some extent the source of the heat evolved, but it is not at present possible to discriminate between the various possible sources of heat in a complex reaction. The fact, however, that both the temperature and intensity of a change of this kind varies with the concentration of the dissolved element finds it analogue in the higher arrest-points of low-carbon steel.

A point of some difficulty yet remains to be dealt with. The data of the cooling-curves show that this heat-evolution diminishes to zero at or near the concentration of the eutectic alloy, and it is therefore evident that the transformation is confined to the structurally free lead constituent, the lead-rich constituent of the eutectic taking no part in the reaction. This fact can only be reconciled with the Phase Rule by supposing that while the structurally free β solution and the lead-rich constituent of the eutectic must be the same phase when first formed, yet the lead constituent of the eutectic retains the β state (in meta-stable equilibrium) when the transition temperature is passed. This explanation is rendered probable by the observation already described, that the crystallites of the lead constituent are generally completely surrounded by a sheath of pure tin which separates them from the lead constituent of the eutectic; this envelope of tin no doubt serves to prevent the propagation of the reaction from the structurally free β body to the corresponding constituent of the eutectic.

The view that owing to the retention of the β state in a meta-stable form the lead-rich constituent of the eutectic is not identical with the stable α body is further borne out by an examination of the densities of the alloys, which have been carefully determined for this purpose. The density of the α body containing 16 per cent. of tin (part of which is present as free "secondary" tin) is found to be 10·31, while the density of pure tin is 7·30. Taking the percentage composition of the pure eutectic at 37·07 per cent. of lead and 62·93 per cent. of tin, and supposing the lead-rich constituent of the eutectic to hold 16 per cent. of tin in solution, the percentage composition of the eutectic in terms of its actual constituent phases becomes 44·13 per cent. of lead-rich β constituent and 55·87 per cent. of tin. From the observed density of the eutectic, an obvious calculation shows that the density of the lead-rich constituent must be 10·38. The density of the lead-rich constituent of the eutectic, *i.e.*, of the β body in the meta-stable state, is thus 0·07 higher than that of the stable α body with the same amount of tin. This result fully agrees with the view that the α body has deposited some of its tin content in the free state, with an increase of volume.

The equilibrium diagram of the lead-tin alloys, as based upon the data and inferences given above, is shown in fig. 30. The diagram consists in all of eight fields or regions corresponding to different states of the alloys. In field No. 1, lying above the liquidus AEB, the alloys are homogeneous liquids. In field No. 2, bounded by the lines AE, EC, CA, the alloys consist of a mixture of liquid and crystals of the lead-rich β body; it should, however, be noted that while the line EC and the position of the point C have been determined, the line AC has not been fixed experimentally and is therefore drawn as a dotted line, but its true position is not likely to depart widely from that indicated. In field No. 3, bounded by AC, CF, FE, EPb, PbA, the alloys consist of the homogeneous β body, which is a solid solution of tin in lead which is saturated at a temperature of 182·5° C. with a tin content of a little more than 16 per cent. The point F, lying upon the line of the α/β transformation at the point where that transformation first reaches its highest temperature (at a concentration of 18 per cent. of tin), probably represents the limit of saturation of the β body at 149° C., and for that reason the limit of the region of pure β has been drawn from C to F; this line also is to be regarded as tentatively drawn. The curve from F towards E has been prolonged vertically downward, since no trace of the β/α reaction can be found in alloys containing less than 8 per cent. of tin.

In region No. 4, bounded by CE, EG, GF, FC, the alloys consist of saturated β plus eutectic or—in terms of phases—of saturated β and tin. In region No. 5, bounded by FG, GK, KE, EF, the alloys consist of the α body (a saturated solution of tin in lead saturated at a lower concentration of tin than 18 per cent.) plus eutectic plus secondary tin, the eutectic itself consisting of tin plus the β body in a meta-stable condition. In terms of phases this region would contain the α body plus tin if complete equilibrium were attained, but in all cases so far studied meta-stable β was present. Region No. 6, bounded by BE, ED, DB, contains alloys consisting of liquid plus crystals of pure or very nearly pure tin. Region No. 7, bounded by ED, DH, HG, GE, comprises alloys consisting of tin plus eutectic or—in terms of phases—of tin plus the β body in a stable state. Finally, in region No. 8, bounded by GH, HSn, SnK, KG, the alloys contain tin plus eutectic or—in terms of phases—tin plus meta-stable β body.

The Eutectic Alloy of Lead and Tin.

The percentage composition of the eutectic alloy has been determined with special care. The method adopted consisted in preparing an alloy of a composition known to be approximately that of the eutectic and preparing a micro-section. On examining the section it was possible to detect the presence of a very slight excess of either of the constituents, thus differentiating between alloys which could not be definitely separated by the indications of the pyrometer alone. It was found that in a small ingot of such an alloy, particularly if slowly cooled from fusion, there was generally a slight concentration of tin towards the top of the ingot and a corresponding small concentration of lead near the bottom. By the aid of the microscope, however, specimens free from excess of either constituent could be picked out, and these were submitted to careful chemical analysis. The composition as thus determined is found to be :—

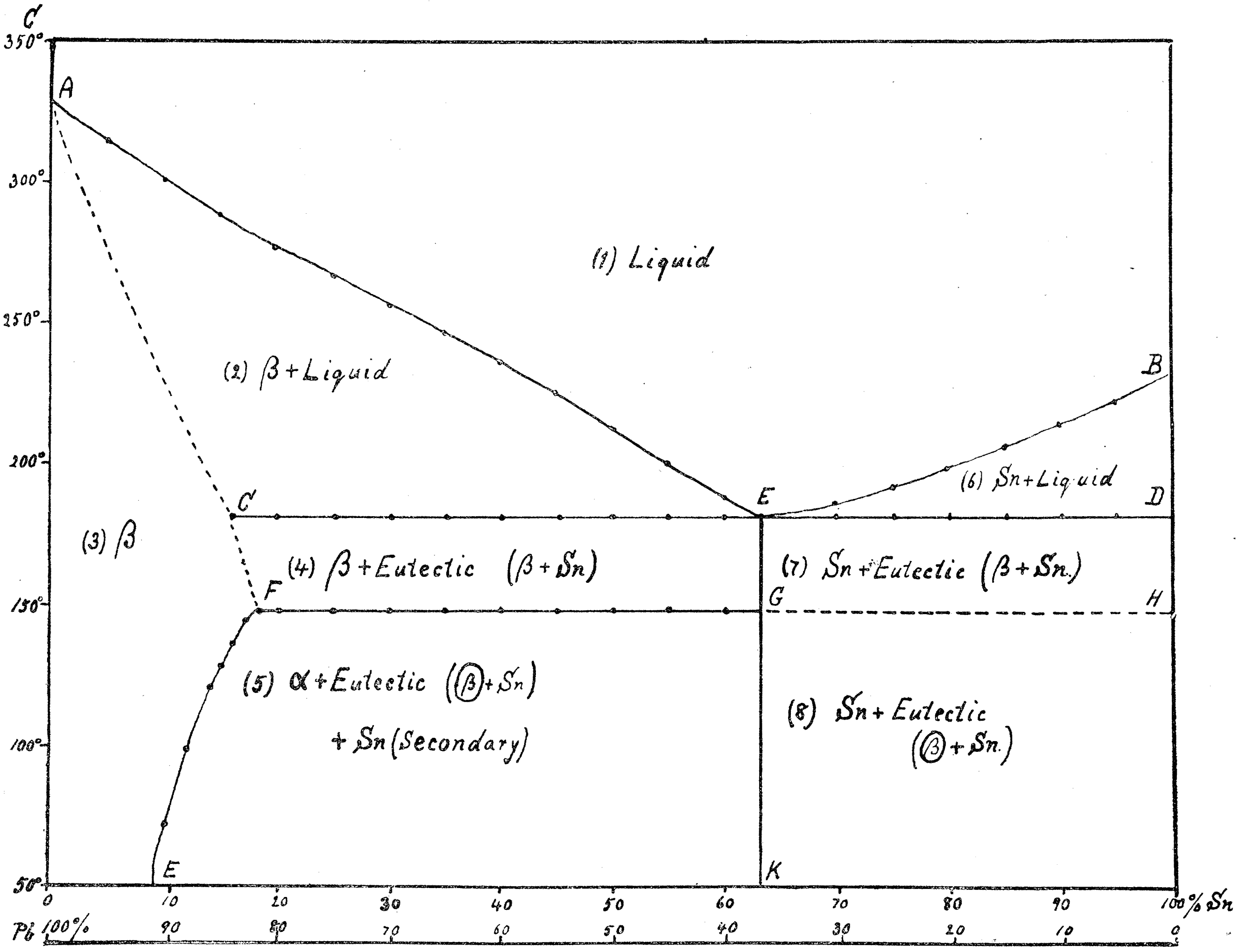

Fig. 30.

Lead	37·07 per cent.
Tin	62·93 ,,

and this result agrees closely with the figures given by Guthrie, and derivable from Roberts-Austen's diagram, although it is believed that owing to the greater refinement introduced by the use of the microscope the present determination is probably more accurate, since even very delicate pyrometric observations fail to detect any difference in freezing-point between alloys lying between 62·5 and 63·5 per cent. of tin; GUTHRIE's method of separation, by liquation, was necessarily subject to the same inaccuracies.

From the data as to the chemical composition, constitution and density of the eutectic alloy and its two component phases as arrived at in the earlier parts of this paper, it is possible to calculate the volume composition of the eutectic alloy. The eutectic has been found to consist of 55·87 parts of tin and 44·13 parts of β per cent., the densities of tin and of the β body being 7·30 and 10·38 respectively, while the density of the eutectic is 8·40. The volumes of free tin and of the β body present in 100 grammes of the eutectic alloy are therefore equal to 55·87/7·30 and 44·13/10·38 respectively; this gives the volume ratio of the two constituents as 7·653 to 4·252 or 1·80 to 1. An attempt was made to verify this volume relationship by means of planimetric measurements of the relative areas of the light and dark constituents of the eutectic as represented in some of the best defined of the photo-micrographs reproduced in figs. 34, 35 and 36, but the results varied too widely to allow of any satisfactory deduction. Consideration of the fact that the structure of the eutectic as shown in these photographs frequently assumes the form of plates or rods of one constituent embedded in the other at once serves to explain these variations; in the case of a bunch of parallel needles of the β body lying in a matrix of tin, the relative areas of the cross-sections as seen in a micrograph would depend upon whether the plane of the section ran parallel to or at right angles to the length of the needles. These variations are, of course, further accentuated by the fact that the eutectic structure is always somewhat minute, so that the areas measured at any one time are confined to a very minute portion of the actual alloy.

Examples of the typical micro-structure of the lead-tin eutectic alloy are given in figs. 31 to 36 inclusive (Plate 8), all of which have been taken from samples of pure eutectic prepared in the manner described above. Fig. 31 (magnification 600 diameters) shows an example of regular lamination, the layers of the two constituents lying approximately parallel; the photograph, however, shows the junction of two regions or "grains" in the eutectic, the general direction of these parallel bands being decidedly different in the adjacent "grains," while more or less constant throughout each region or "grain." In figs. 32 and 33 (magnification 300 diameters) a similar feature is shown over a larger area, fig. 33 showing the junction of three areas of different and more or less regular orientation. In figs. 31 and 32 it should be noticed that the regular pattern of the eutectic remains undisturbed up to the very edges of each region (the black dots in fig. 31 are small holes in the metal, not areas of β). As close observation has shown, this is a severe test of the accuracy with which the true eutectic composition has been attained in the synthesis of the alloy, the first effect of a slight addition of either constituent being to produce a slight coarsening of the structure—combined with a slight relative increase in the amount of the excess constituent—at the boundaries of these regions of similar orientation. To a very small extent this is the case in fig. 33, but it is clearly illustrated in figs. 36 and 37, which represent alloys containing a slight excess of tin (No. 36 represents an alloy with 64 per cent. of tin, magnified 200 times, while No. 38 represents an alloy with 65 per cent. of tin, magnified 600 times).

Figs. 34 and 35 show, under higher magnification (600 and 1200 diameters respectively), other types of eutectic structure of the "laminated" variety, but in this case the lamination is not rectilinear, while still preserving a certain regularity throughout well-defined regions. Study of these structures suggests certain conclusions as to the manner in which they have originated and as to their physical nature. Important evidence as to this may be obtained by viewing a specimen of pure eutectic, properly polished and etched, under oblique illumination with a low magnification. Fig. 39 is a photo-micrograph of such a specimen taken with a magnification of 12 diameters. A single photograph, however, gives a very feeble idea of the true appearance of such a specimen. Viewed in this manner the various regions of similar orientation already referred to are clearly differentiated in colour and brightness, owing apparently to the manner in which the incident light is reflected by the facets arising from the etching out of one constituent. The lustrous appearance, with its brilliant diffraction colours, however, is strikingly different from the "oriented lustre" observed when a similar section of pure metal is viewed in this way. The conclusion which is to be drawn from this difference is probably that while the eutectic has some form of crystalline structure, that form is different from that of pure metals. When the specimen of eutectic is rotated under oblique light, this difference becomes still more evident, and its character is revealed. In pure metals the various regions or grains—which are now well understood to be simply holomorphic crystals—characteristically exhibit a uniform brightness over their entire area, and, when the specimen is rotated, increase and decrease in brilliance according to the incidence of the light uniformly so far as the entire area of each crystal is concerned. The regions or grains of the lead-tin eutectic behave differently; in every position of the specimen the incident light appears to pick out some radial line or sector in each grain, and this line or sector appears bright; as the specimen is rotated the lighted sector appears to rotate in each crystal, thus giving rise to an appearance strikingly similar to that which is observed when a transparent section of a spherulitic mineral crystal is rotated under crossed Nicol prisms, except that the dark cross is not seen as such in the eutectic "grains." Examination of a number of such specimens has led the author to the view that the grains or regions into which masses of pure eutectic are always found to be divided probably represent true spherulitic crystals, *i.e.*, crystals which possess a radiating structure, but which in other respects are similar to the holomorphic crystals of pure metals. The effect of the radial structure on the mechanical behaviour of the metal must, however, be very marked. The detailed study of the phenomena accompanying plastic deformation of these alloys is, however, rendered very difficult by the presence of the second constituent. In the present case the β body is so much softer than the tin that on deformation it is immediately driven out at the surface, thus obscuring the deformation phenomena of the tin matrix which constitutes the greater bulk of the alloy.

A study of the micro-structure of the lead-tin eutectic shows—as would be anticipated from the volume-relation of the two substances—that in most sections the β body can be seen definitely embedded in and surrounded by the tin, which has therefore been called the matrix. Whether the two bodies actually crystallise simultaneously or whether there is a slight interval of time or of temperature between their solidification has yet to be ascertained, but it would appear probable that at each point of the eutectic where solidification was beginning the crystallisation of the predominant constituent determined the arrangement of the whole mass; on that view, in the present case, the tin crystallised out in the form of radiating dendrites whose arms met and more or less interpenetrated those of adjacent dendrites, the lead—liquid or solid—being forced into the interstices, whose shape would vary according to the form of each particular dendrite. Whether this picture of the solidification process be accurate or not, the existence of clearly marked spherulitic structure throughout the individual grains of the eutectic proves quite definitely that the solidification of each grain must have proceeded from a centre, and that therefore one or both of the constituents are arranged in some definite crystalline manner throughout each grain; the alternative view that each separate particle of each constituent might be a minute independent crystal, having no systematic connection with its neighbours, being thus entirely discredited.

In the hope of throwing further light on the nature and structure of eutectic alloys, the micro-structure of lead-tin alloys of eutectic composition was investigated under other conditions. In one experiment the specimen of alloy, which originally showed the laminated structure usually associated with the term "eutectic," was exposed to prolonged heating at a temperature of 175° C. (just below the melting-point of the eutectic). On subsequent examination it was found that the β body of the alloy had segregated into relatively large masses in the manner shown in fig. 38. In all other respects the alloy had preserved its true eutectic character, thus serving to show that the ordinary "typical" eutectic structure is a consequence only of the manner in which these alloys usually solidify from fusion, and is not an inherent property of alloys of that particular composition.

In connection with this line of enquiry it occurred to the author that a solid alloy of lead and tin of the eutectic composition might be produced by the method of SPRING,* *i.e.*, by strongly compressing clean fresh filings of the two metals by means of an hydraulic press. A small compressing apparatus was therefore prepared (by the kind co-operation of Dr. T. E. STANTON), and powdered lead and tin, mixed in the correct proportion of the eutectic composition, were compressed in it by the aid of a

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* SPRING, 'Bull. de l'Acad. Roy. de Belgique,' (2), vol. xlv. (1878), No. 6.

small testing-machine, pressures up to 35 tons per square inch being put on the metal. The small buttons of solid metal produced in this way were subsequently cut and polished for microscopic examination, and their appearance under a magnification of 80 diameters is shown in figs. 40 and 41. Fig. 40 is taken from a part of the specimen which had been subjected to severe flow under the action of the plunger, while No. 41 is taken from a part where the pressure had acted uniformly in all directions. It will be seen at once that this compound mass of metal can scarcely be regarded as a true alloy at all; the particles of lead and tin are merely juxtaposed and held together by surface cohesion. It is intended to observe these specimens from time to time, both when kept at the ordinary temperature and when maintained at temperatures just below the melting-point of the eutectic, with a view to detecting the process of diffusion which will probably occur, but so far the time has been too short to allow of definite results being observed.

For the purpose of furnishing a more delicate test of such a diffusion process, specimens of an alloy containing 17 per cent. of tin were prepared in a similar manner; their micro-structure is shown under a magnification of 80 diameters in fig. 42. Prepared from fusion and very slowly cooled, this alloy would be very nearly homogeneous, so that the difference between the true alloy and the mechanical mixture obtained by the compression process is very marked in this case.

The author is indebted to Dr. R. T. GLAZEBROOK, F.R.S., the Director of the Laboratory, for his kindly interest in the progress of the present research, and to his colleagues on the staff of the Laboratory for much valuable help in various details of the work.

DESCRIPTION OF PLATES (5–9).

PLATE 5.

Fig. 14. Alloy with 15 per cent. Sn after four weeks at 175° C. V. × 100 diameters.
„ 15. Alloy with 20 per cent. Sn after prolonged heating. V. × 300 diameters.
„ 16. Alloy with 45 per cent. Sn. V. × 200 diameters.
„ 17. Alloy with 63 per cent. Sn (eutectic alloy). V. × 300 diameters.
„ 18. Alloy with 65 per cent. Sn. V. × 200 diameters.
„ 19. Alloy with 74 per cent. Sn. V. × 200 diameters.

PLATE 6.

Fig. 20. Alloy with 85 per cent. Sn. V. × 200 diameters.
„ 21. Alloy with 95 per cent. Sn. V. × 200 diameters.
„ 22. Alloy with 99 per cent. Sn. V. × 200 diameters.
„ 23. Alloy with 10 per cent. Sn cooled from fusion. V. × 150 diameters.
„ 24. Alloy with 15 per cent. Sn cooled from fusion. V. × 150 diameters.

PLATE 7.

Fig. 25. Alloy with 16 per cent. Sn quenched in liquid air from 160° C. V. × 1000 diameters.
„ 26. Alloy with 16 per cent. Sn very slowly cooled after prolonged heating. V. × 1000 diameters.
„ 27. Alloy with 16 per cent. Sn very slowly cooled after long heating. V. × 1000 diameters.
„ 28. Alloy with 18 per cent. Sn quenched in liquid air from 160° C. V. × 1000 diameters.
„ 29. Alloy with 18 per cent. Sn very slowly cooled after prolonged heating. V. × 1000 diameters.

PLATE 8.

Fig. 31. Eutectic alloy showing regular lamination. V. × 600 diameters.
„ 32. Eutectic alloy showing junction of two "grains." V. × 300 diameters.
„ 33. Eutectic alloy showing junction of three "grains." V. × 300 diameters.
„ 34. Laminated eutectic alloy. V. × 600 diameters.
„ 35. Laminated eutectic alloy. V. × 1200 diameters.
„ 36. Alloy with 64 per cent. Sn. V. × 200 diameters.

PLATE 9.

Fig. 37. Alloy with 65 per cent. Sn. V. × 600 diameters.
„ 38. Segregated eutectic alloy. V. × 200 diameters.
„ 39. Eutectic alloy showing "spherulitic lustre." Oblique. × 12 diameters.
„ 40. Alloy of eutectic composition made by compressing the powdered ingredients. V. × 80 diameters.
„ 41. Alloy of eutectic composition from compressed powder. V. × 80 diameters.
„ 42. Alloy containing 17 per cent. Sn from compressed powder. V. × 80 diameters.

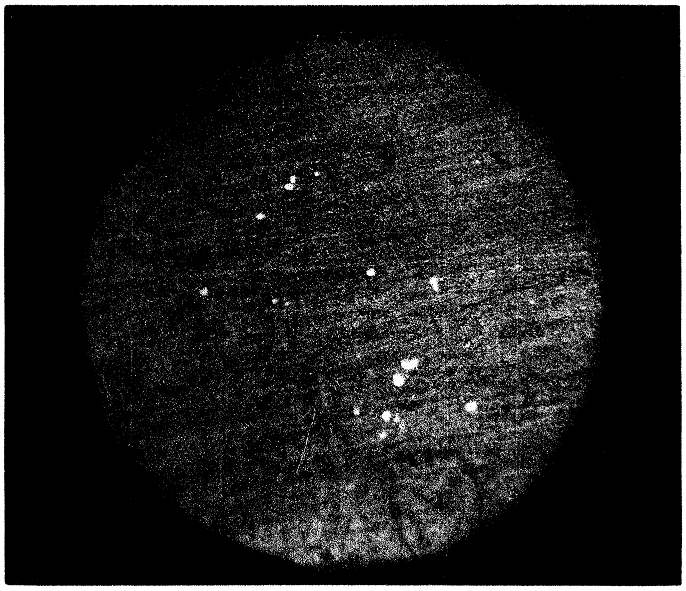
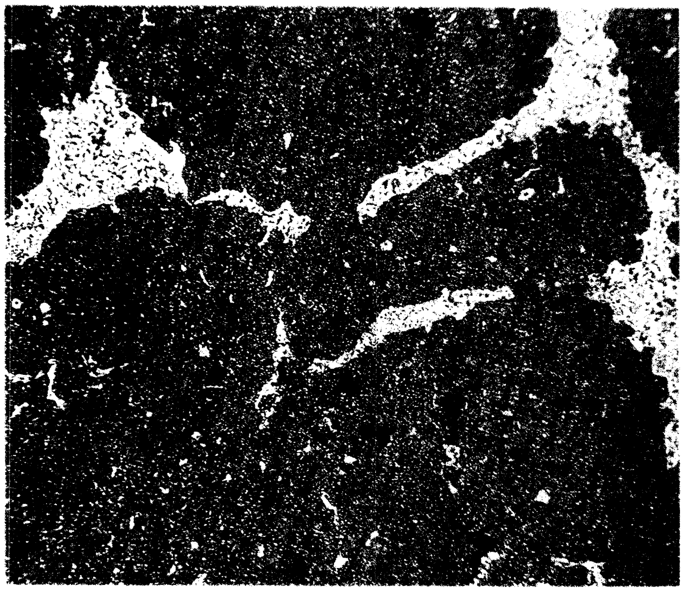


FIG. 14.



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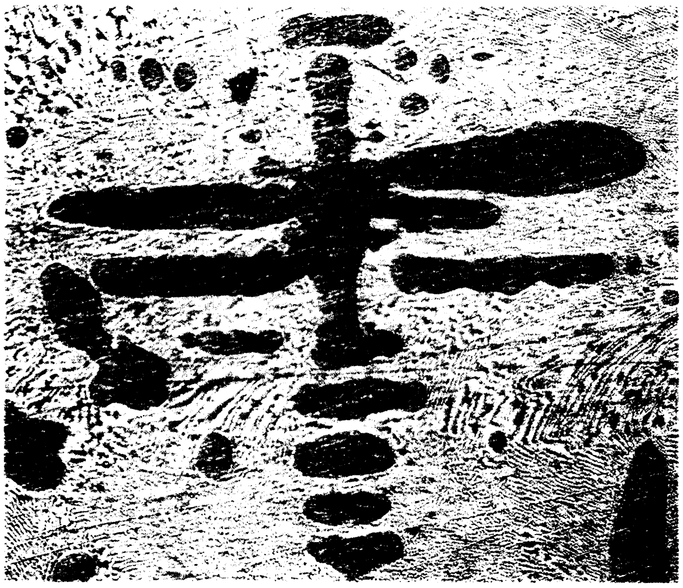

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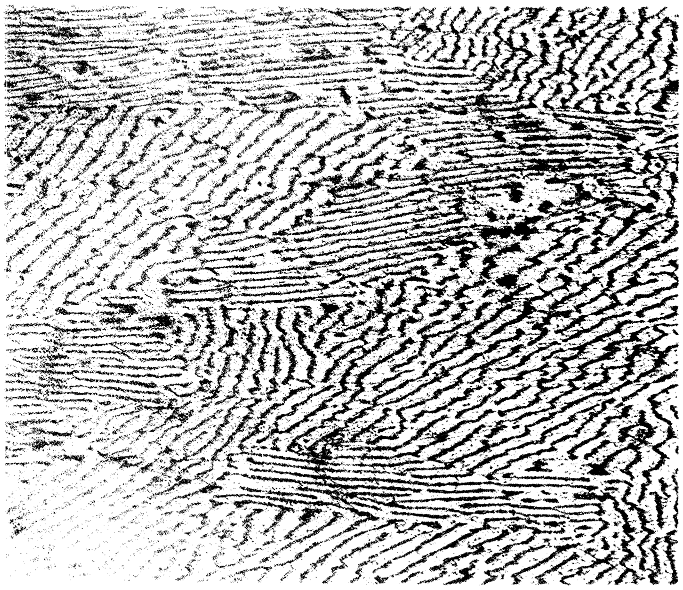

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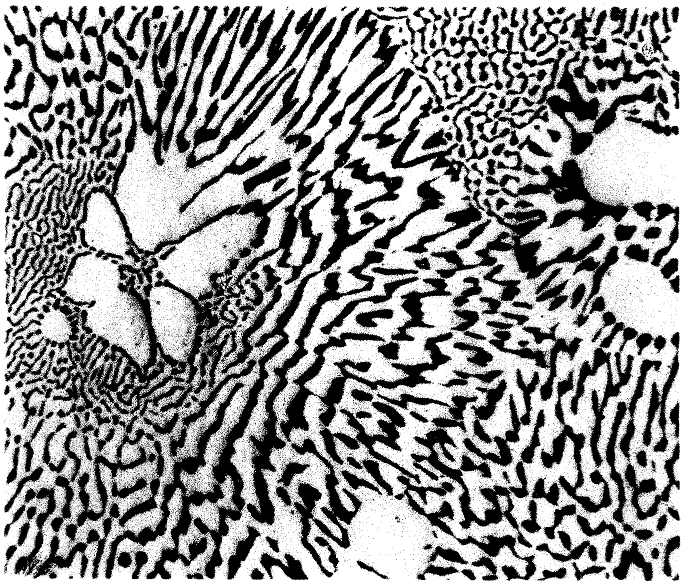

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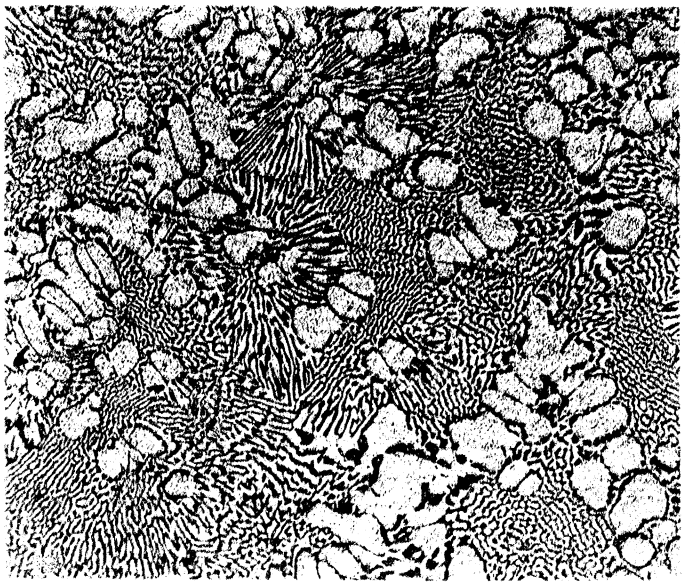

FIG. 19.

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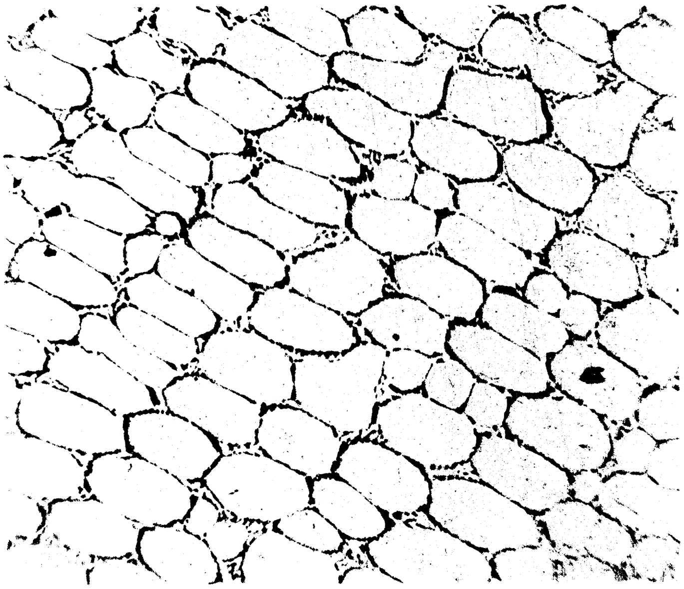

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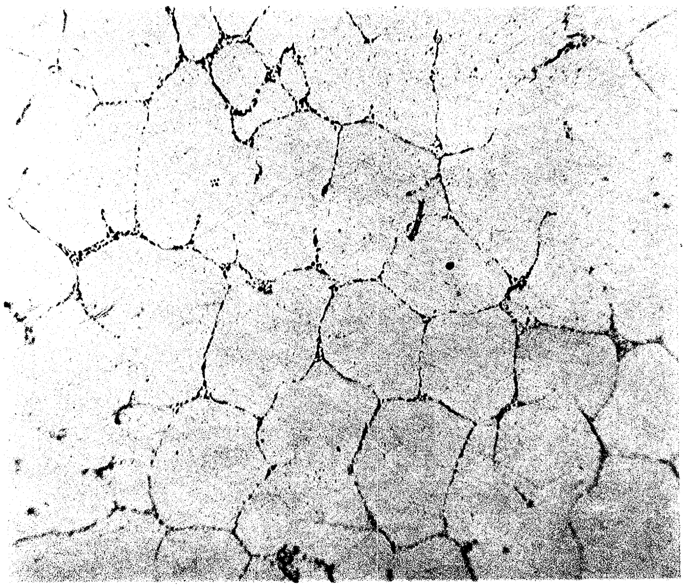

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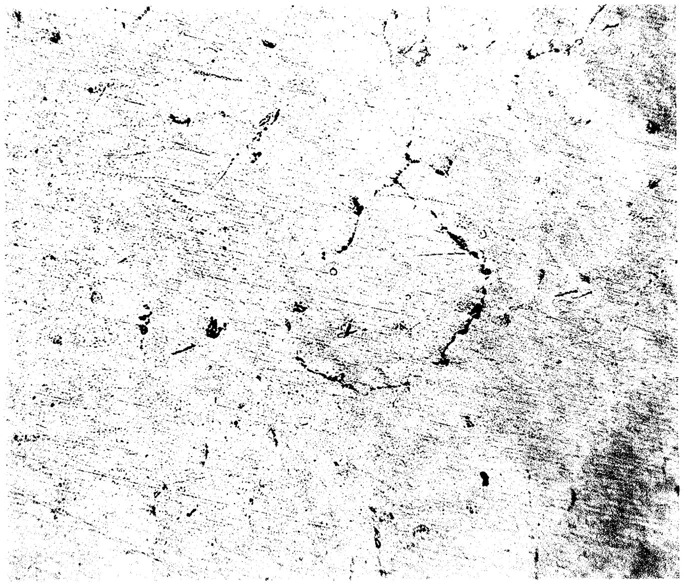

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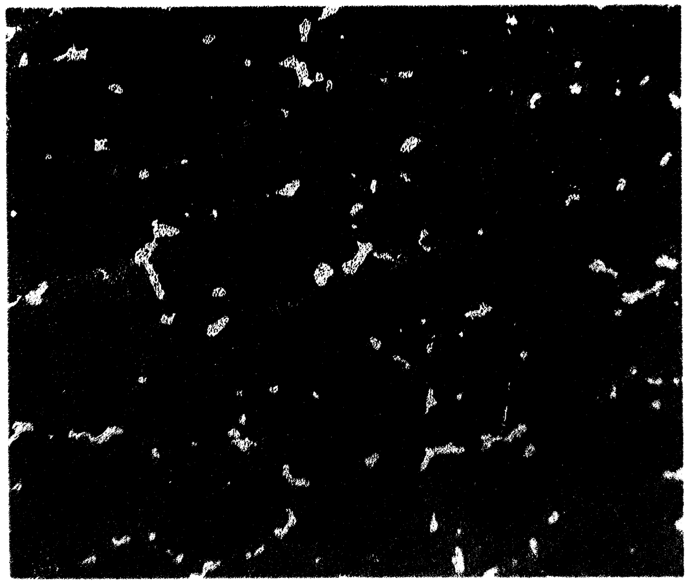

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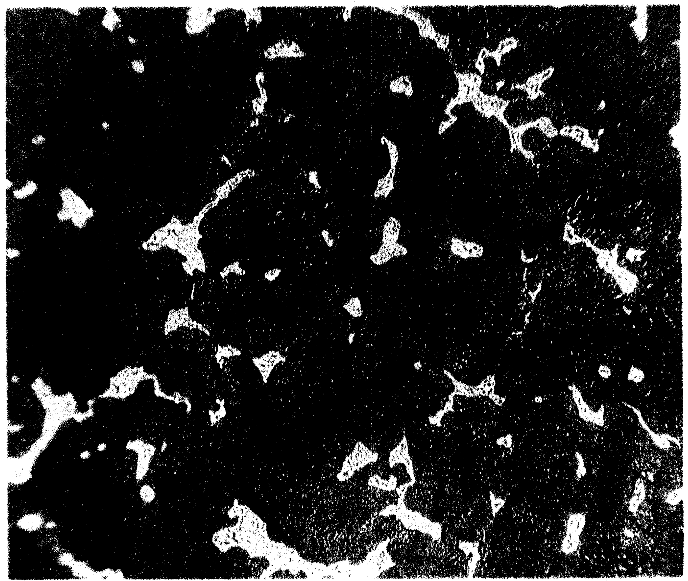

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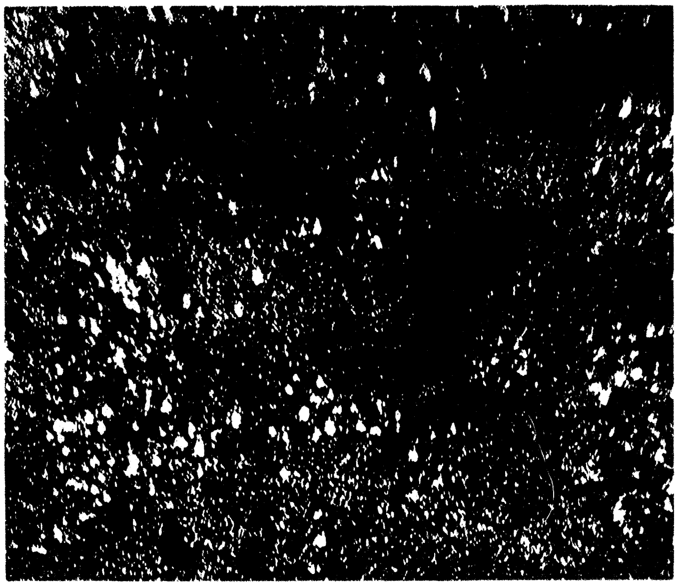

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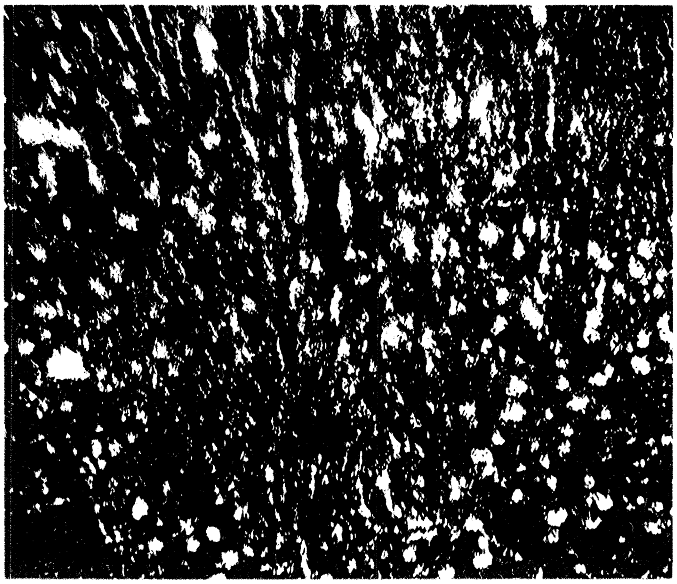
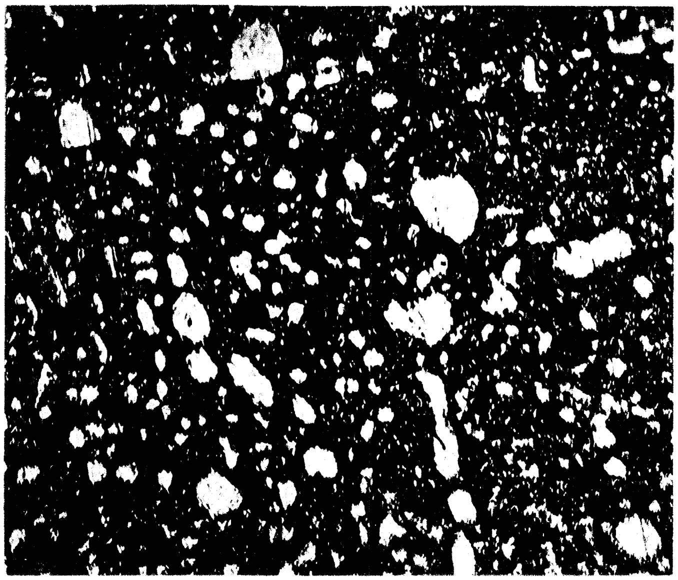


FIG. 26.

FIG. 27.

FIG. 28.



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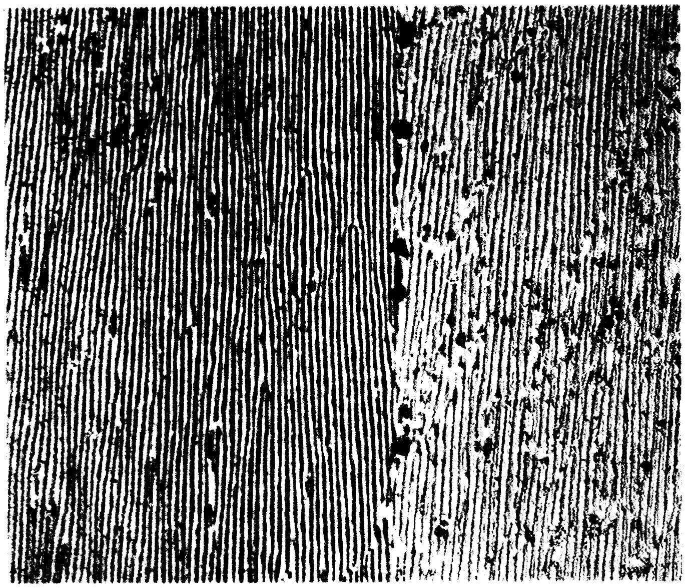

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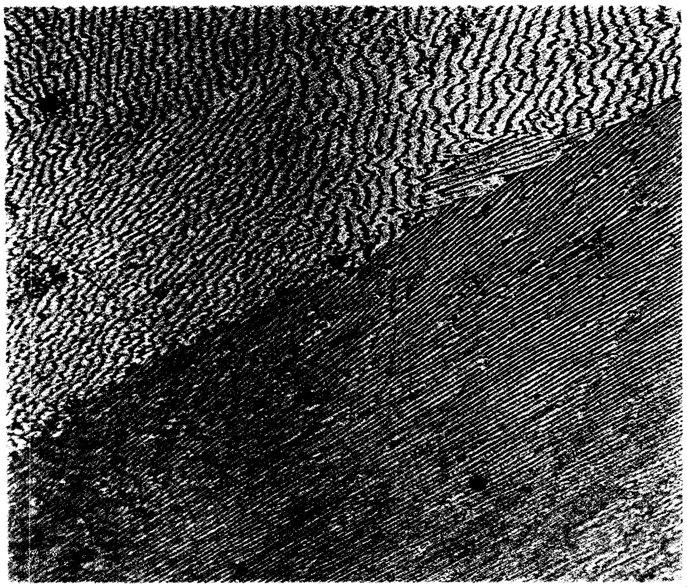

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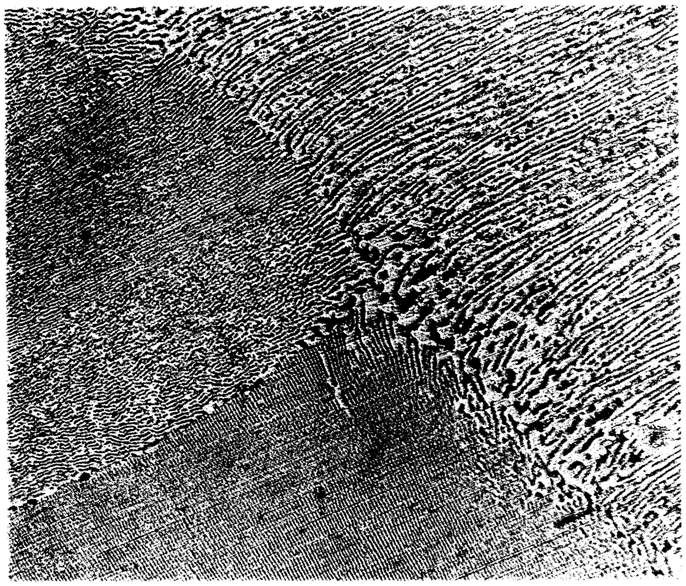

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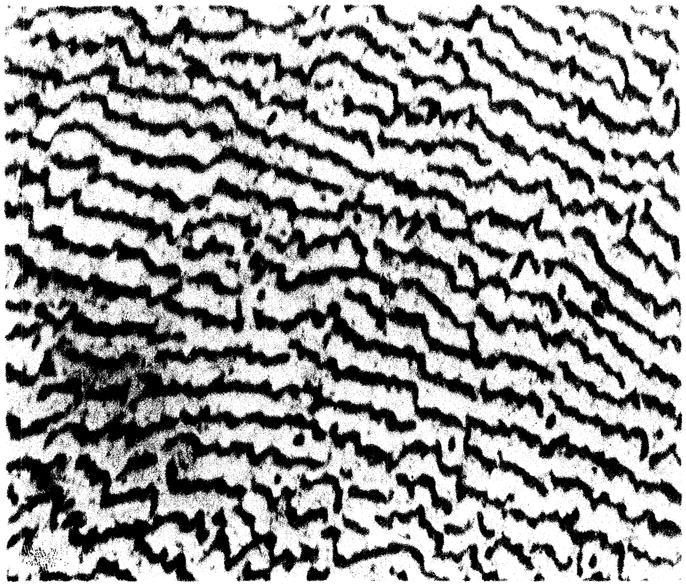

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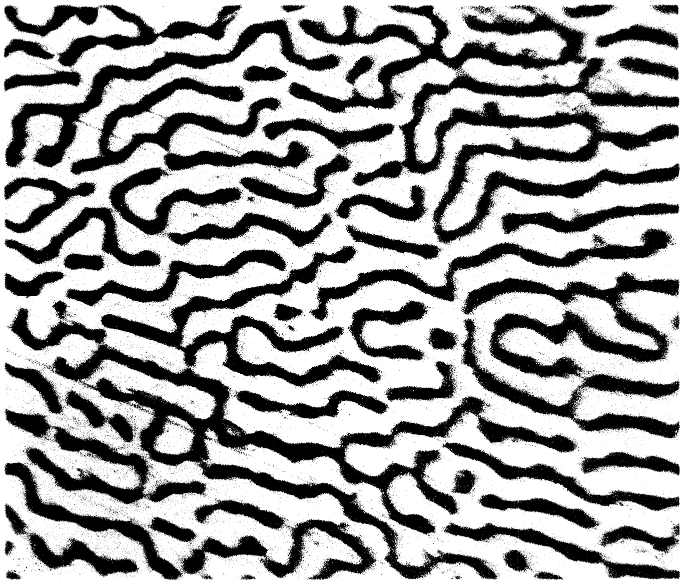

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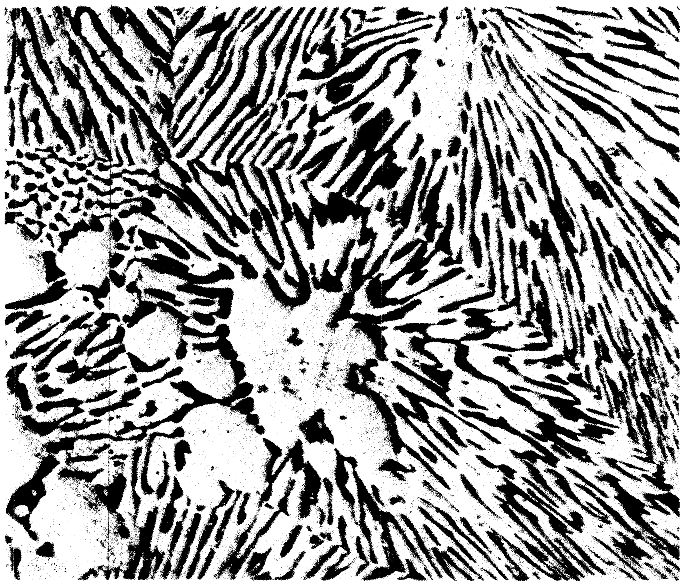

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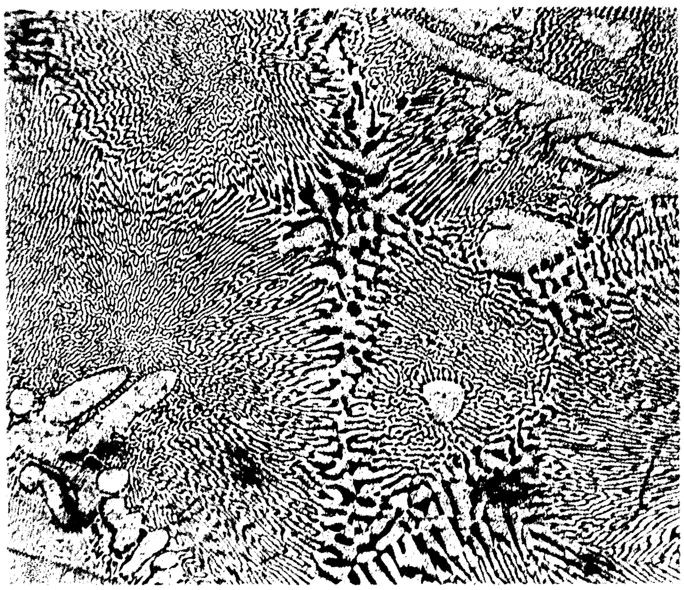

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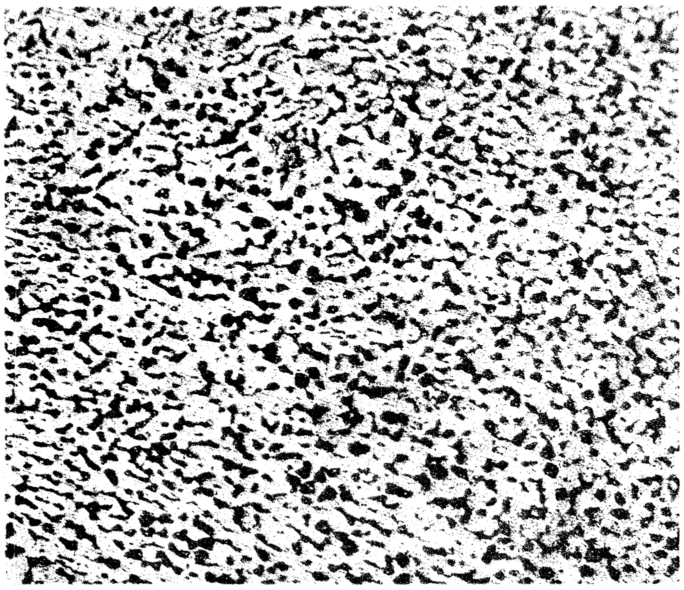

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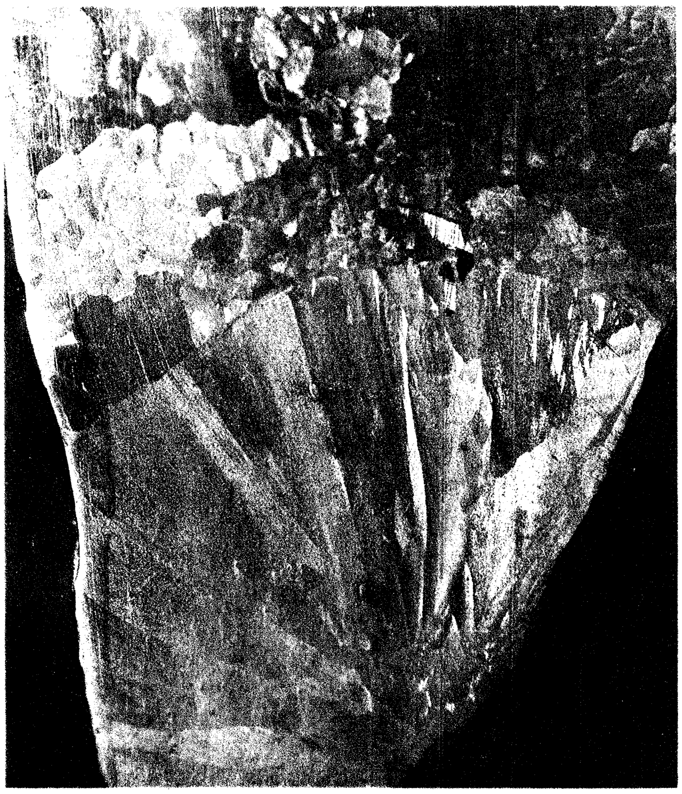

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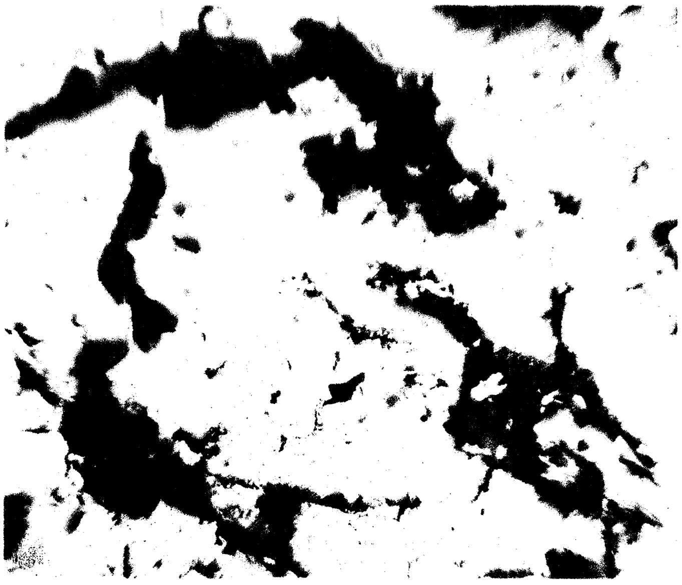

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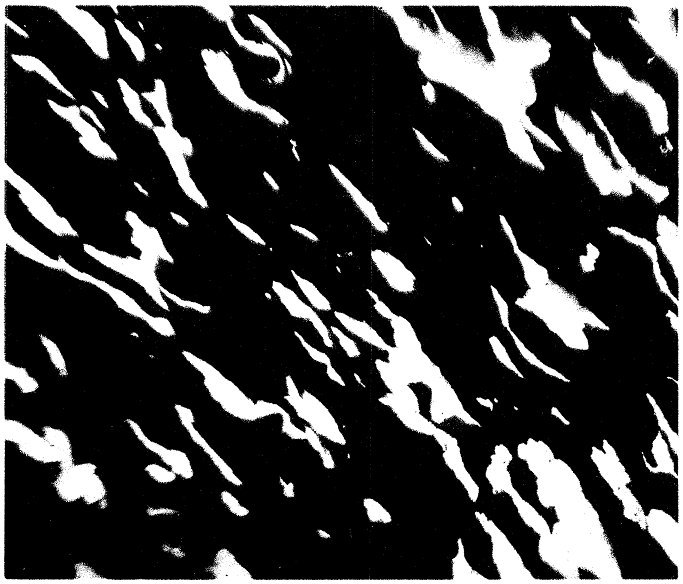

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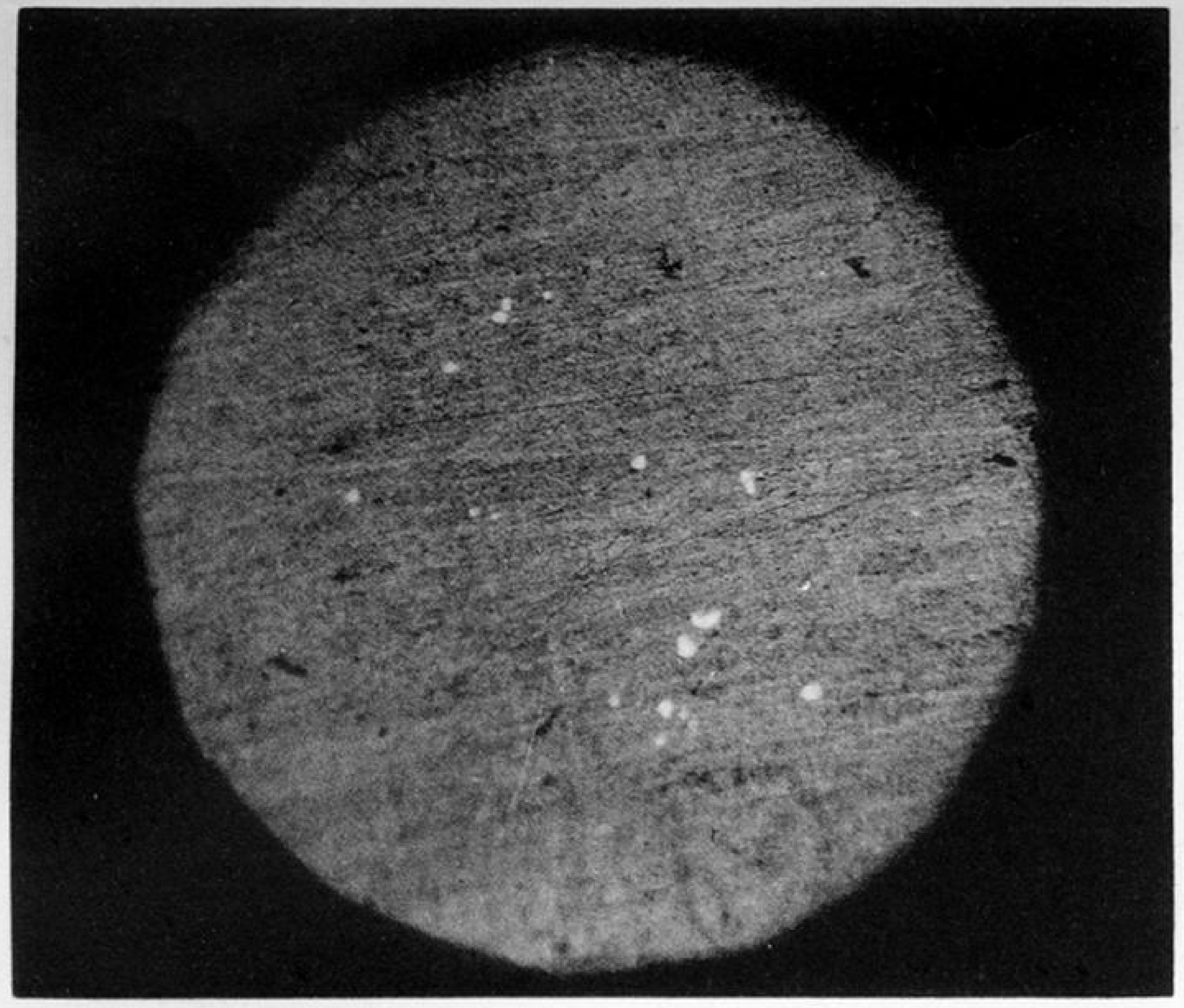

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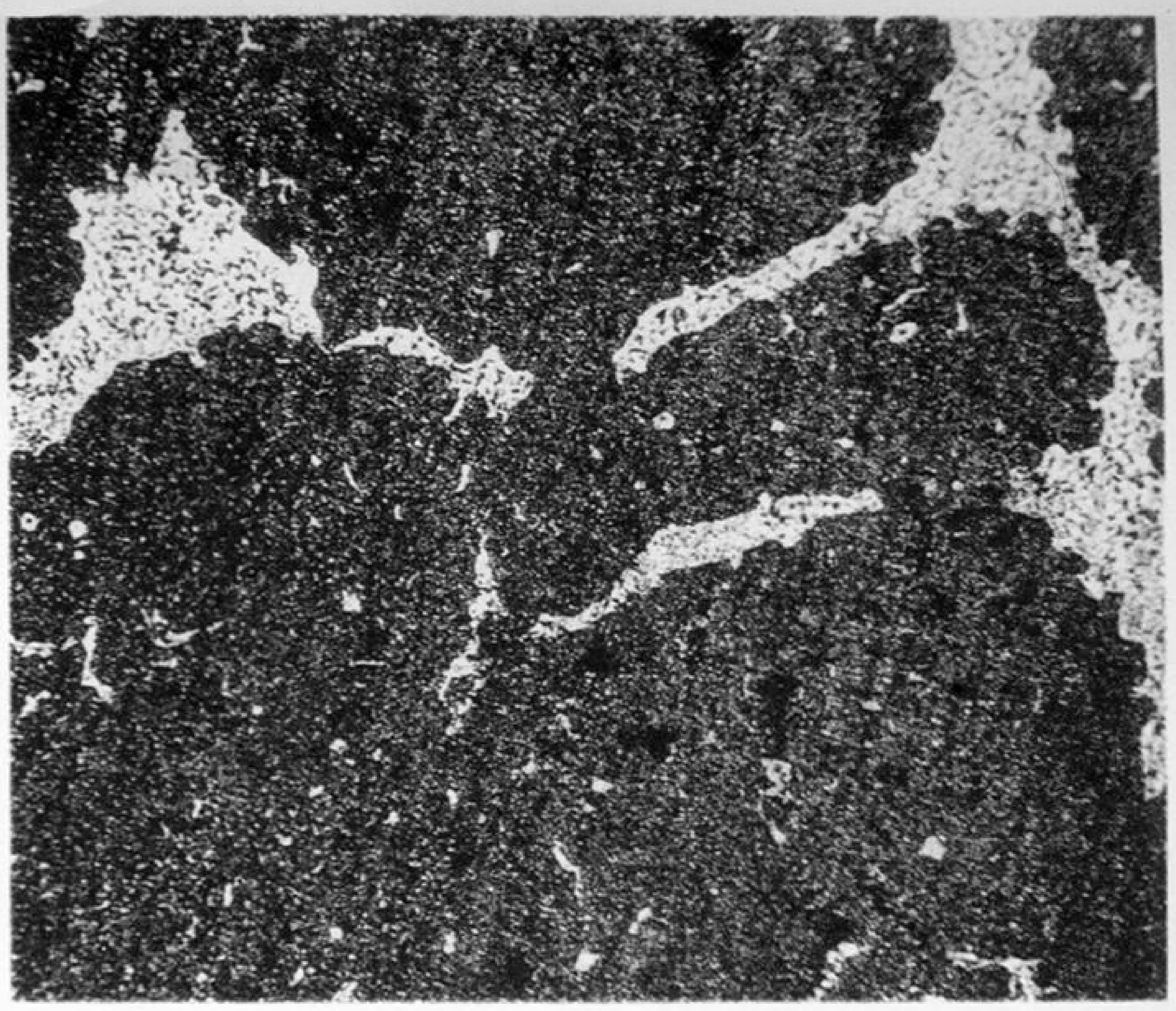

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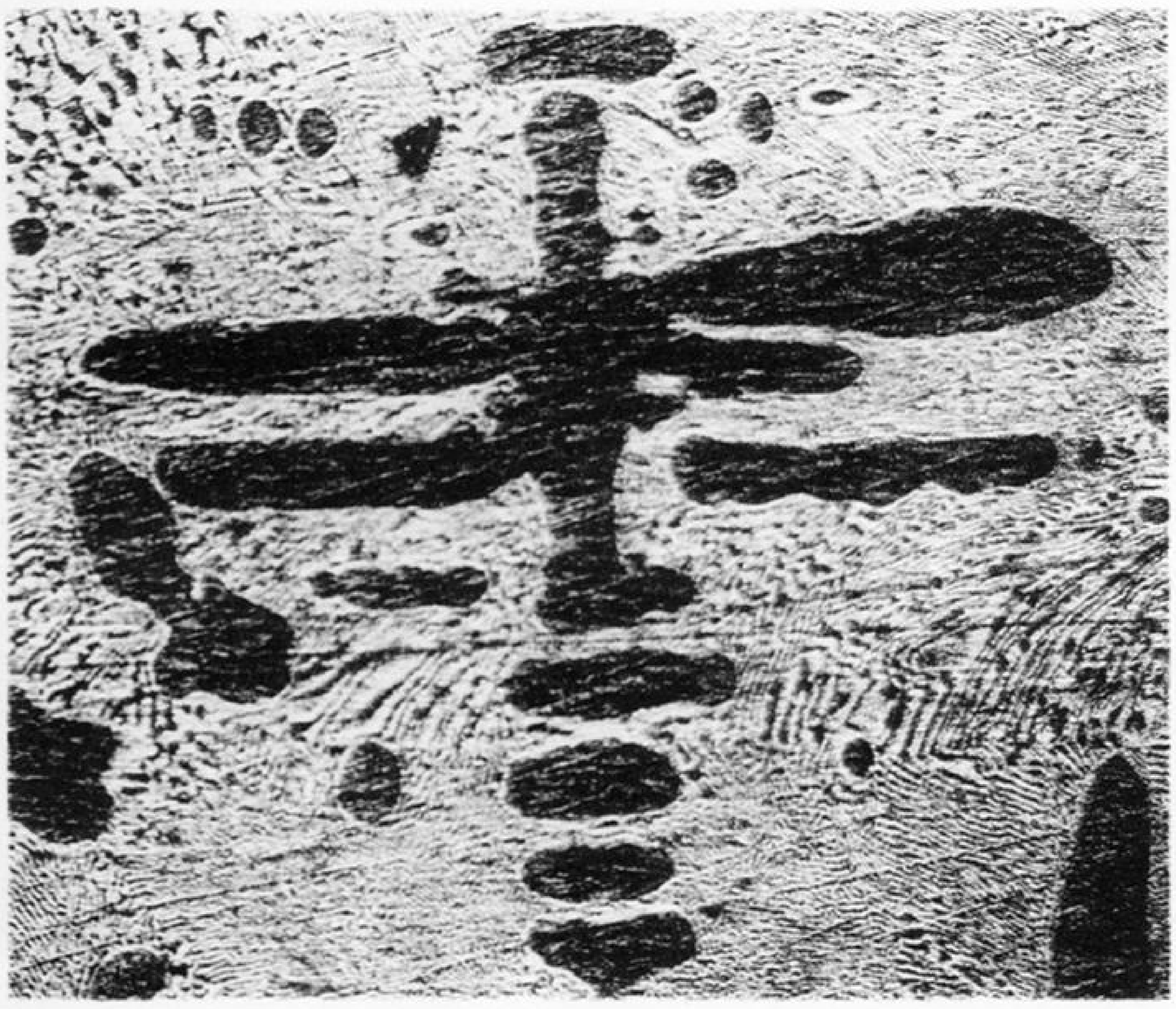

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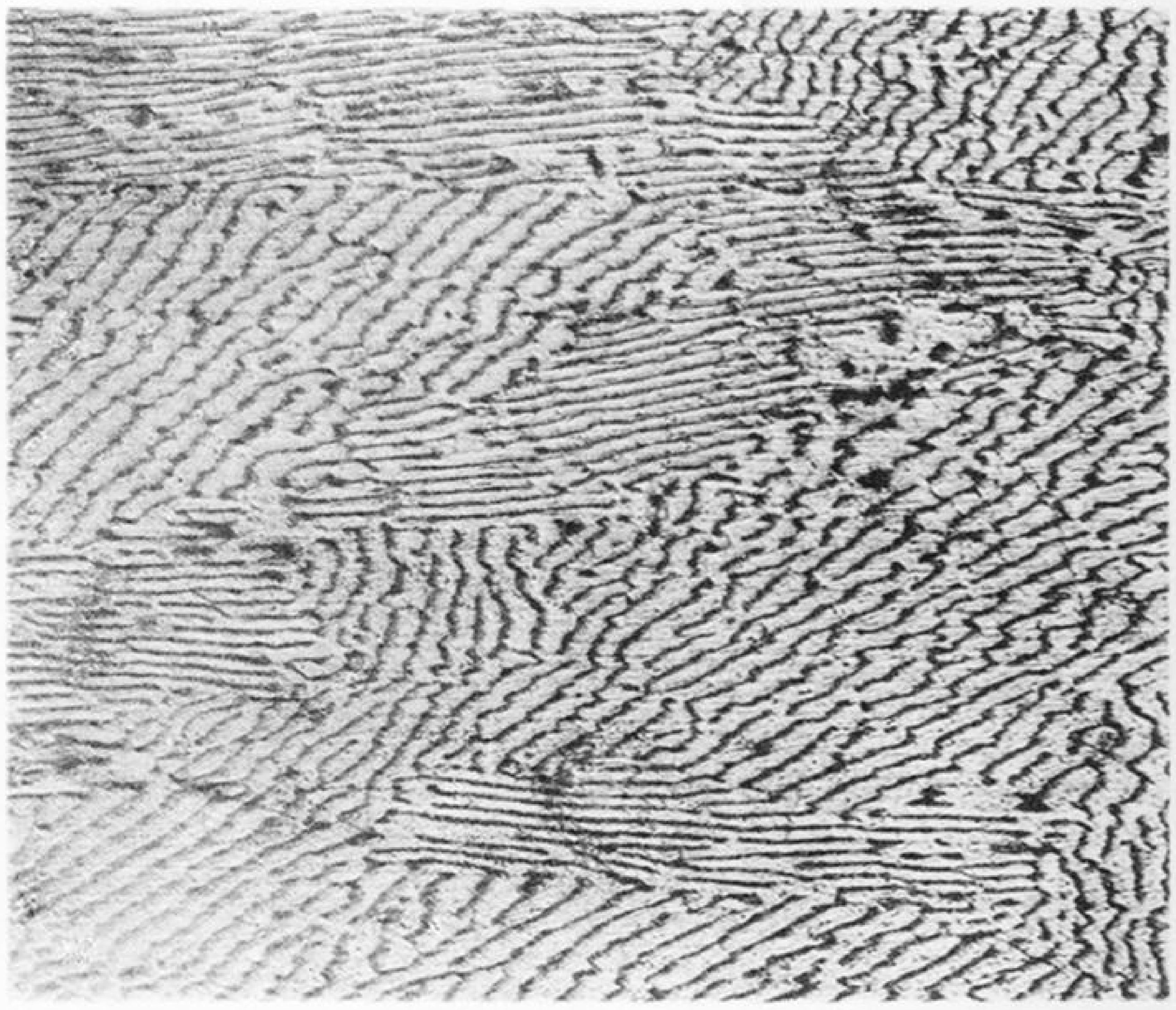

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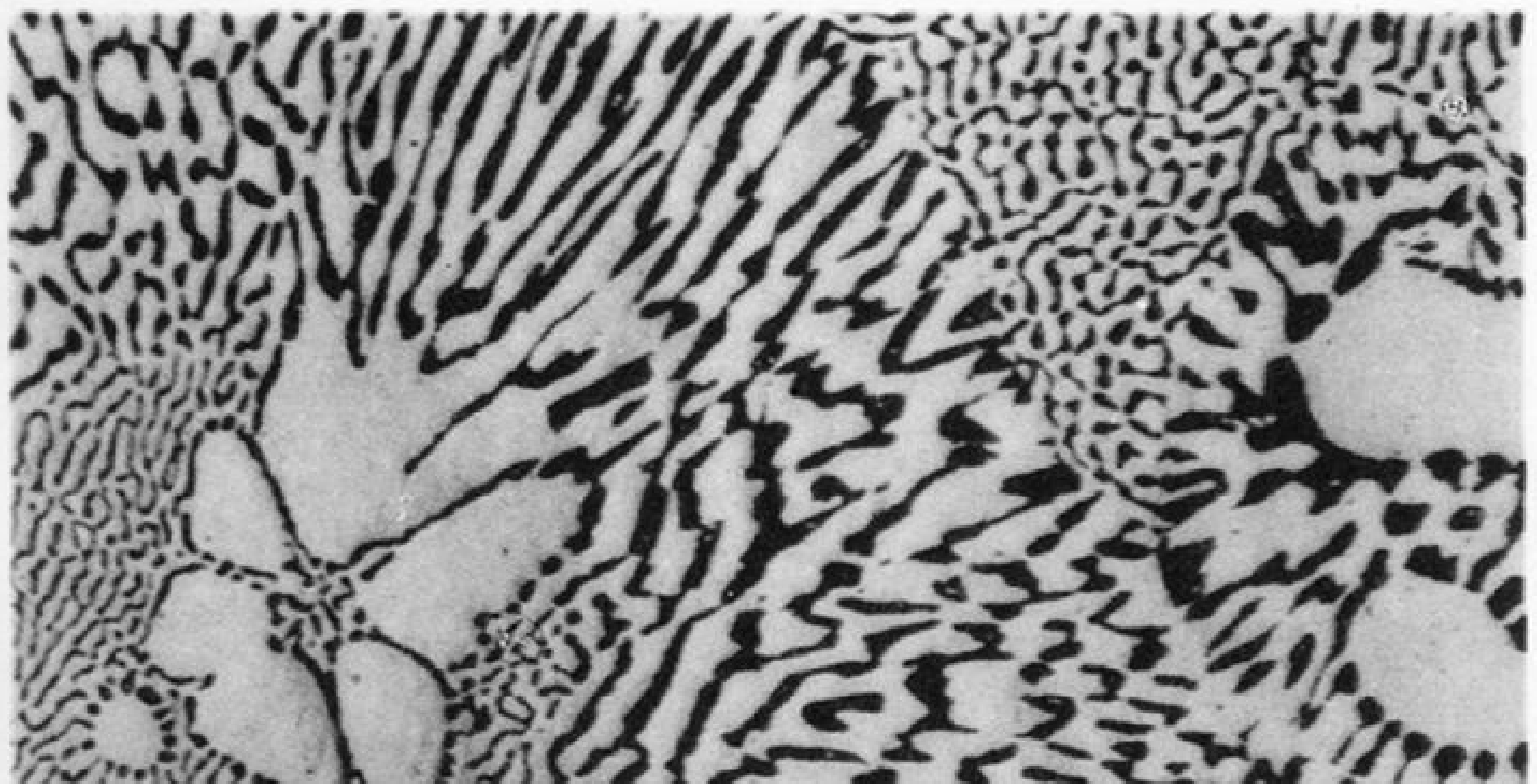

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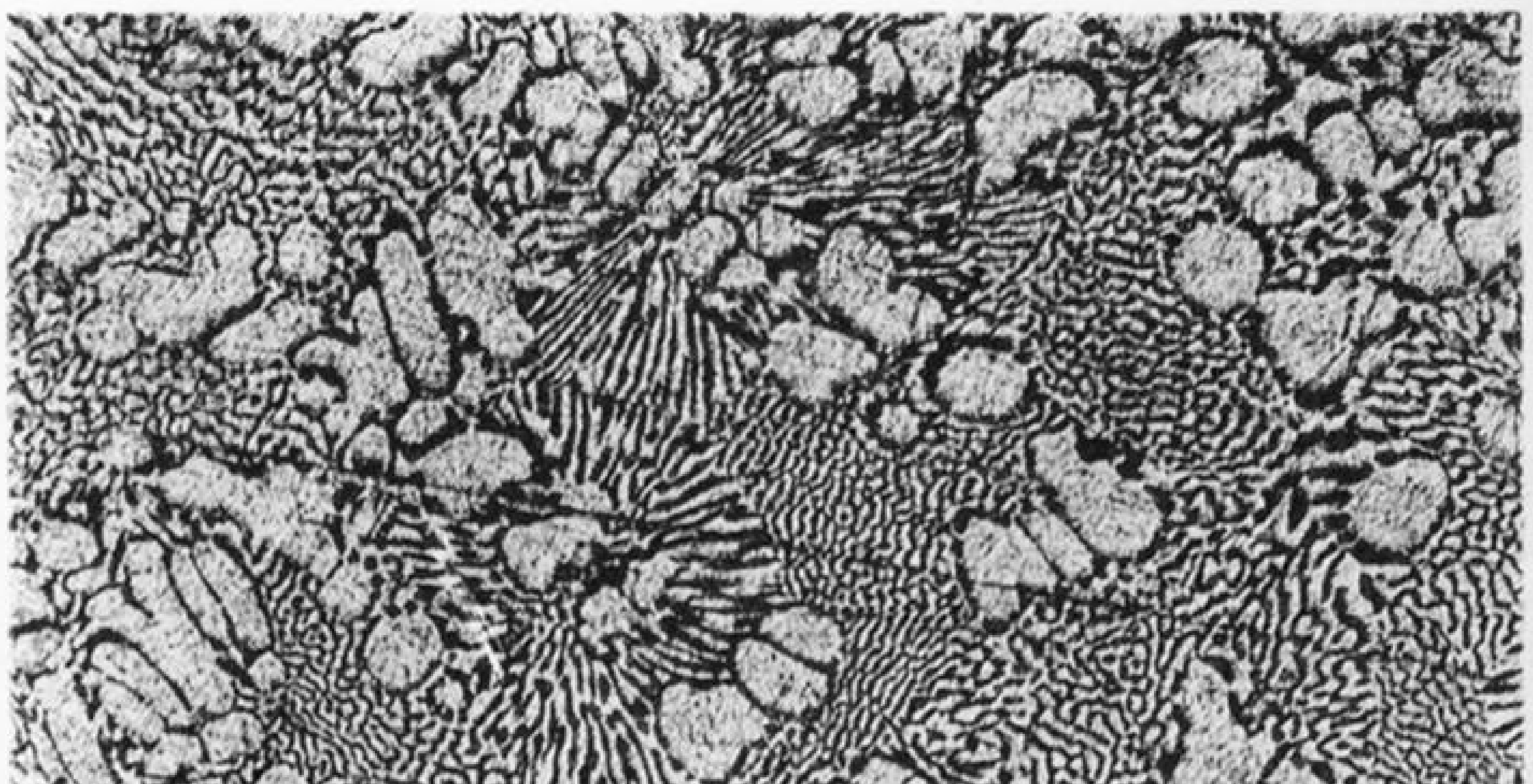

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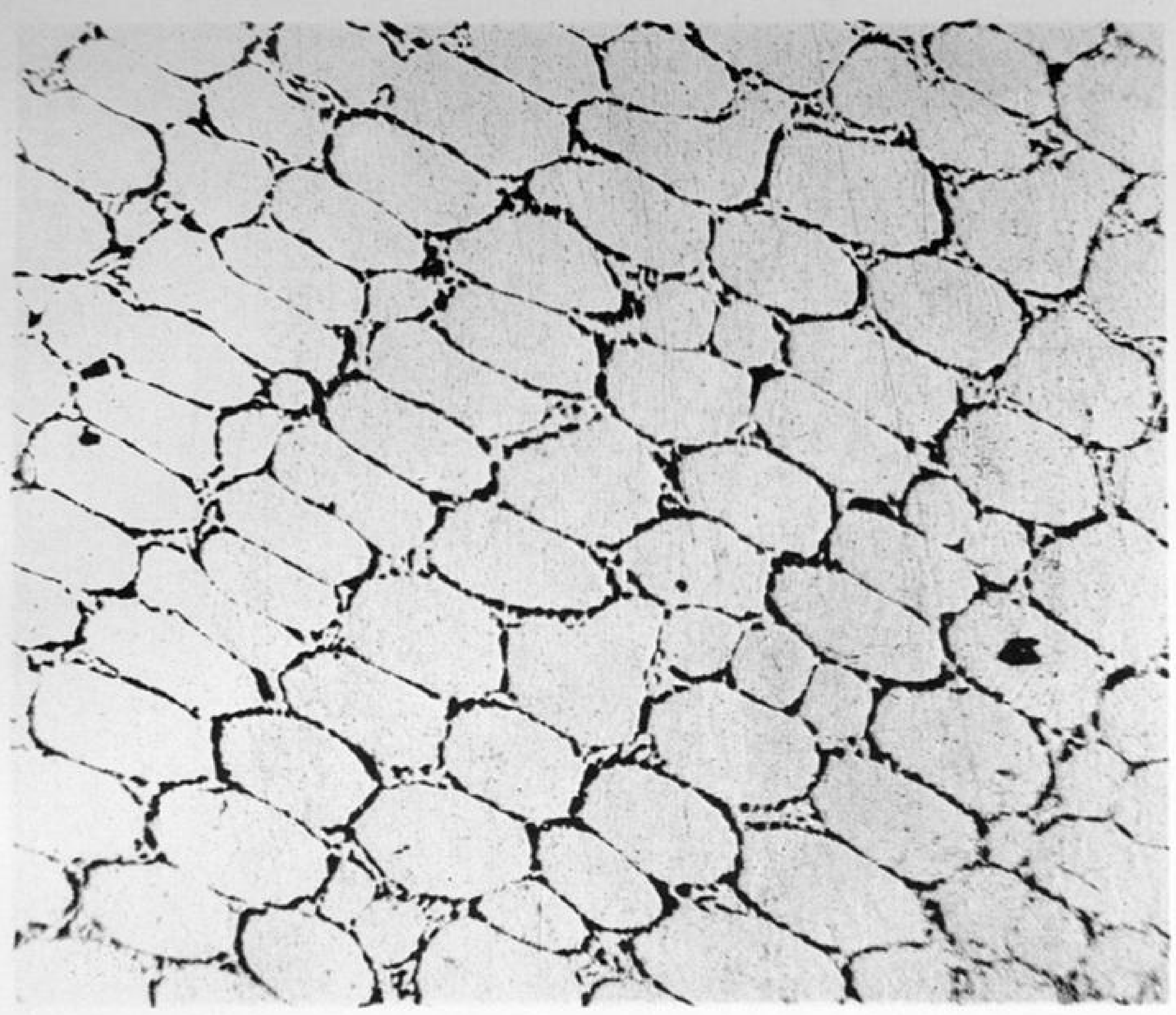

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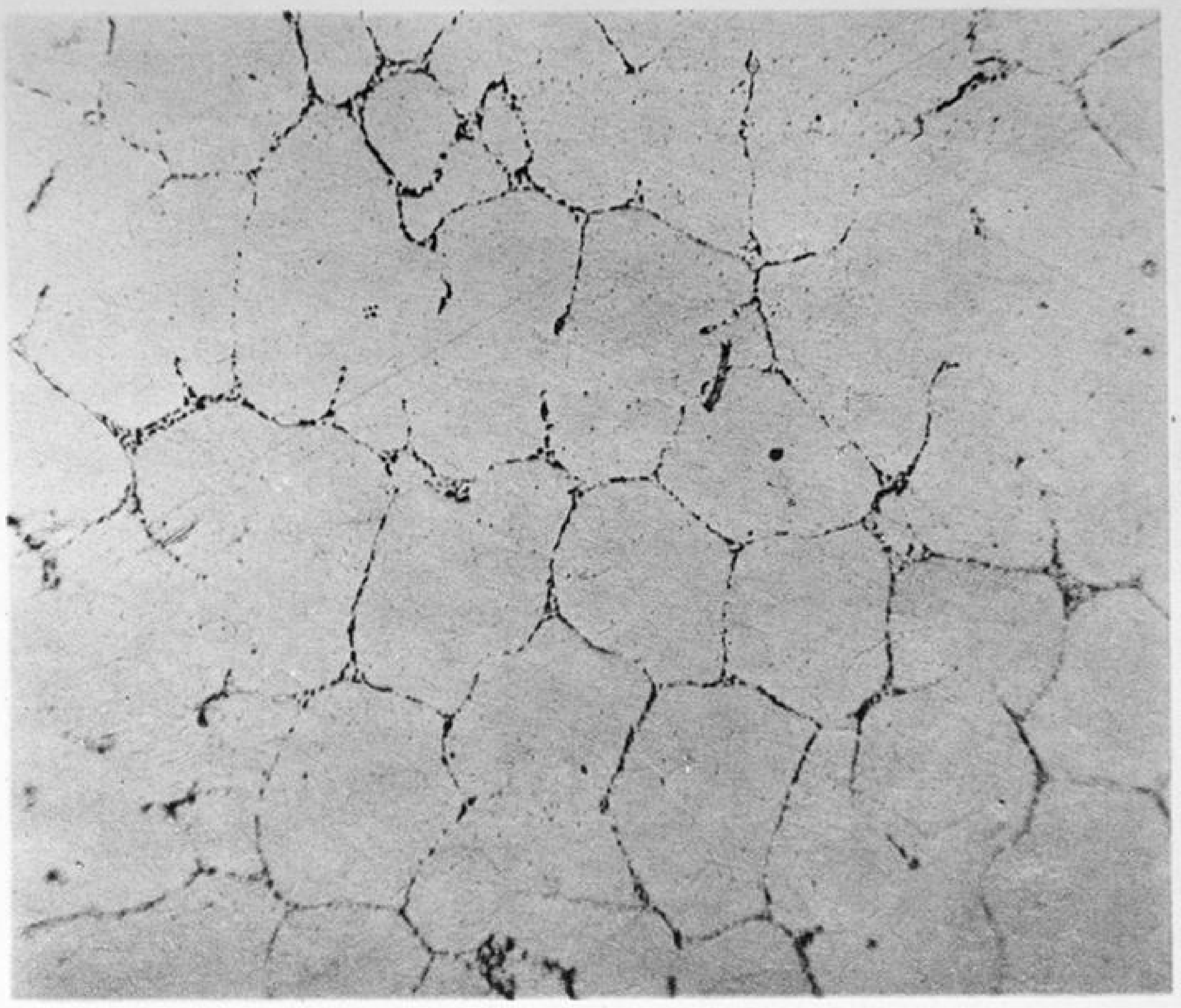

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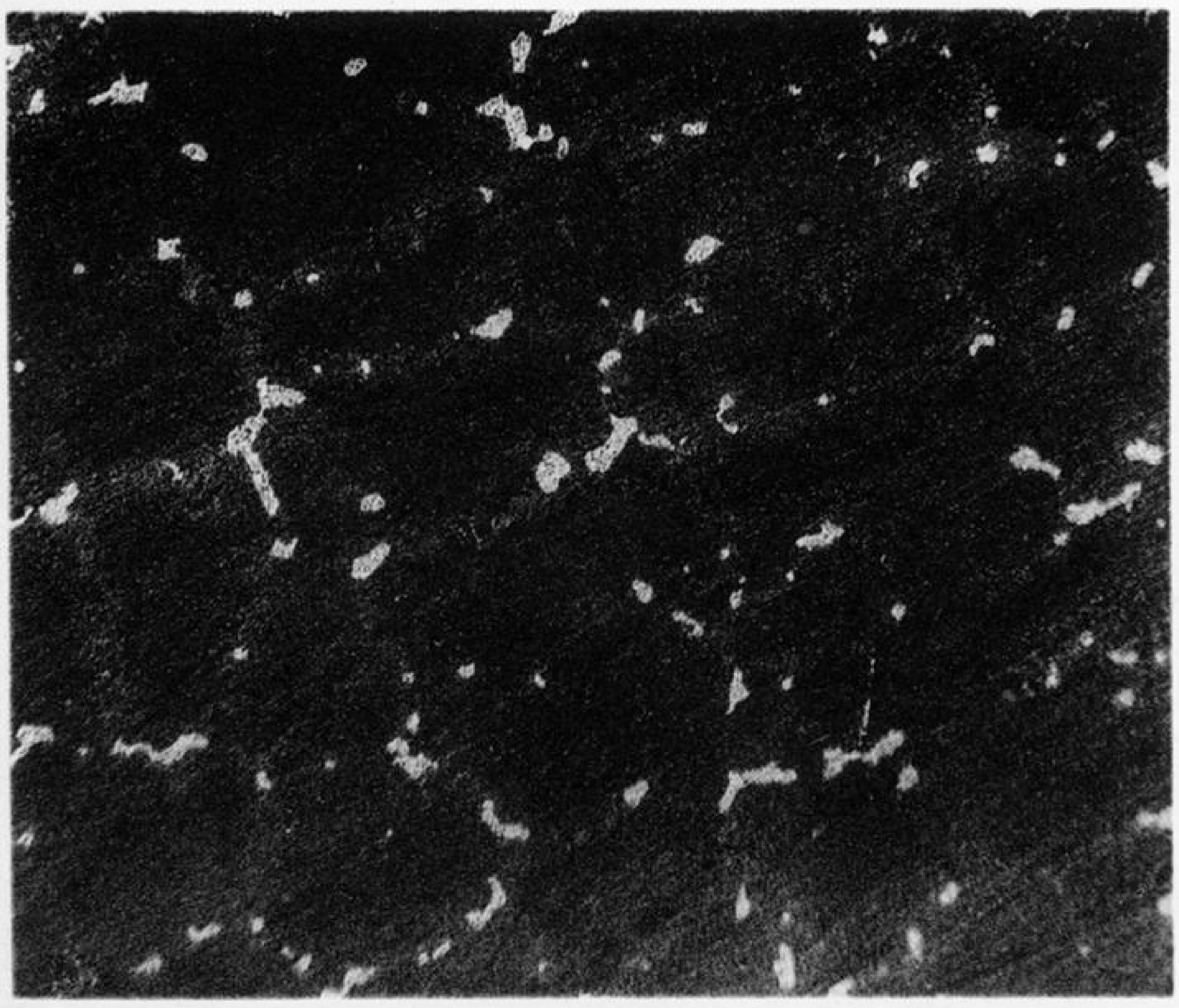

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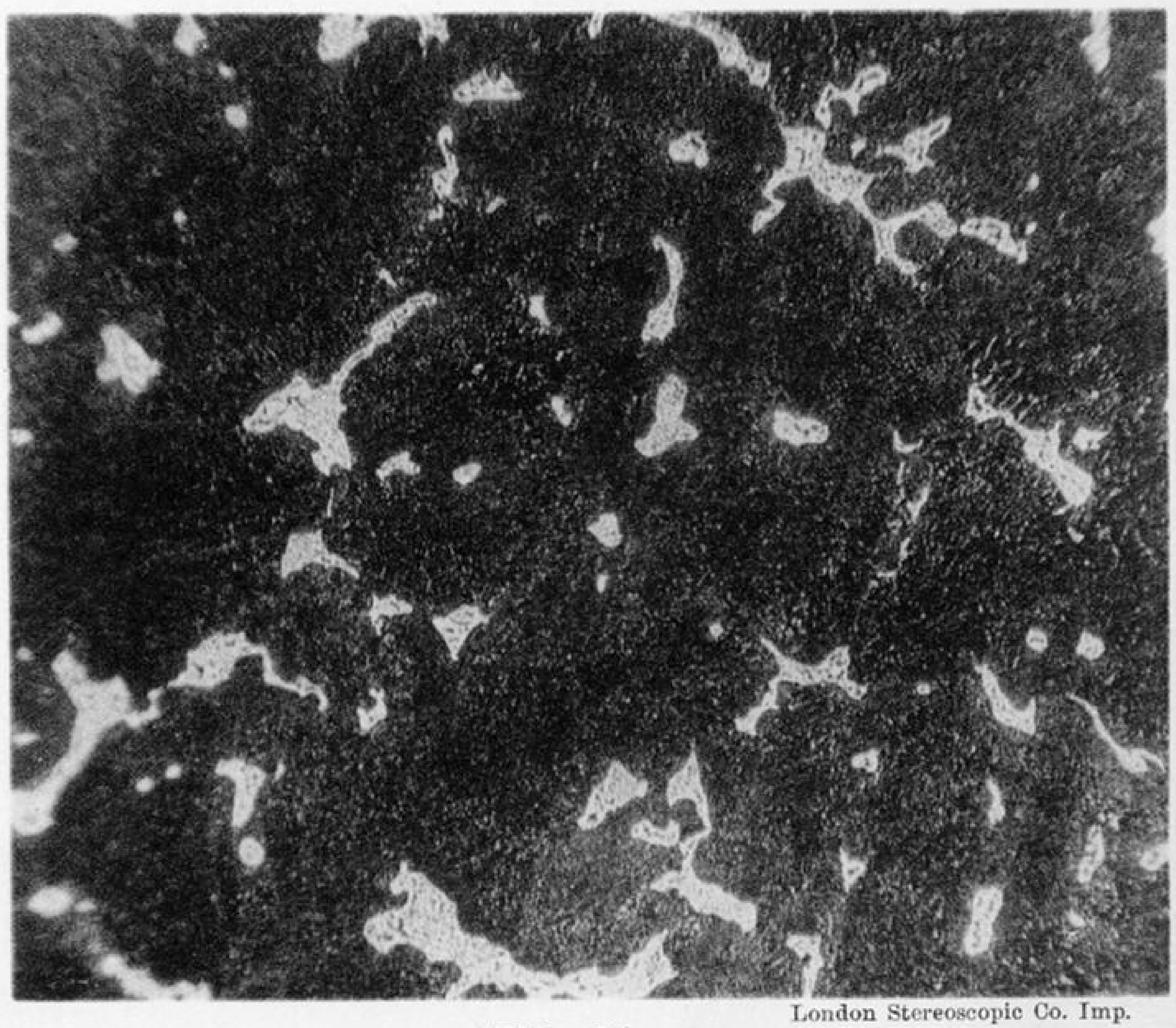

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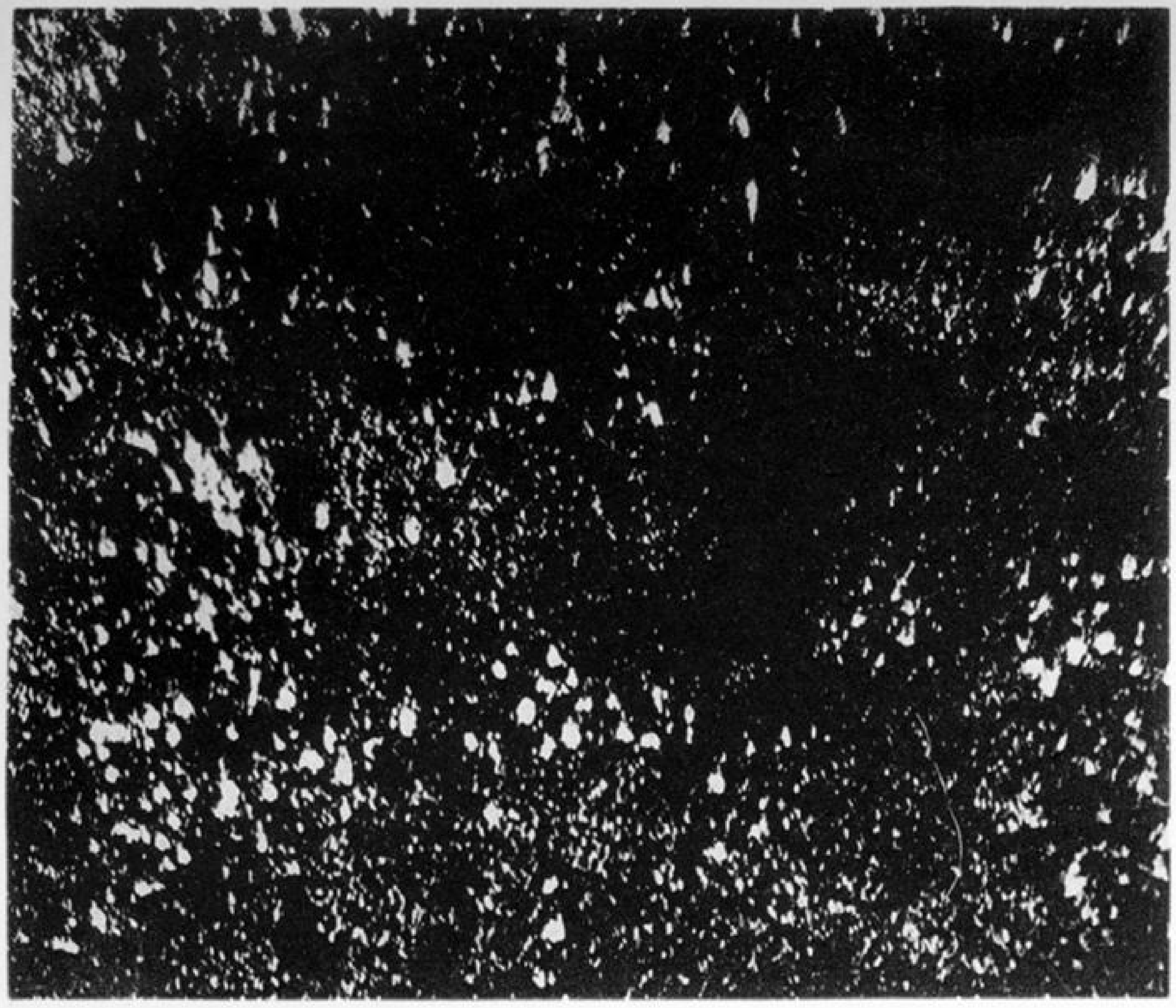

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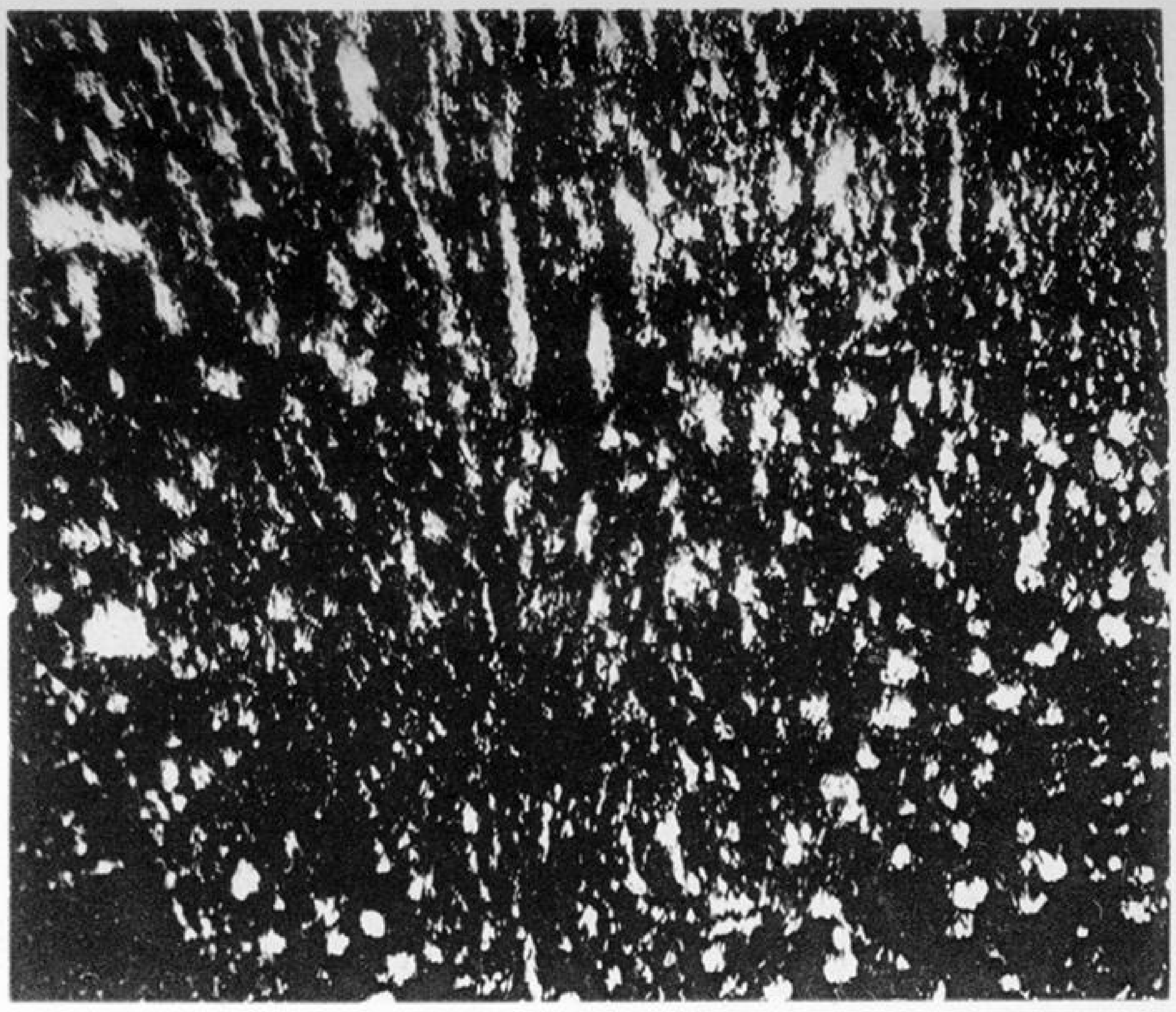

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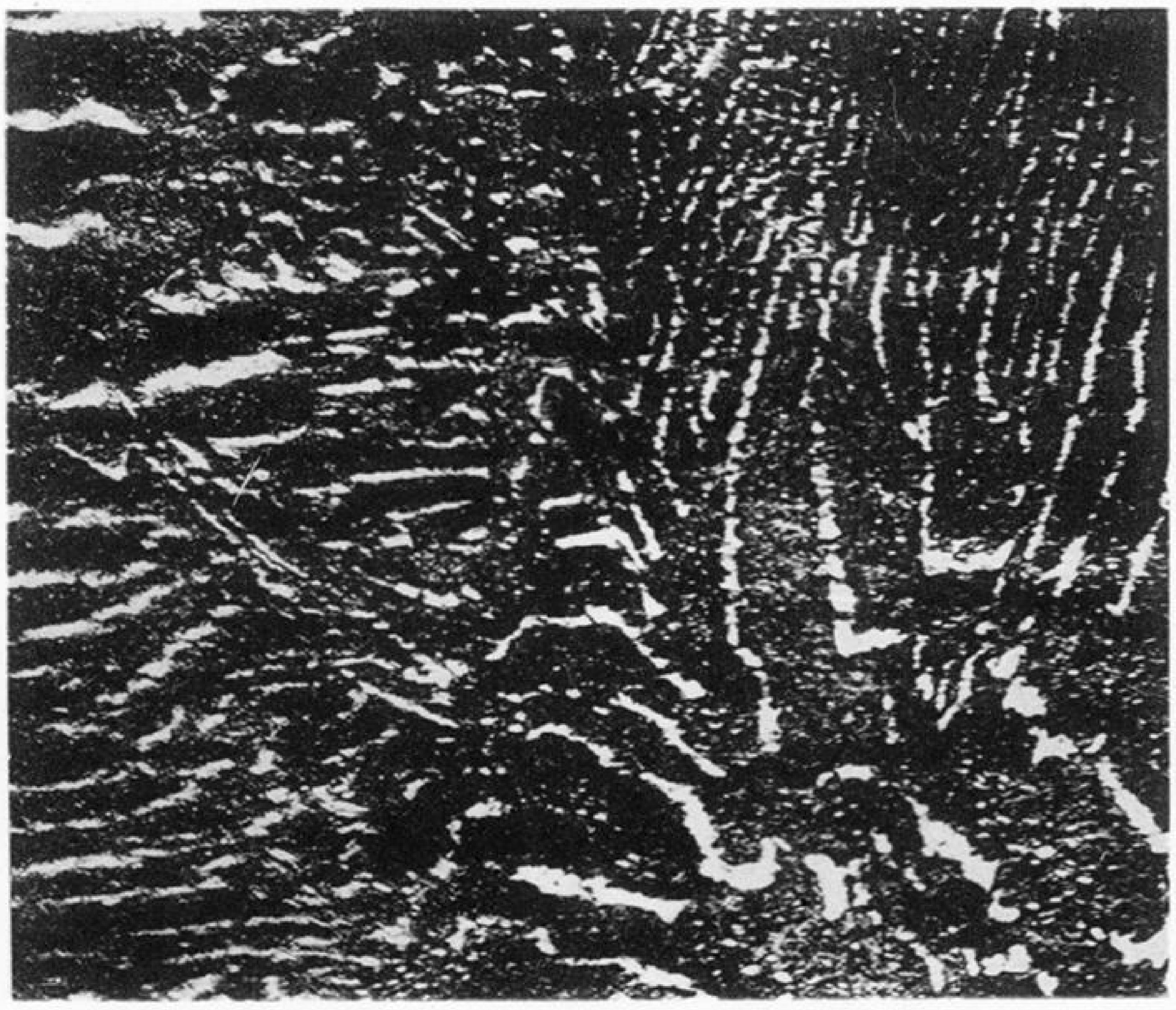

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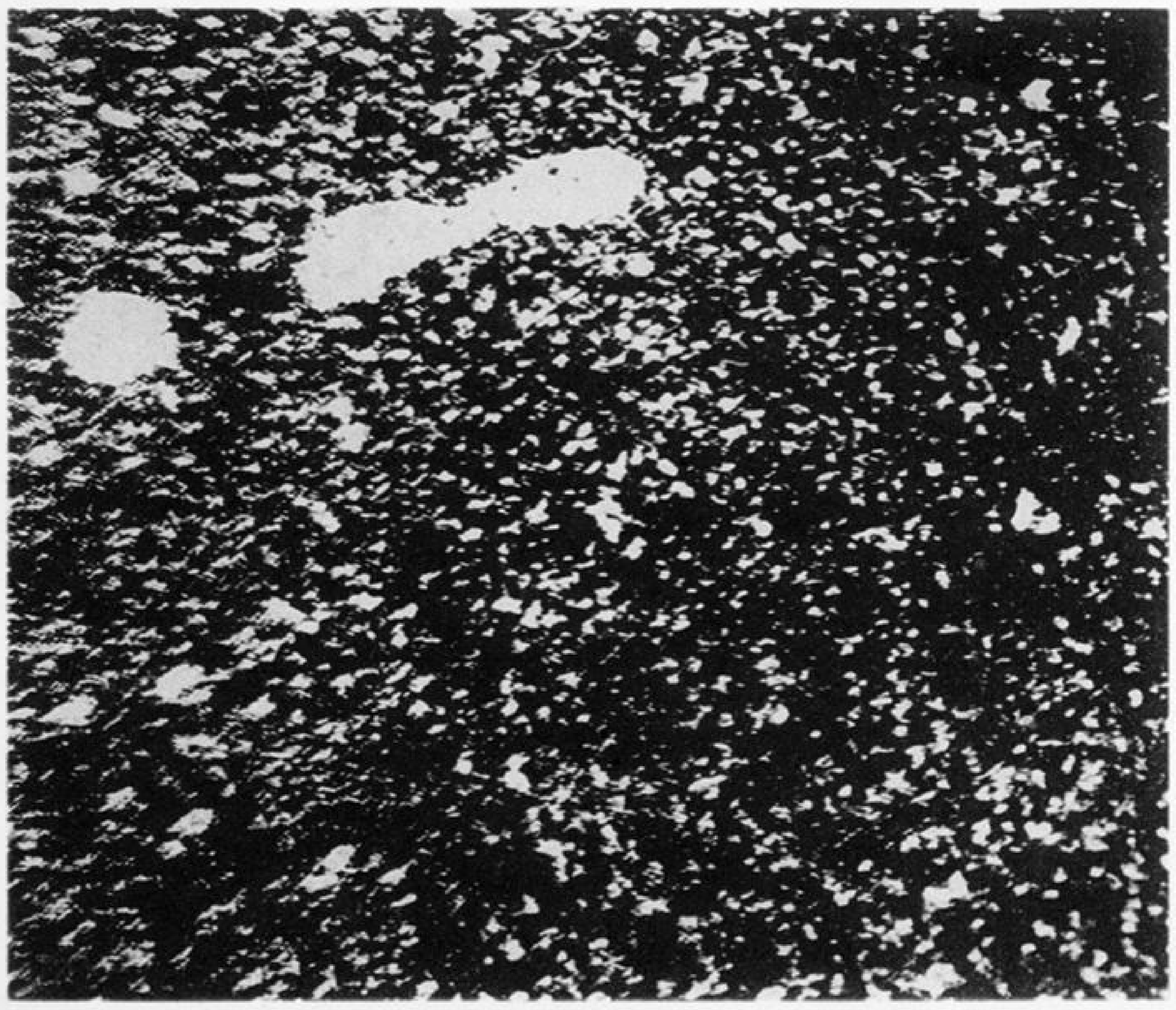

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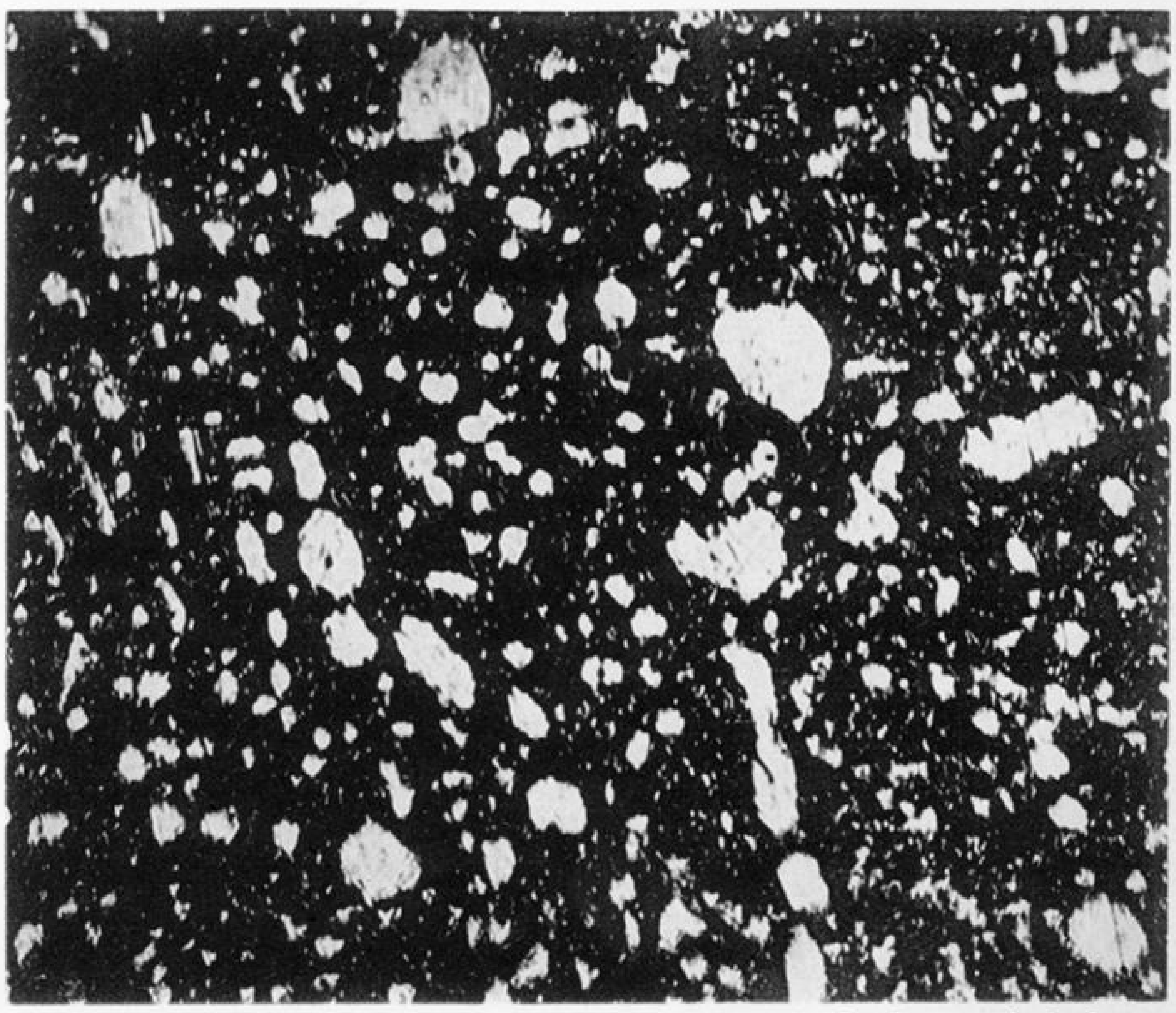

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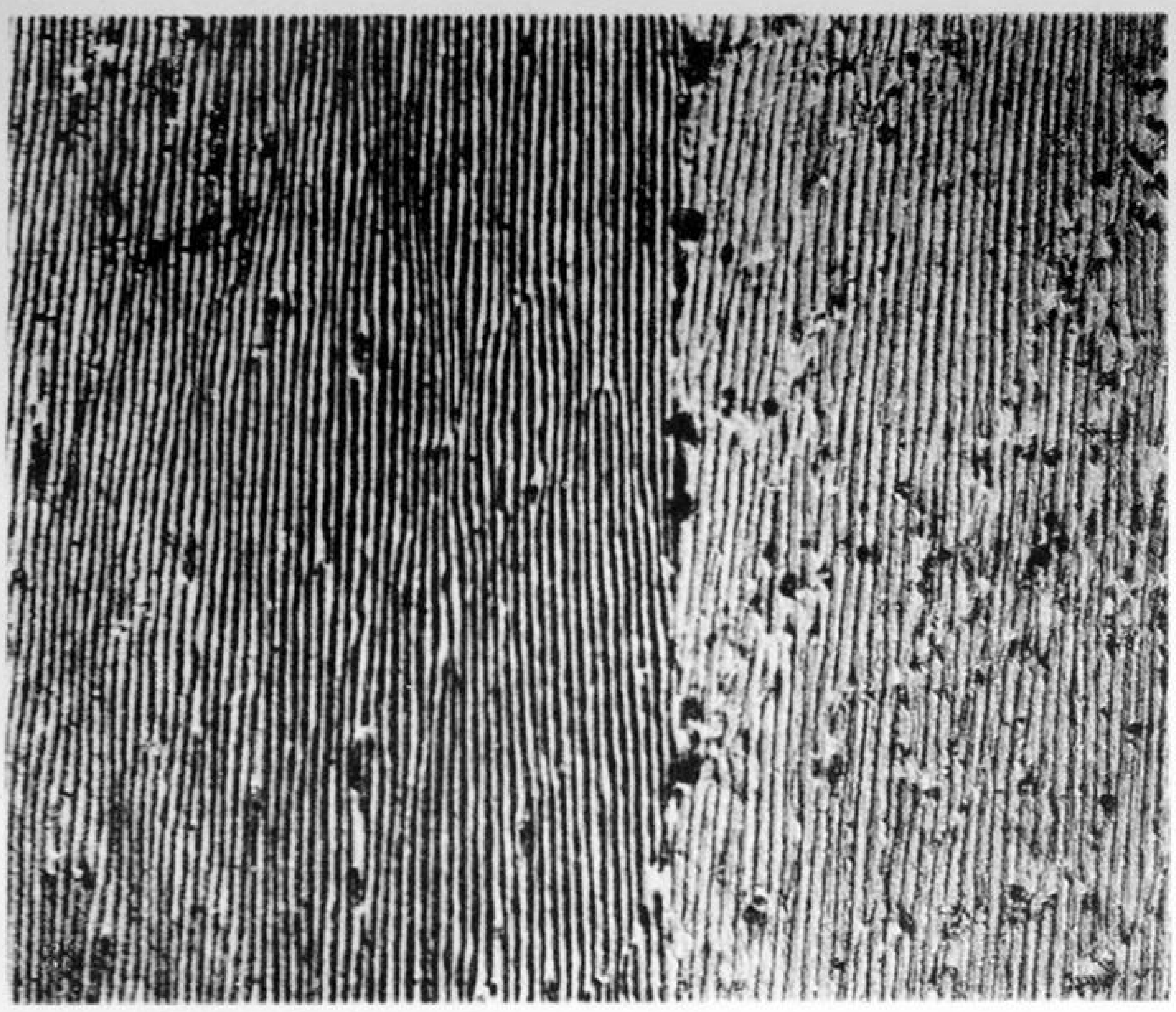
FIG. 29.



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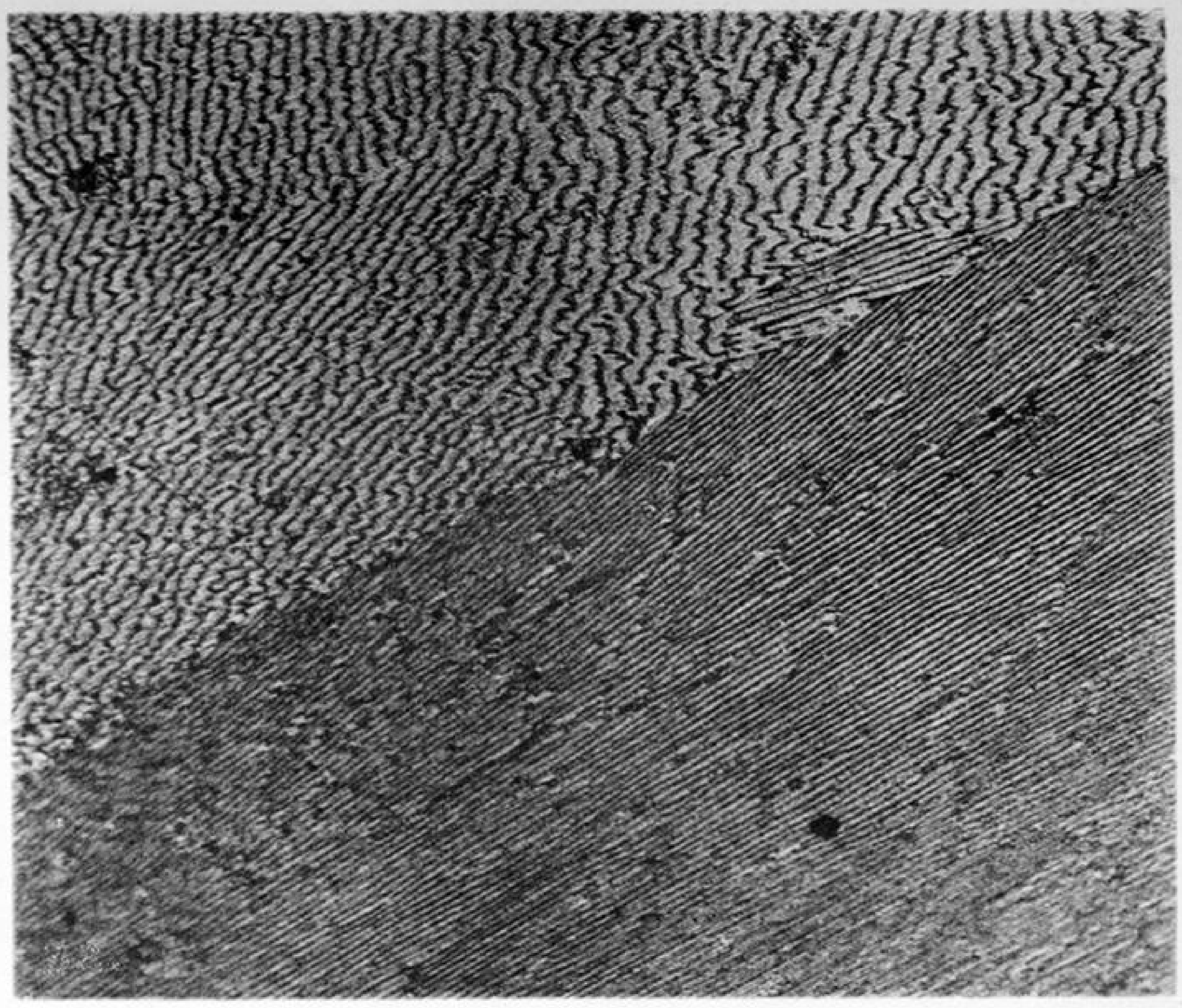

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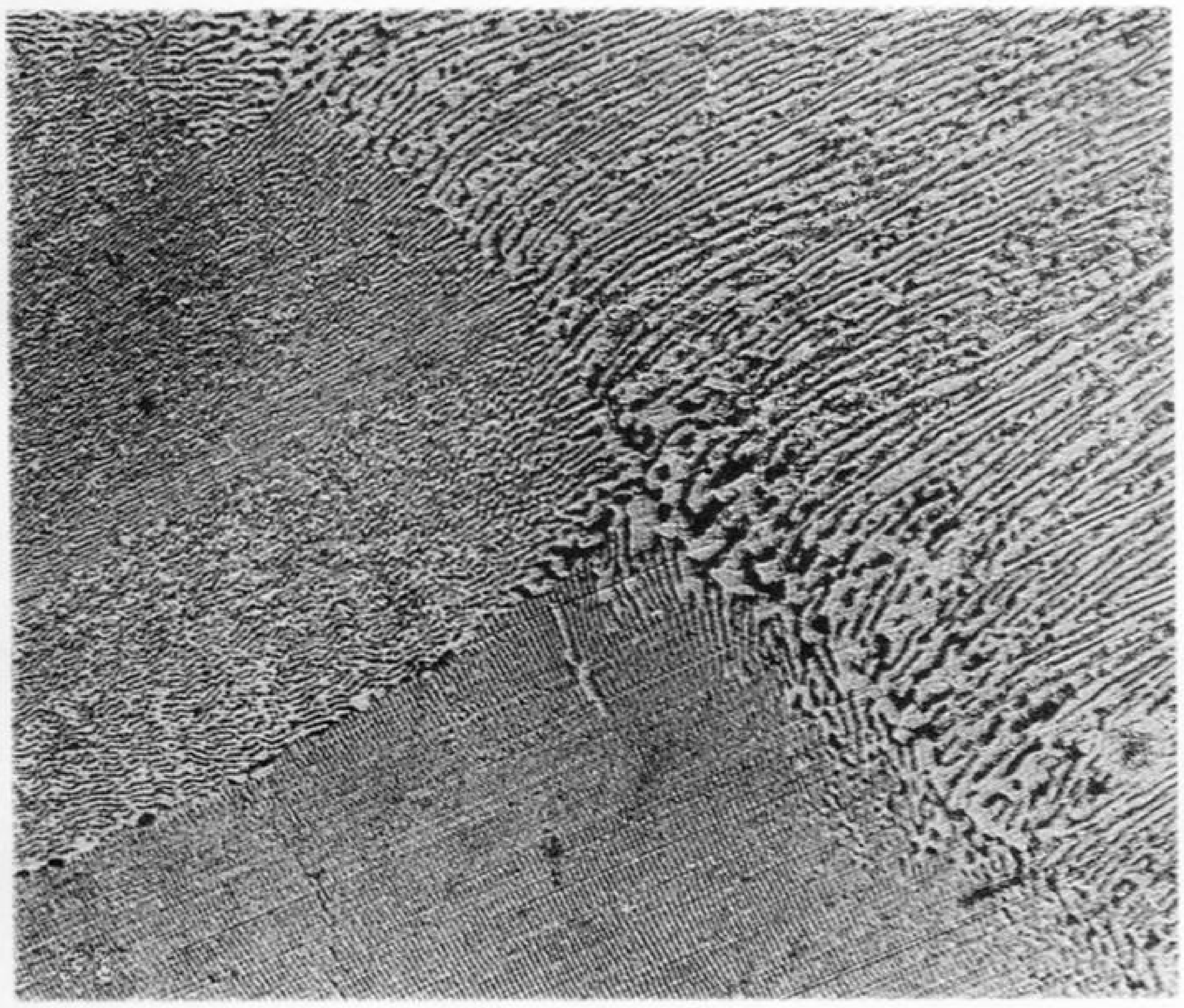

FIG. 33.

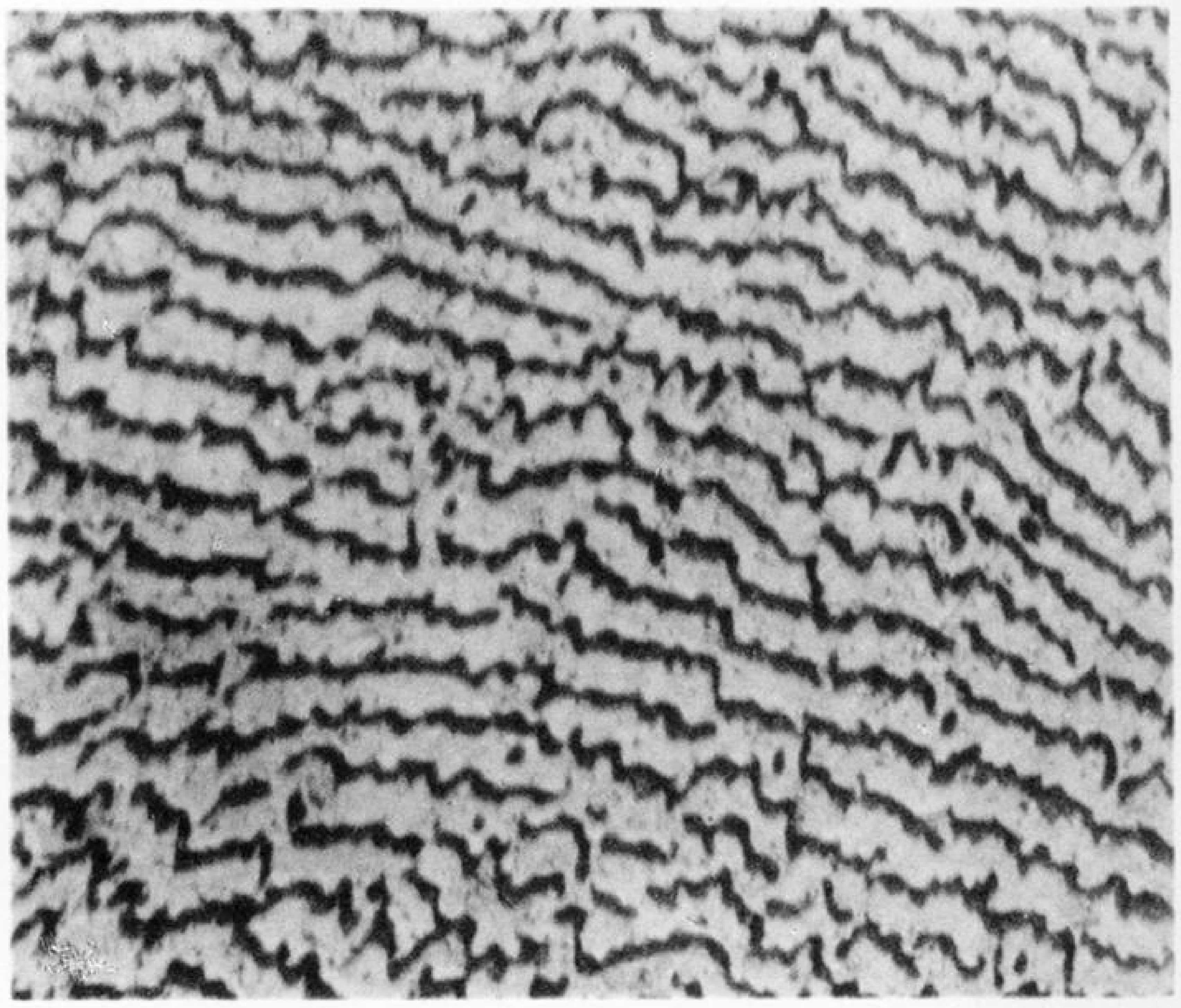

FIG. 34.

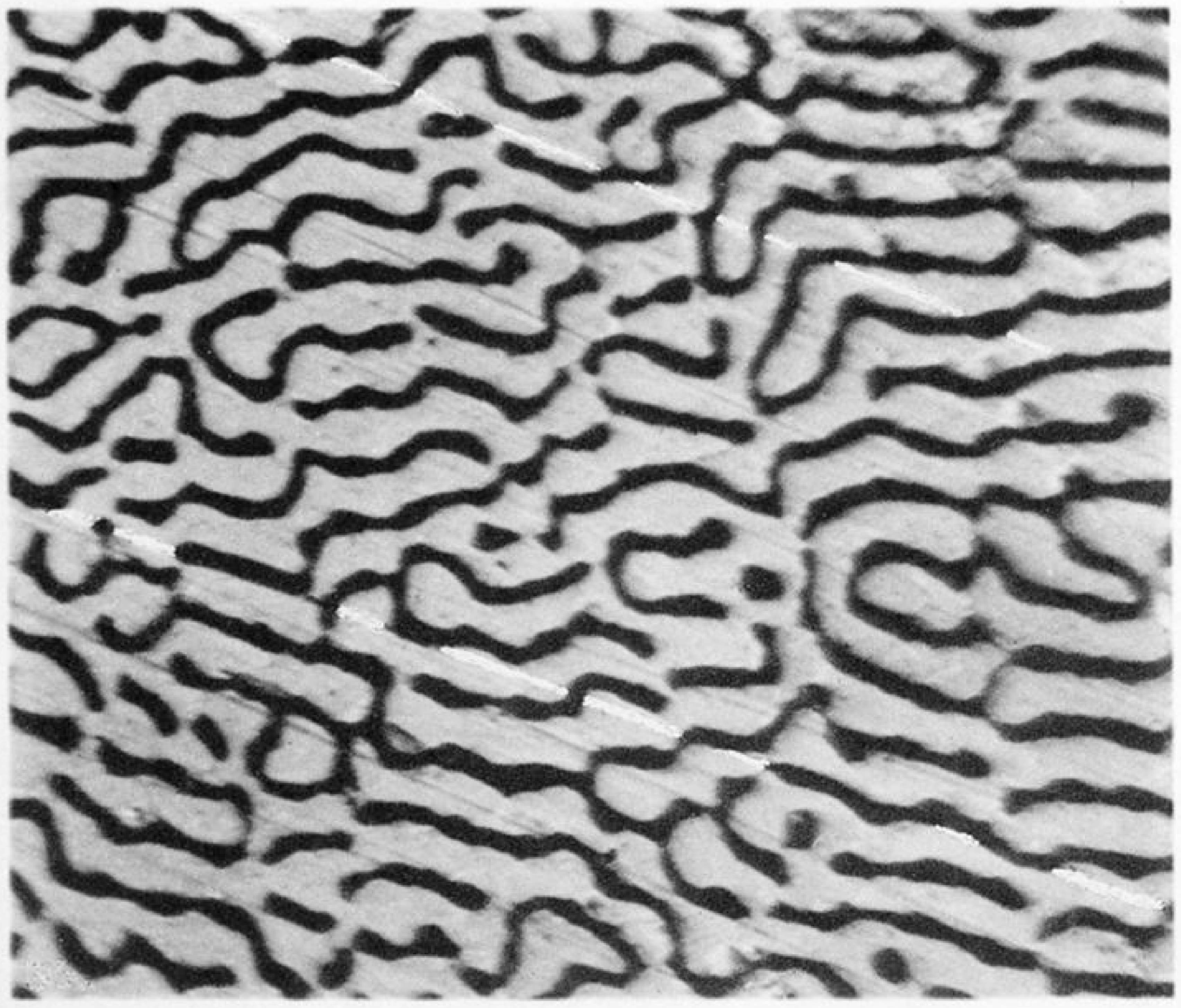

FIG. 35.

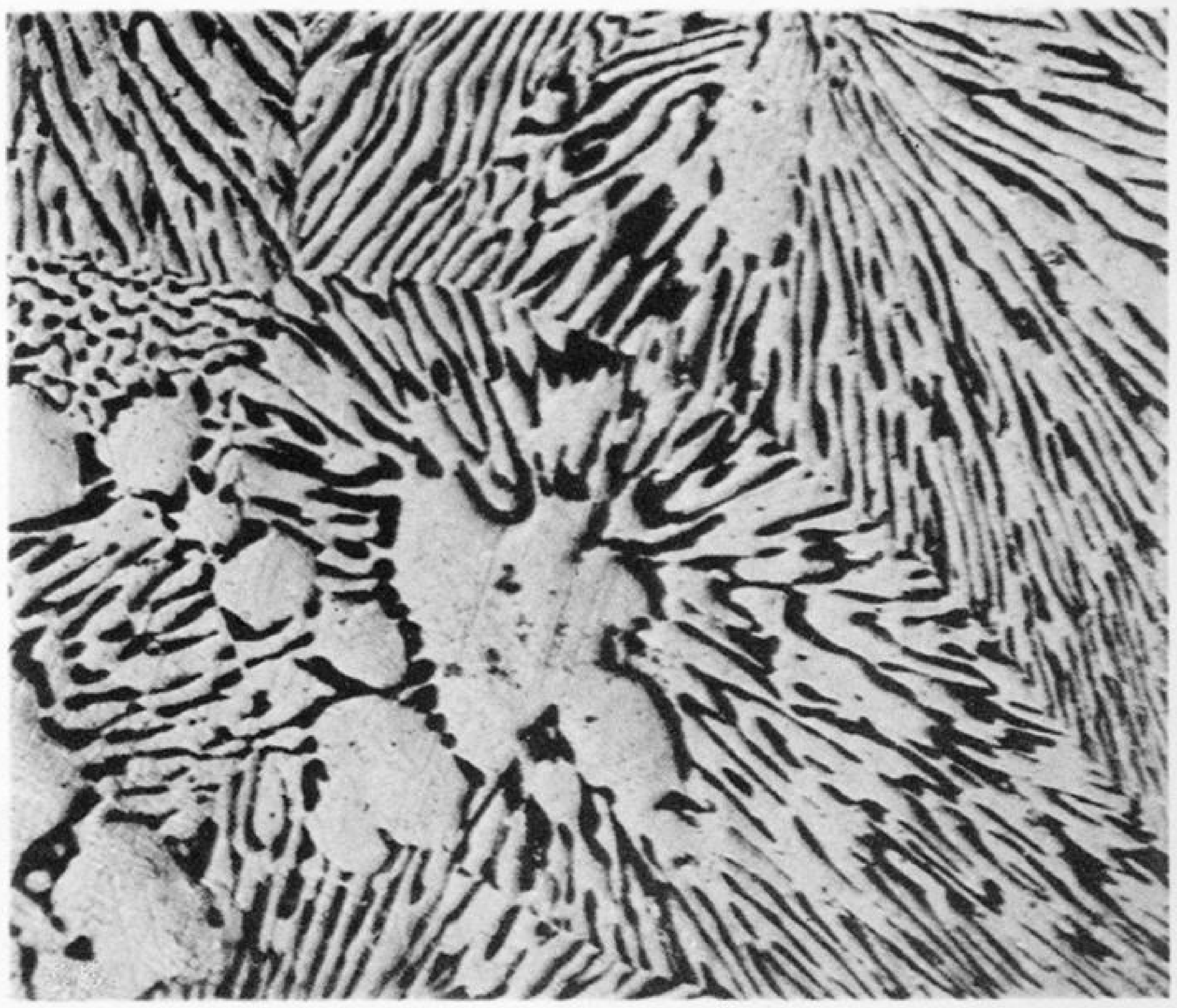

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FIG. 36.

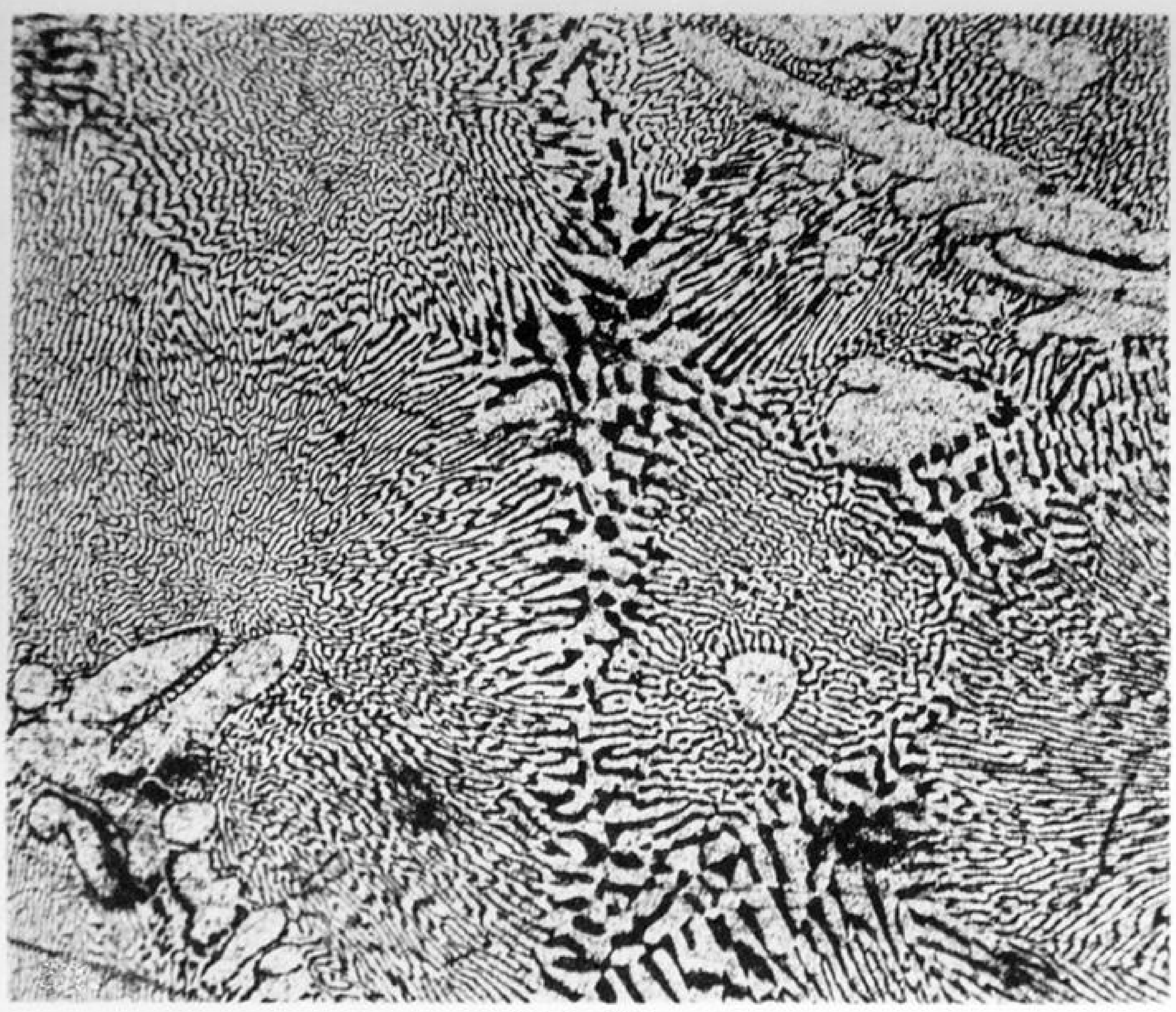

FIG. 37.

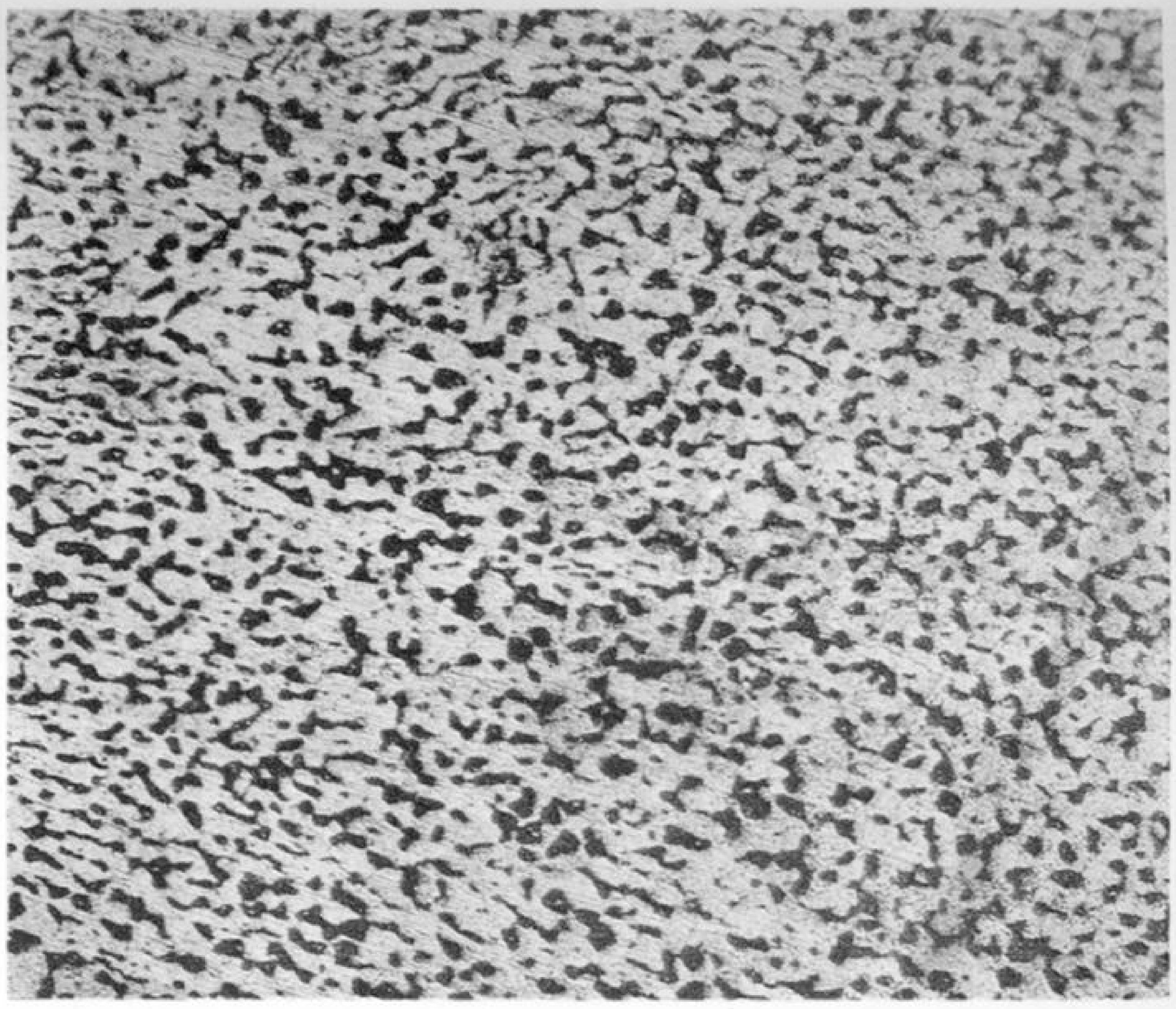

FIG. 38.

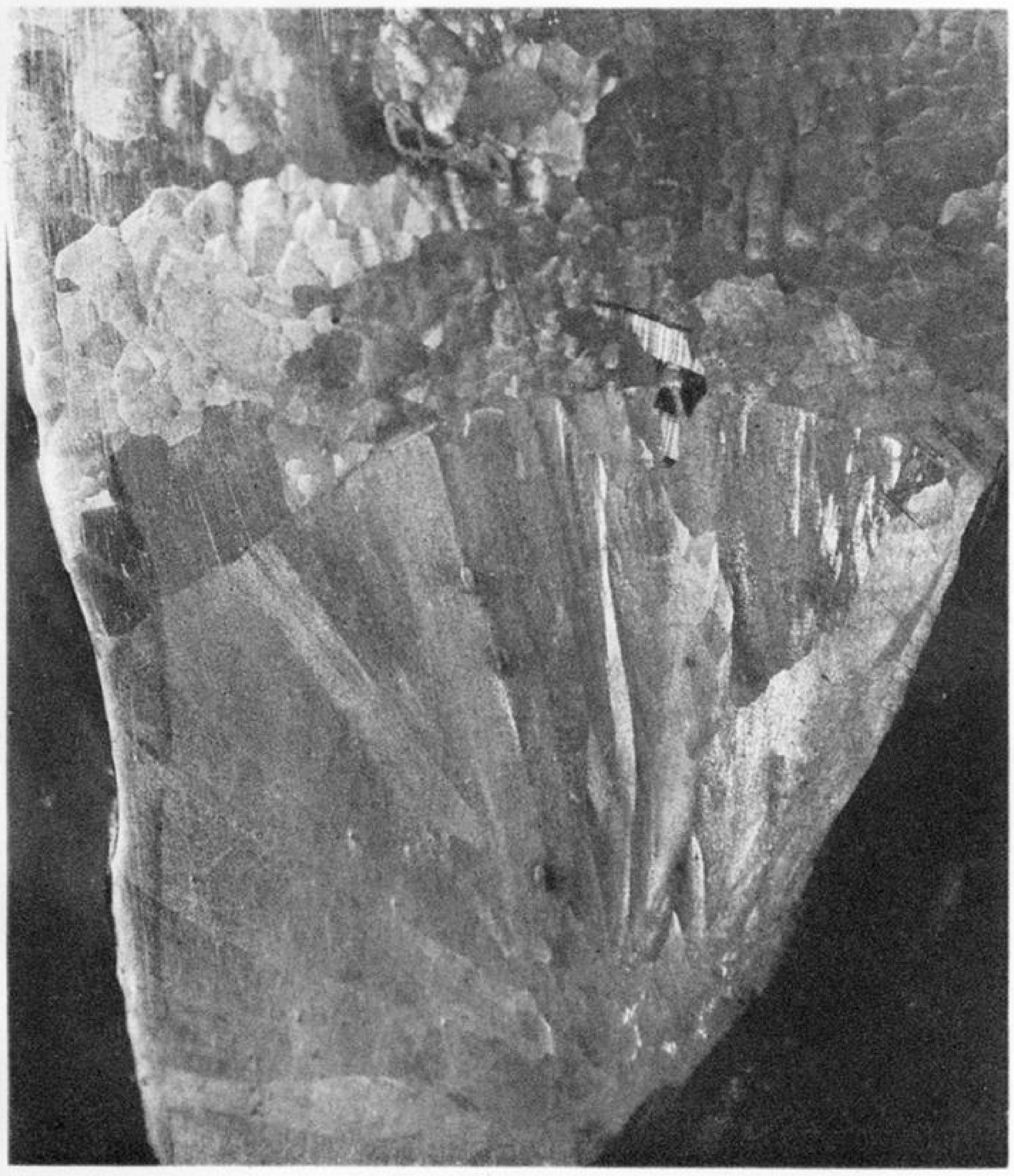

FIG. 39.

FIG. 40.

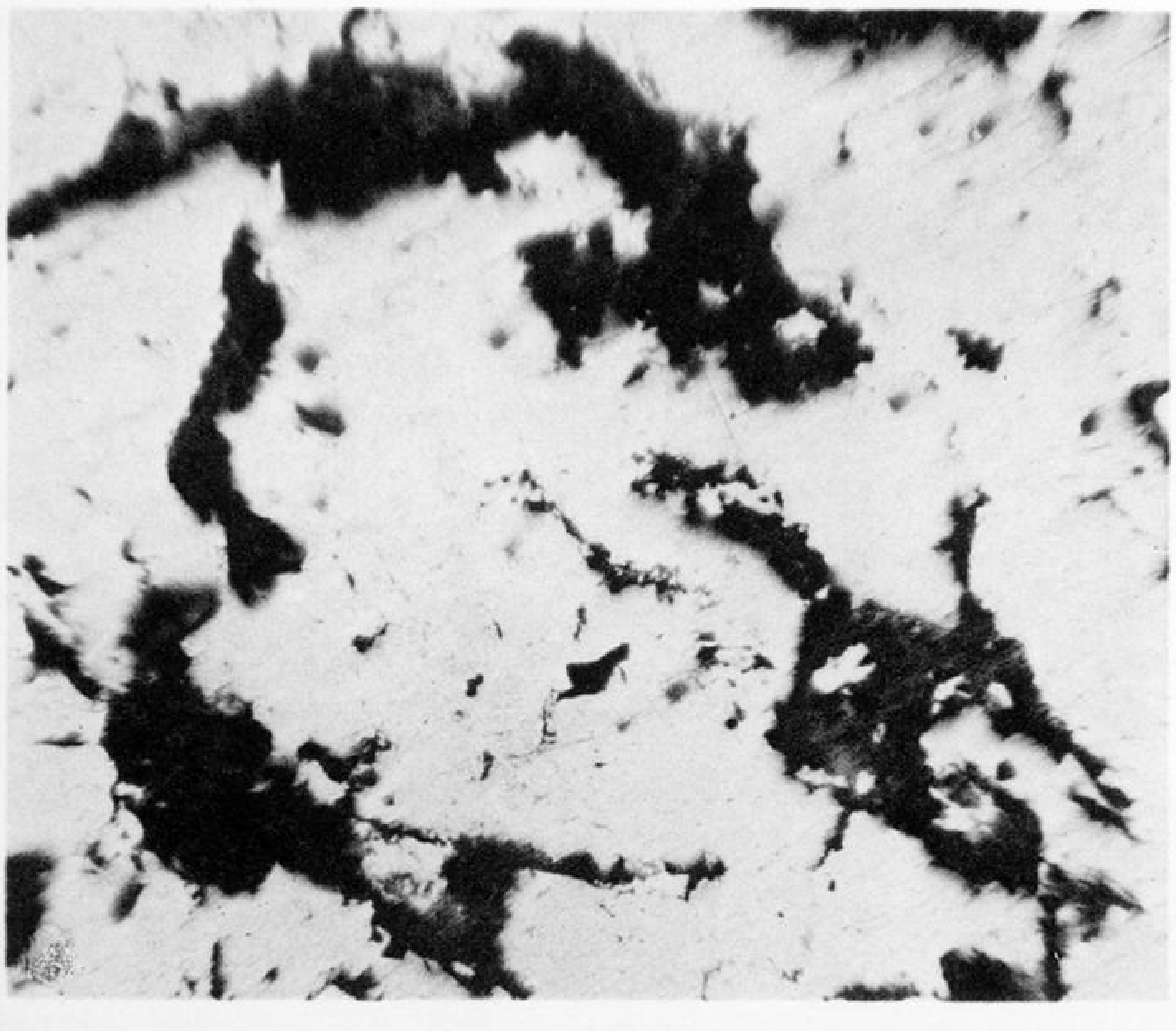

FIG. 41.

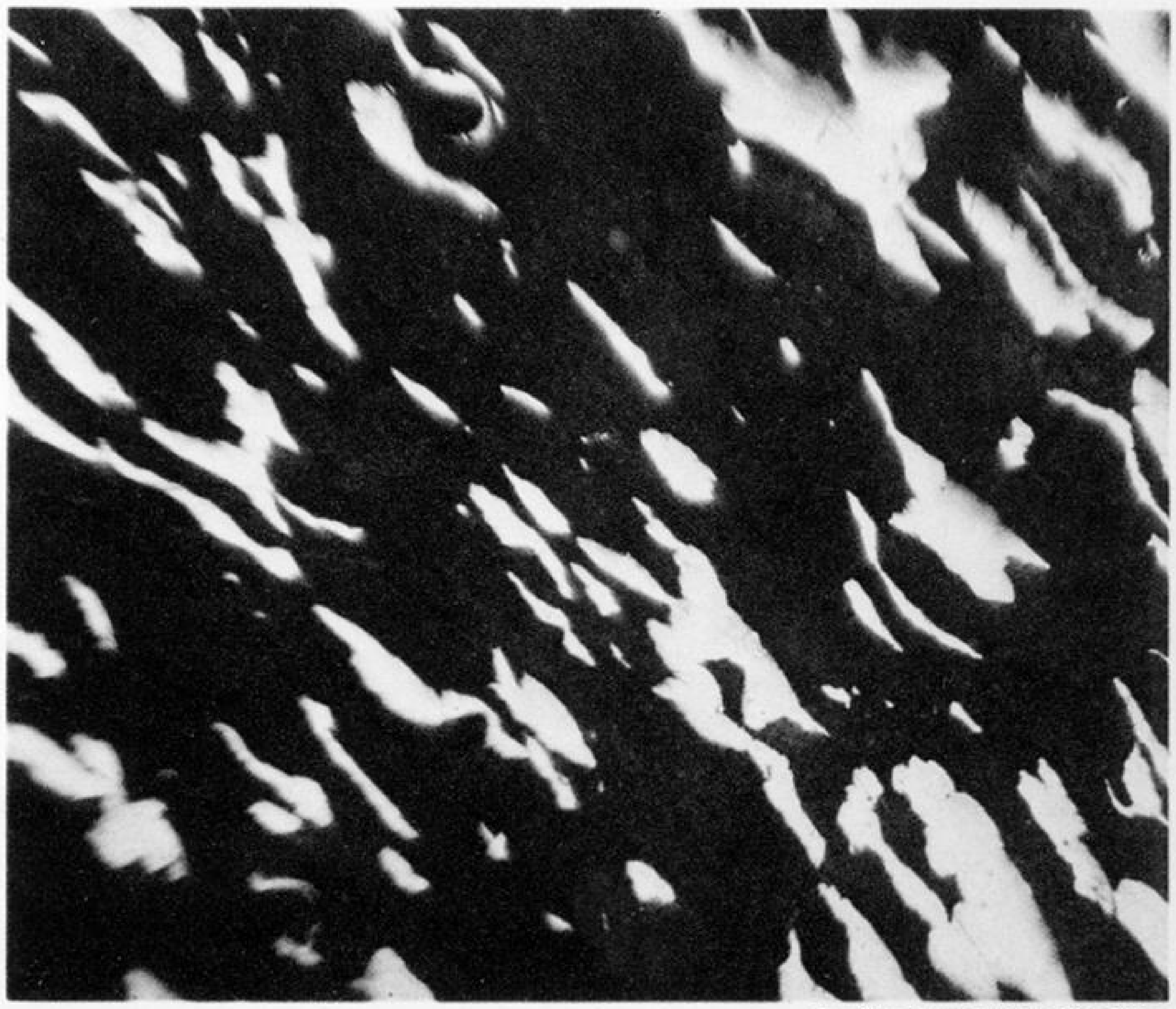

FIG. 42.

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