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Dilute Solutions of Aluminium in Gold

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VII. *Dilute Solutions of Aluminium in Gold.*

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[PLATES 4–5.]

THE following is an account of an attempt we have been making to determine the complete equilibrium diagram of aluminium and gold. We have been occupied with the problem during the last two years, and, as the experiments consume a great deal of labour and time, we are not likely to complete the work for at least another year; we therefore venture to ask the Royal Society to accept a *résumé* of the portion which is practically complete.

The results, in part embodied in the accompanying diagram, are based on two kinds of experiment—the tracing of cooling curves and the microscopic examination of ingots that have been annealed at certain temperatures, specially treated, and finally chilled by sudden immersion in water, the chill preserving to a great extent the structure existing a moment before the chill.

The diagram, fig. 1, is a temperature-concentration diagram, the temperature being expressed in degrees Centigrade and the concentration in atomic per cents. of aluminium. We also give a table stating the percentage by *weight* of aluminium at important points. It will be seen that none of the alloys contains more than 5 per cent. by weight of aluminium. It may very well be thought that the percentage compositions at points, such as *b* and B, *c* and C, respectively, differ by amounts comparable with possible experimental errors. This is to a certain extent true, but, for reasons which we give towards the end of the paper, we think that the only probable error of any importance is that we may have slightly overestimated the amount of aluminium in the alloys; this error will be of the same sign and almost of the same amount for all the alloys, and its only effect will be to shift a little to the left the points *b*, L, and perhaps *c*, a matter of no importance for our conclusions.

The points B and, to a less degree, C were determined very exactly in a previous research; *b* and *c* were fixed partly from theoretical considerations and partly from a minute study of the alloys.

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The upper line, or liquidus, ABCD, was taken from our previous memoir ('Phil. Trans.,' A, 1899). The solidus begins at A, the freezing-point of gold, and the first branch ends at *a*, with 13 atomic per cents. of gold, or, in our notation, at Al 13; it continues horizontally to *b*, then probably follows the line *bc*, and is continued horizontally through C to a point *d*, which lies nearly under the summit D of the liquidus. It is, perhaps, unnecessary to say that at points below the solidus all alloys are wholly solid.

The diagram deals with three substances—the solid solutions alpha and beta, which are of variable composition, and with a third substance, D, which is the sole constituent of the alloy Al 28 at the summit D of the liquidus. D may very well be the compound Al_3Au_8; it is very constant in appearance in all the alloys from Al 18 to Al 28, in which we have studied it, and from the fact that second freezing-points occur along the line C*d* to a point almost under the summit D of the liquidus it does not appear probable that D is a solid solution.

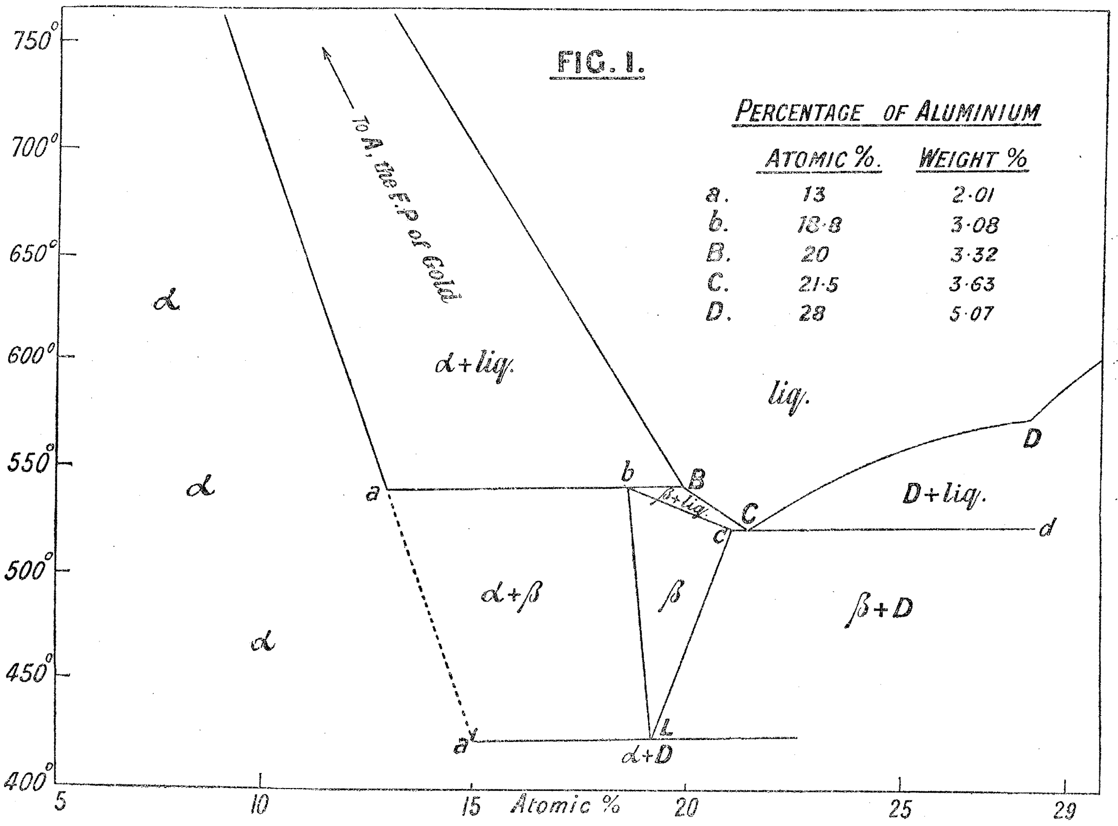


FIG. I.

The diagram ends at 400° C., and all alloys considered in it are supposed to have been melted, cooled to a temperature not below 400° C., and chilled. This limitation is important, as alloys cooled below 400° C., even if afterwards heated, generally require another diagram.

Microscopic Structure.

All alloys whose percentage composition places them to the left of the line Aaa' show the same patterns of uniform polygons or counties; these are closely packed, there being no interstitial matter, and they often meet in straight lines (Plate 4, fig. 1). In other words, the alloys contain only one phase—the solid solution that we call alpha. The alpha of the point a contains 2 per cent. by weight of aluminium, but at lower temperatures alpha can apparently contain a little more aluminium, as indicated by the slope of the line aa'; we are, however, not quite satisfied as to the exact position of the point a'.

In the region aa'Lb the ingots consist of a complex of alpha and beta, the alpha decreasing in amount as we go to the right and vanishing as we cross the line bL (figs. 2 and 3). The alpha vanishes at or about Al 19, and for about 2 atomic per cents. we have in the solids at a high temperature beta only (figs. 4 and 18).

Polished and etched surfaces of beta that have been chilled at a high temperature always present the appearance of angular rocks seen in relief, a high power showing groups of fine parallel lines, the direction of the lines changing from grain to grain so as to give the effect of shading. This is due to a laminated structure in the beta, perhaps to an incipient decomposition. In some cases the ruled structure is extraordinarily regular and resists etching, remaining bright when the rest of the beta is darkened (fig. 5).

The triangle bLc contains all the alloys that can exist in equilibrium as pure beta; it will be seen that this substance becomes unstable at 424° C. To the right of the point C, which appears to be an eutectic point, we get primaries of the substance D embedded in beta, the D generally etching bright; indeed everywhere to the right of the line Lc the alloys are a complex of D and beta (figs. 6 and 16).

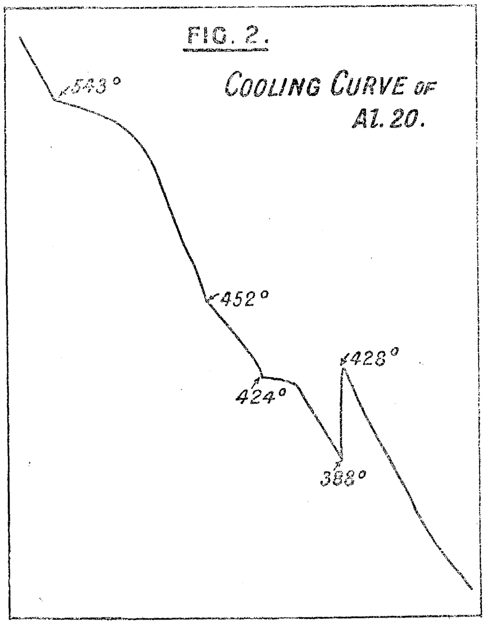
We are hardly entitled, as far as experimental evidence goes, to separate the points C and c, for we have no certain evidence of eutectic structure in any alloys of the BC branch, but we think it probable that the solidus of these alloys ends a little to the left of C as we have drawn it. It must be remembered that the C eutectic can only contain a very small proportion of D, and would be hard to detect; alloys such as Al 22, Al 23, and Al 25, when appropriately treated, do show a minute network of D in the matrix, this is perhaps the eutectic (fig. 7).

The relations of the three bodies alpha, beta, and D are, so far as this diagram extends, very similar to other cases already studied, for example, in the copper-tins. The lines bL and cL are the lines of incipient crystallisation of alpha and of D out of the solid beta; they correspond to the liquidus in crystallisation out of a liquid. The point L is an eutectoid point; when any alloy containing beta cools slowly through the L temperature the residual beta in it breaks up into a complex of alpha and of D. We have verified this in alloys ranging from Al 18 to Al 23 (figs. 8, 9, and 14). If the composition of the alloy as a whole lies to the left of L, the primary, or pseudo-primary, crystals are alpha, if to the right of L they are D. In this way the microscope shows that L lies between Al 19 and Al 19·5.

Cooling Curves.

We have determined the cooling curves of a number of alloys; we will discuss that of Al 20, of which we give a reproduction. This curve, fig. 2, shows a period of heat evolution beginning at the B temperature and continuing for some time with a slightly falling temperature; this is due to the solidification of the solid solution beta, and is very characteristic of the solidification of solid solutions. The next heat evolution, near 450° C., is probably due to the crystallisation of D as the solid solution cools across and below the *c*L line. The formation of the L eutectoid is indicated by a well marked flat at 424° C., the invariable temperature at which this phenomenon occurs. But the most striking feature of the curve is the recalescence that began at 388° C. and, almost instantly, raised the temperature to 428° C.

FIG. 2.



COOLING CURVE OF Al. 20.

A similar recalescence can be detected in all alloys from Al 10 to Al 27, though in those remote from Al 20 it is slight, while in those near Al 20 the effect is almost as marked as in that alloy. Both the initial temperature and the rise in temperature are very variable, the latter being sometimes as much as 70° C. This is essentially an explosion phenomenon, that is, a change commencing below the temperature at which it ought to take place, and the temperature to which the recalescence carries the ingot may not reach that at which the new system would be in equilibrium with the old one. We have also traced the *heating* curves of Al 20 and neighbouring alloys. In these heating curves the first marked absorption of heat, causing a flat, is seen to begin at 520° C., and we think that it indicates the equilibrium temperature of the recalescence reaction. A strong reason for this opinion is that if we take several pieces of an ingot that has undergone recalescence and heat them, annealing and chilling at successively higher temperatures, we find, on examination with the microscope, that the pattern produced by the recalescence persists up to 520° C., but that if the alloy be ever so little further heated this pattern disappears and is replaced by that characteristic of the pre-recalescence state.

By introducing a thermocouple into a molten ingot, tracing the cooling curve, remelting, cooling to selected points on the curve and chilling at these points, we can by microscopic examination correlate the change in structure with the thermal changes. The change in structure occurring at the recalescence is especially remarkable. For example, Al 14 chilled at any temperature above 420° C. is a uniform solid solution of closely fitting polygons showing no trace of a second material, but chilled at 400° C. it becomes filled with polygons, bars, and sprays of a second material, and from the fact that the new substance shows a tendency to margin the old polygonal divisions, it is probable that it is richer in aluminium than the original alpha (Plate 5, fig. 10).

The same change occurs spontaneously in all alloys from Al 14 to Al 20 when they are cooled below 400° C. and either chilled or not. Ingots of Al 15 and of Al 18, chilled the first at 380° C. and the second at 410° C., show the striation in the alpha and the specks and crinkles in the beta, both alpha and beta having been uniform before the recalescence (figs. 11, 12, and 13). The change in the beta seems to be the most important and to contribute most of the heat evolved.

The recalescence may occur in the beta itself before the temperature has fallen low enough to allow of the formation of the L eutectoid, but, as a rule, the eutectoid forms before the recalescence, and in such cases we can analyse the phenomenon more minutely. In the case of an ingot in which the eutectoid already exists, the chemical change causing the recalescence is, essentially, a reaction between the two phases alpha and D which make up the eutectoid complex; it results in the complete disappearance of all the D and of most of the alpha of the complex, a new body, which for the moment we will call Y, being formed. Hence, if an ingot, which has been successively through the eutectoid and the recalescence changes, be chilled immediately after the latter, we find, instead of the L complex, a very delicate reticulation of threads which etch bright, while in the cells of this network there is the Y body, etching a uniform brown. The primary, or pseudo-primary, whether it be of alpha or of D, is unaffected at this stage. Ingots of Al 23, chilled one at 420° C. the other at 400° C., are excellent examples, the first of the eutectoid, the second of what it becomes after the recalescence (figs. 14 and 15. Compare also figs. 8 and 8A, 9 and 9A).

As the recalescence of the eutectoid always leaves a slight excess of alpha, it follows that the substance Y must contain rather less gold than the pure eutectoid of the L point; this points to the hypothesis that Y is the compound $AlAu_4$.

Such an alloy as Al 23, chilled at 400° C. immediately after recalescence, contains three phases, alpha, Y, and D, while the Phase Rule only allows of two; this anomaly is removed by annealing, when the D primaries slowly react with the residual alpha to form more Y, the process resulting in the disappearance of the D or of the alpha, according to whether the one or the other was in excess; in Al 23 the alpha disappears, while in Al 20 a long anneal after spontaneous recalescence always leaves us with a trace of alpha (fig. 17). Two ingots of Al 20, the first (fig. 16) chilled at 440° C., before recalescence, and the second (fig. 17) chilled at 410° C., after spontaneous recalescence and a long anneal at that temperature, show the enormous change caused by recalescence followed by annealing. The white pattern of the 440° C. chill is of D, and is characteristic of the D that crystallises out of uniform beta when the temperature of the ingot reaches that of the *c*L line. In the second ingot, at one time like the first, the L complex has been formed and destroyed, and the reaction between the alpha, remaining from the complex, and the D bars has removed the latter completely. A comparison of these two ingots only might lead one to think that the residue was D, but a study of ingots intermediate in temperature of chilling proves that the white residue is alpha.

Forced Recalescence.

The fact that recalesced ingots lose all trace of the recalescence pattern when heated above 520° C., at which temperature the beta is solid, makes us doubt if it would be possible to trace the liquidus of Y by seeding liquid alloys with fragments of a recalesced alloy. But we have been able to show that beta, which, spontaneously, does not often recalesce above 410° C., can be stimulated to do so at all temperatures up to 515° C.

The experiment was conducted as follows:—An ingot was melted, a thermocouple placed in it and the ingot allowed to cool slowly while its cooling curve was traced on the recorder. At a selected temperature the ingot was touched with a cold steel wire. The contact generally caused a slight and momentary drop in temperature followed by a sudden jump which sometimes rose as high as, but never above, 524° C. We have in this way forced the recalescence of alloys varying in composition from Al 15 to Al 23.

The recalescence of Al 15 could not be effected above 408° C. The change of structure is well seen by comparing the pattern of a recalesced ingot with that of a control ingot that was not recalesced but otherwise had precisely the same thermal treatment. In the case of Al 15 the control proved to be uniform solid solution with hair-line boundaries between the polygons and a few small triangular pools of matrix. In the recalesced ingot there are broad jagged edges of a new material separating the polygons, as well as a certain amount of this material inside the polygons.

The change in the case of Al 15 took place in the alpha and is not altogether comparable with the cases of forced recalescence of the beta that we are about to describe. In all the cases in which a uniform beta was forced to recalesce two new substances appear, a network or diaper of a somewhat golden material that resists etching and has all the character of alpha, and which we shall call alpha, and another material the crystallisation of which determines the pattern; this second substance etches dark and is eaten away by the etching reagent, it fills the cells of the alpha network; we have already called this substance Y. These two substances preserve their character in all the cases of forced recalescence from Al 18 to Al 23.

Al 18 was forced to recalesce at 500° C. and the temperature rose to 504° C. The recalescence produces a fine diaper of alpha, but the alpha primaries previously existing remain uniform, as apparently the alpha cannot change at this temperature.

An ingot of Al 19 was, as the etched surface shows, forced to recalesce at 507° C.; although no thermal effect was noticed it shows a network of alpha with no primaries. Another ingot of Al 19 was recalesced at 504° C., the temperature rising to 515° C., and was chilled a few minutes later at 510° C. It shows a magnificent pattern of bars, many of them large, and of feathery masses of Y, this substance being everywhere outlined by bright alpha. It is very evident in this case that a complete recrystallisation has taken place throughout the ingot, the new pattern being determined by the shape of the crystals of Y. The control ingot was fine-grained, rocky, very uniform beta.

We have forced the recalescence of Al 20 at 397° C. and 445° C., these two experiments only confirming our previous results. A forced recalescence at 498° C., rising to 520° C., is a remarkable example of the recrystallisation of a solid being brought about by a stimulus. The picture is one of broad bands, bars, and sprays of Y, margined as usual by alpha; at the highest temperature reached the Y must have been very near its melting point. Another ingot, recalesced at 514° C., rose to 524° C. and remained at that temperature for some minutes. The pattern shows that a good deal of the Y melted in consequence of the high temperature attained. The pools of matrix are not pure alpha but a complex resembling the feathery pattern of a high chill of beta. Here we have a case of a solid that, when touched by a cold wire, rises ten degrees, completely recrystallises and partly melts. Another ingot was recalesced at 508° C. and rose to 523° C. The figures 18 to 21, inclusive, illustrate forced recalescence.

These results confirm the view that Y cannot exist much above 525° C. Another experiment supports this conclusion. A portion of the ingot recalesced at 498° C., and described above, was reheated to 525° C., kept at this temperature for 12 hours, and then chilled. The pattern shows that quite half the Y melted, or disappeared, the solid part appearing to have remained in equilibrium with the liquid; but we do not know whether the matrix continued liquid until the chill or solidified previously as beta. The solidified matrix has a coarse striation and might be a complex of alpha and Y. The equilibrium between Y and liquid, that we perhaps see here, could only be arrived at in an indirect way; if we had attempted to reach it by cooling molten Al 20 the alloy would, at 525° C., have become a mass of solid beta.

Al 22 was recalesced at 478° C., the temperature rising to 520° C., the ingot cooling in a few minutes to 486° C., when it was chilled. A control was treated in the same way but not recalesced. Both ingots have large crystals of D approximating in shape to those that separate along the *c*L line, but the recalesced ingot, alone, has a golden network of alpha in the matrix identical with that of the recalesced Al 20. We have also forced a recalescence in Al 23, but the pattern shows very little change.

The recalesced ingots retain the new pattern when annealed at any temperature below 520° C., the only changes produced by the anneal being to segregate any fine pattern into larger particles and, if there is a redundant phase, to remove it by the reaction alpha + D = Y.

It would now be possible to determine the complete equilibrium diagram of Y, by giving a prolonged anneal, at successive temperatures, to a number of recalesced alloys.

Experimental Details.

The alloys used in determining the liquidus, and also for many of the cooling curves, were in large quantities of several hundred grammes and were carefully analysed at the end of each experiment; but such a large number of alloys had to be made that, as a rule, we dispensed with analysis, each alloy being prepared by weighing out appropriate quantities of pure gold and pure aluminium and melting them together in a vacuous silica tube. This method of making the alloy seems to exclude the probability of any error except perhaps that of assuming the percentage of aluminium to be slightly higher than the true value.

Etching.

The etching reagents were bromine water or *aqua regia*; the two give practically the same pattern, *aqua regia* being more rapid and clean in removing the smear of metal produced in polishing. Alpha always etches bright whatever other phase is present. D etches bright in the presence of beta or of Y, but generally darkens if alpha is present. Beta and Y both etch dark, and are rapidly eaten away, in the presence of either of the other two phases. The result is a curious one in the case of alloys containing primaries of D; if the ingot is chilled above the temperature of the L eutectoid the D is bright and the ground is dark, but if the eutectoid is present, then the alpha in it generally causes the D to darken; if the alpha is removed, by recalescence and annealing, the D again etches bright, so that even without the microscope one could pretty safely infer what phases were present. Perhaps the only case where it is difficult to distinguish between alpha and D is in such an alloy as Al 20, after spontaneous recalescence and a long anneal (fig. 17). In this case there is so little of the bright substance, and the particles are so minute, that the microscope, alone, would leave us uncertain.

We have to thank Mr. F. E. E. LAMPLOUGH for very valuable help in the thermometric work and for devising an excellent method for the automatic regulation of high temperatures.

We have also to thank Prof. POPE, F.R.S., for his kindness in placing the resources of the University Laboratory at our disposal, and, in especial, for lending us valuable apparatus and lenses for microscopic photography.

DESCRIPTION OF THE MICROPHOTOGRAPHS (Plate 4).

1. Al 15. 50 diameters.
Plunged molten into bath at 470° C., annealed for 20 hours and chilled.
A uniform solid solution of alpha.

2. Al 15. 50 diameters.
Annealed at 545° C. for 23 hours and chilled.
The white is alpha, the dark matrix is beta.

3. Al 18. 50 diameters.
Plunged molten into bath at 520° C., annealed for 8 hours, chilled.
Shows the decrease in the alpha as the content of Al grows.

4. Al 20. 18 diameters, oblique illumination.
Plunged molten into bath at 535° C., annealed for 17 hours, chilled.
Beta only. The relief effect is due to minute striations.

5. Al 18. 350 diameters.
Plunged molten into bath at 470° C., annealed 20 hours, chilled.
The greater part of the beta of this ingot etches the usual uniform dark, but some patches give the bright ruling of the photo. This is, no doubt, due to a very perfect laminar crystallisation of the beta, or of a body derived from the beta. The smooth parts are alpha primaries. This bright ruling can be found in a good many alloys from Al 18 to Al 23 when chilled above 440° C. Almost equally perfect ruling can be found in the dark beta.

6. Al 23. 20 diameters.
Plunged molten into bath at 506° C., annealed for 3 hours, cooled to 410° C., annealed for 18 hours, chilled.
The white is D, the ground is now, presumably, Y. The photo shows three crystal skeletons of D. It is typical of all the primaries of D.

7. Al 25. 50 diameters.
Plunged molten into bath at 535° C., annealed 20 hours, chilled.
The white is D, the dark is beta. The small pattern, which must have formed rapidly during the chill, but a good deal of it at the eutectic temperature of the point C, seems to be made up hexagonal rods of beta surrounded by a margin of D. This is the nearest approach to the C eutectic that we have.

8. Al 20. 160 diameters.
Plunged molten into bath at 510° C., annealed 1 hour, cooled to 440° C.; annealed 3 hours, cooled to 418° C.; annealed 9 hours and chilled.
The large dark bars are pseudo-primary of D that separated when temperature fell to the *c*L line. The small pattern is the L eutectoid of alpha and D.

8A. Al 20. 160 diameters.
The same ingot as that of fig. 8, but after the further treatment of dropping the ingot cold into bath at 400° C. and so provoking the recalescence. The ingot was annealed for 10 minutes at 400° C.
The small white is the alpha left after the decomposition of the eutectoid. The dark ground is Y. The large white is the residue of the pseudo-primary of D; this would be removed by a longer anneal and would leave a pattern like that of fig. 17.

9. Al 18. 300 diameters.
Plunged molten into bath at 418° C., annealed 22 hours and chilled.
A pre-recalescence pattern. The large white is primary alpha. The smaller complex is the L eutectoid of alpha and D.

9A. Al 18. 300 diameters.
The same ingot as that of fig. 9, but after recalescence brought about by heating for 10 minutes to 400° C.
The large primaries of alpha are no longer uniform, but are full of the recalescence pattern (compare with fig. 10). The small white is the residue of alpha left over after the decomposition of the L eutectoid.

9B. Al 23. 350 diameters.
Plunged molten into bath at 560° C., cooled in 2 hours to 420° C., chilled.
A pre-recalescence pattern. The large dark masses are primary D, the complex is the L eutectoid.

Plate 5.

10. Al 14. 80 diameters.

Molten and annealed at 535° C. for 4 hours, cooled to 440° C.; annealed for 17 hours, cooled to 418° C.; annealed 4 hours, cooled to 400° C.; annealed 1·5 hours, chilled.

Shows the effect of the recalescence on the alpha; a control ingot similarly treated, but chilled at the termination of the anneal at 418° C., has no pattern except traces of hair-line polygonal boundaries.

11. Al 15. 200 diameters.

Annealed at 545° C. for 23 hours, chilled.

Shows the white, uniform, alpha, and the dark, almost uniform, beta. A pre-recalescence pattern.

12. Al 15. 200 diameters.

Plunged molten into bath at 535° C., annealed for 6 hours, cooled to 520° C.; annealed 2 hours, cooled to 380° C.; annealed 12 hours and chilled.

A post-recalescence pattern, showing new detail in alpha and in beta.

13. Al 18. 350 diameters.

Plunged molten into bath at 506° C., annealed 3 hours, cooled to 410° C.; annealed for 18 hours and chilled (compare with fig. 3).

Shows the recalescence detail in both alpha and beta.

14. Al 23. 320 diameters.

Melted and plunged into bath at 560° C., cooled in 1·5 hours to 420° C. and chilled. Same ingot as that of fig. 9B.

The large dark is D primary. The small pattern is the L eutectoid complex of alpha and D.

15. Al 23. 320 diameters.

Similarly treated to the preceding, but cooled to 400° C. before chilling.

Shows the effect of the recalescence on the eutectoid.

16. Al 20. 20 diameters.

Plunged molten into bath at 530° C., annealed 1 hour, cooled to 440° C.; annealed 17 hours and chilled.

The white polygons of D crystallised out of the uniform solid beta when the temperature fell to the *c*L line.

17. Al 20. 50 diameters.

Plunged molten into bath at 506° C., annealed 3 hours, cooled to 410° C.; annealed 18 hours and chilled.

This represents the final condition of Al 20 after recalescence and a long anneal; it consists of Y with a trace of residual alpha in small particles.

18. Al 20. 50 diameters.

A control ingot to the forced recalescences of the alloys described below. The ingot was placed molten in bath at 560° C., cooled to 508° C., and chilled.

It consists of uniform beta; under oblique lighting it resembles fig. 4.

19. Al 20. 50 diameters.

Similar treatment to the preceding, but, in addition, the ingot was forced to recalesce at 508° C. by touching with a cold wire, the reaction causing the temperature to rise to 523° C. A few minutes later, when the temperature had again fallen to 508° C., the ingot was chilled.

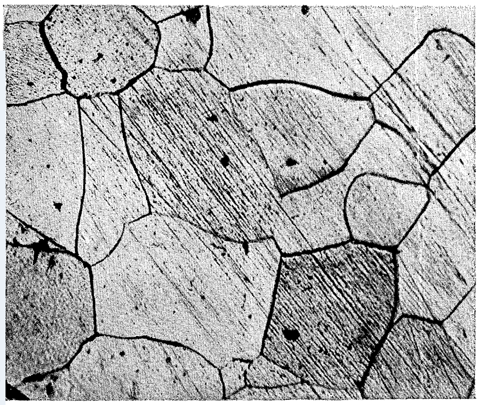
There are large crystal skeletons of the new body Y bordered by a white substance which is, presumably, alpha.

20. Al 20. 160 diameters.

The same ingot and treatment as that of fig. 19. An enlarged view.

21. Al 20. 50 diameters.

A forced recalescence at 514° C. Temperature rose to 524° C. and remained at that temperature for some minutes through the heat evolved in the reaction. There was consequently some fusion and the dark matrix is beta reformed on solidification. The crystal skeletons are of Y.



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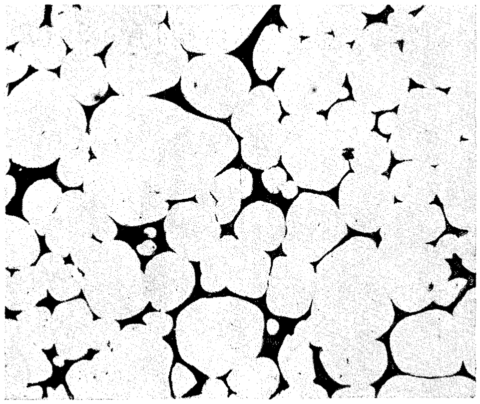

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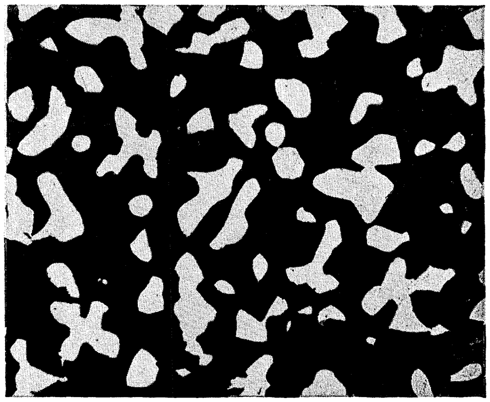

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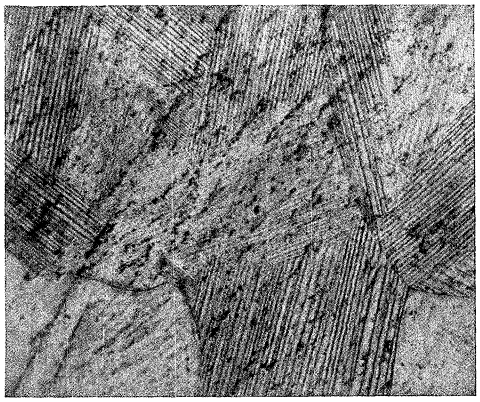

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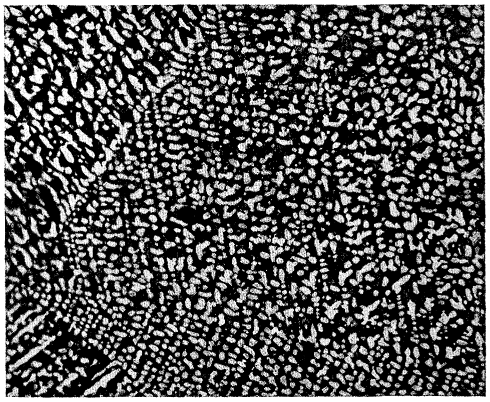

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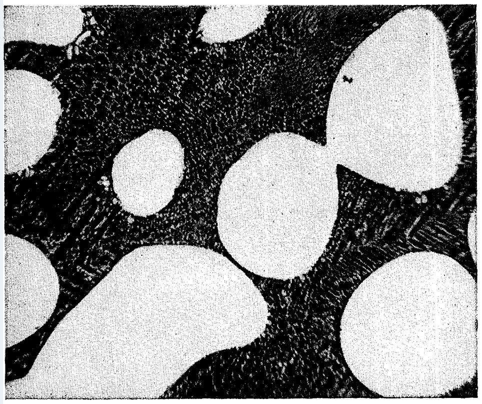

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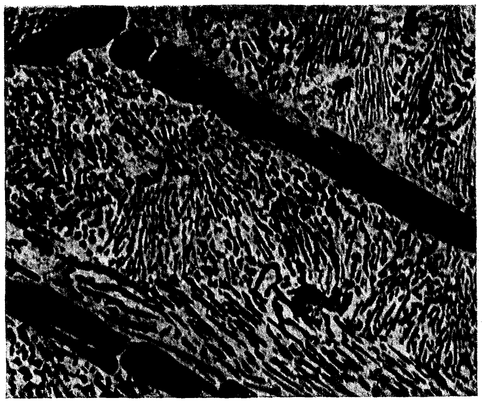

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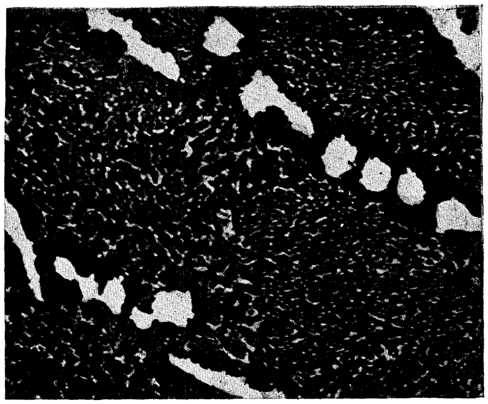

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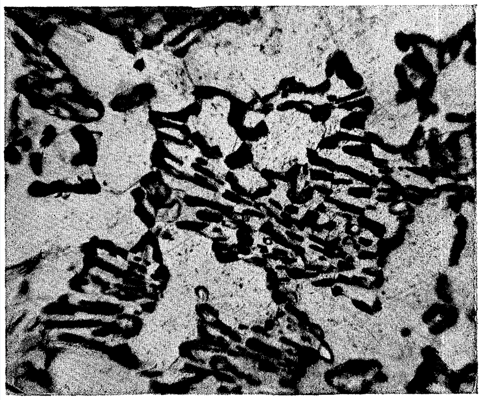

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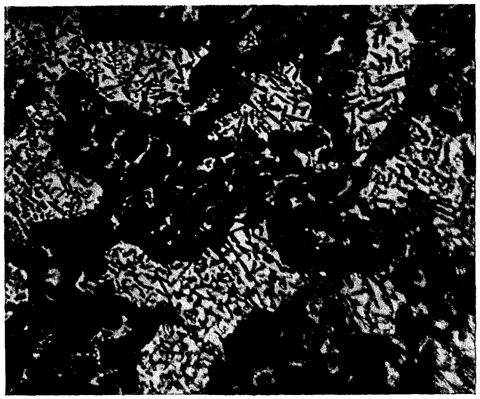
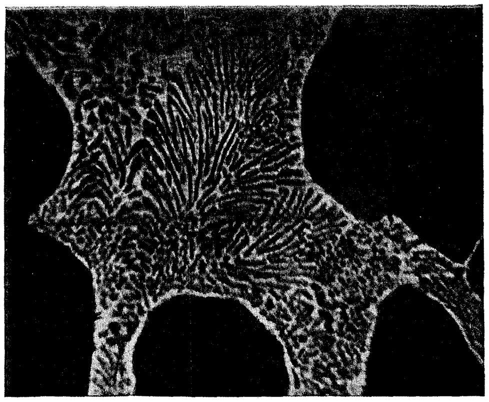


9A.



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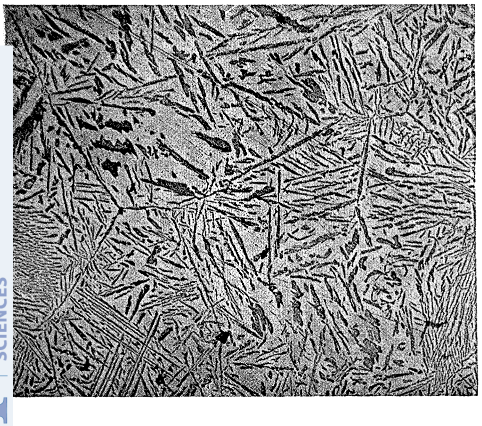

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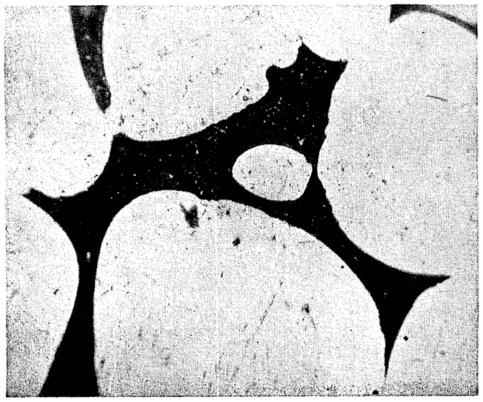

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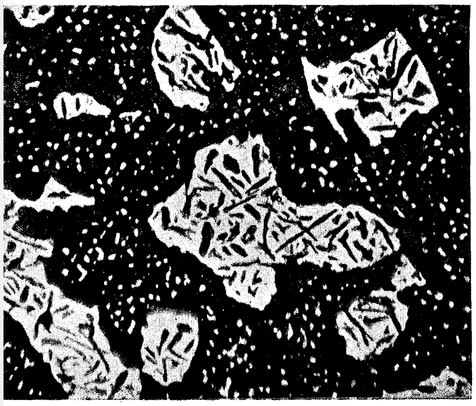

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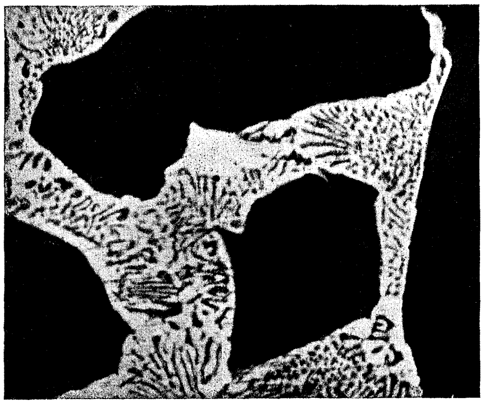

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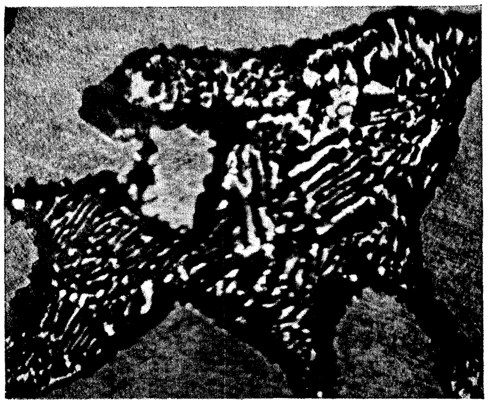

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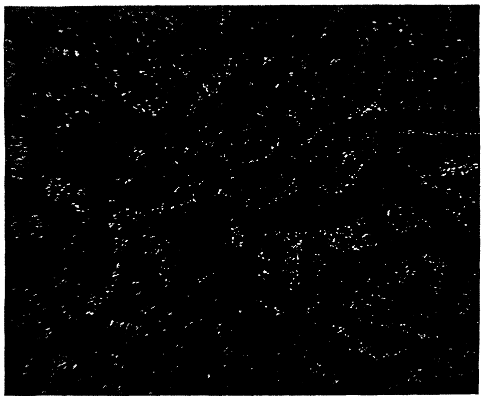

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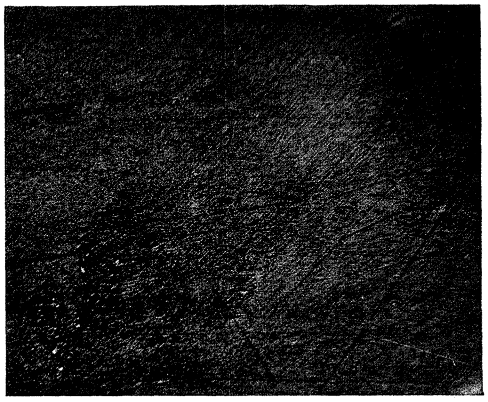

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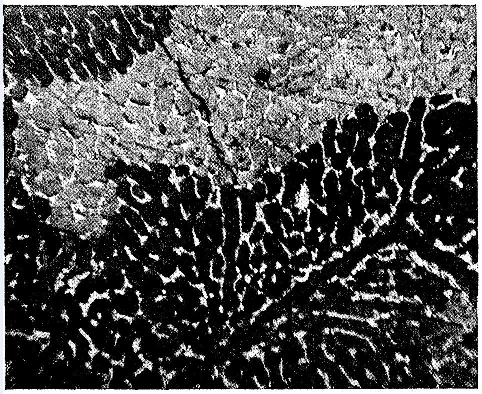

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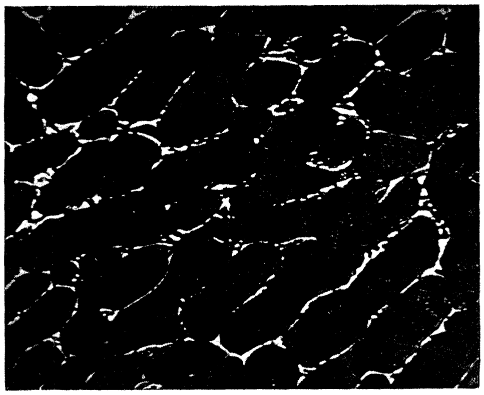

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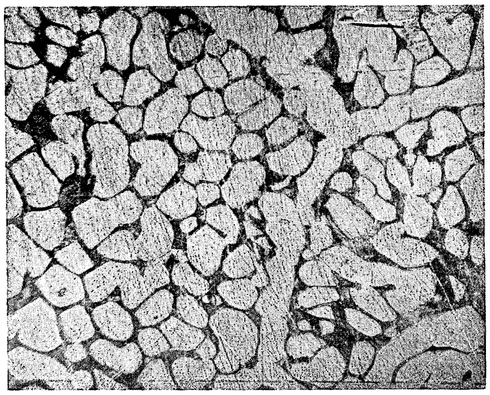

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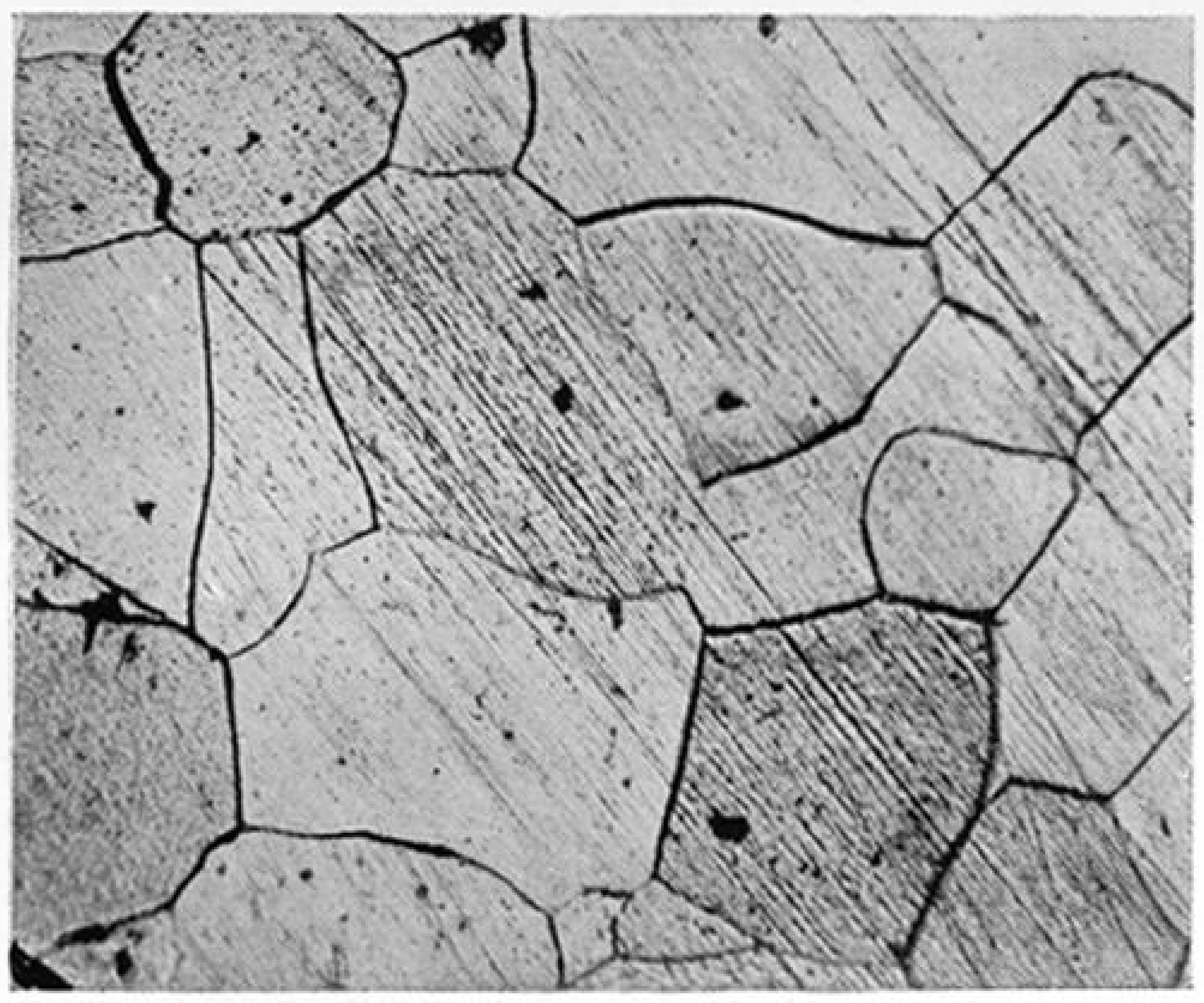

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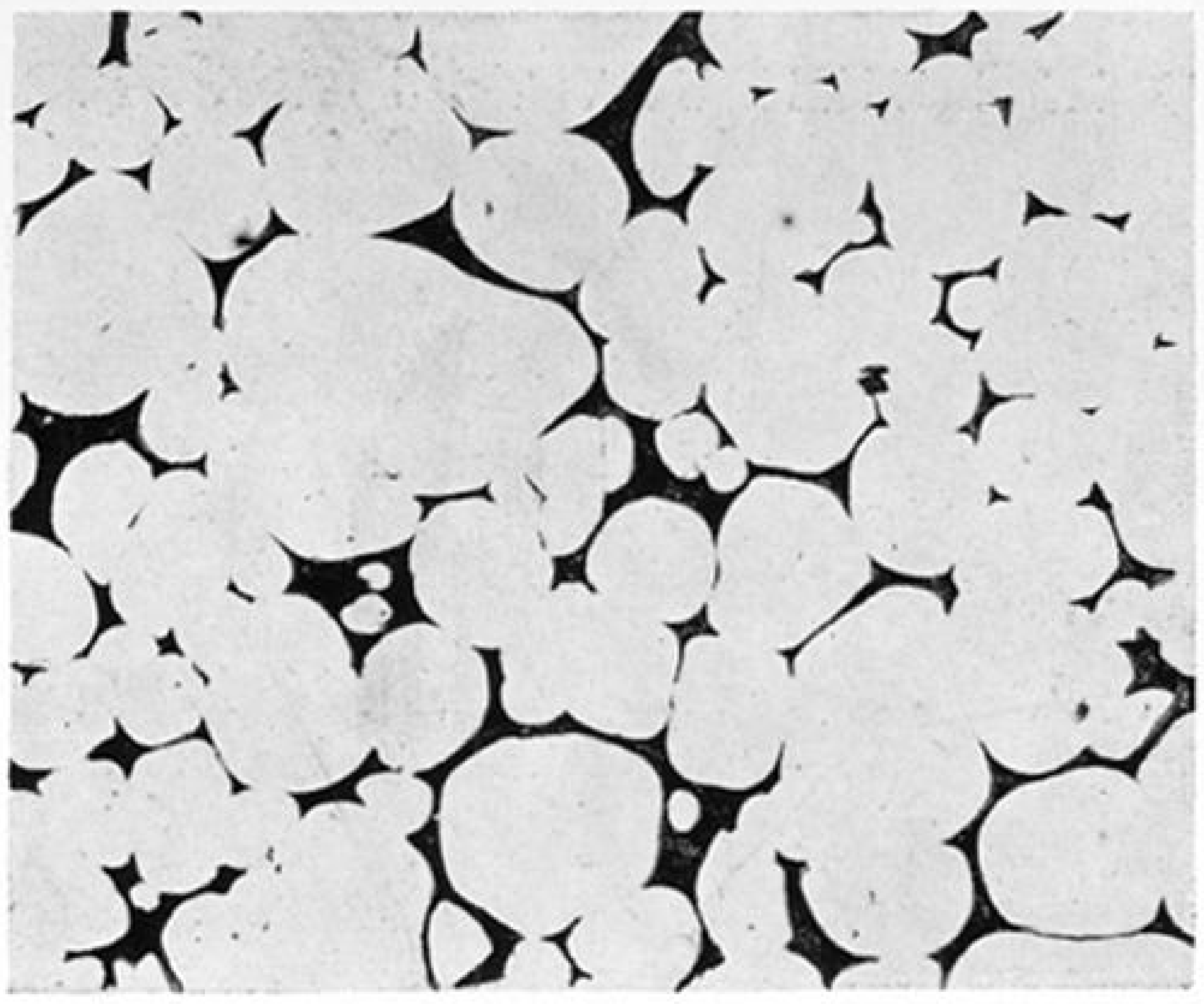

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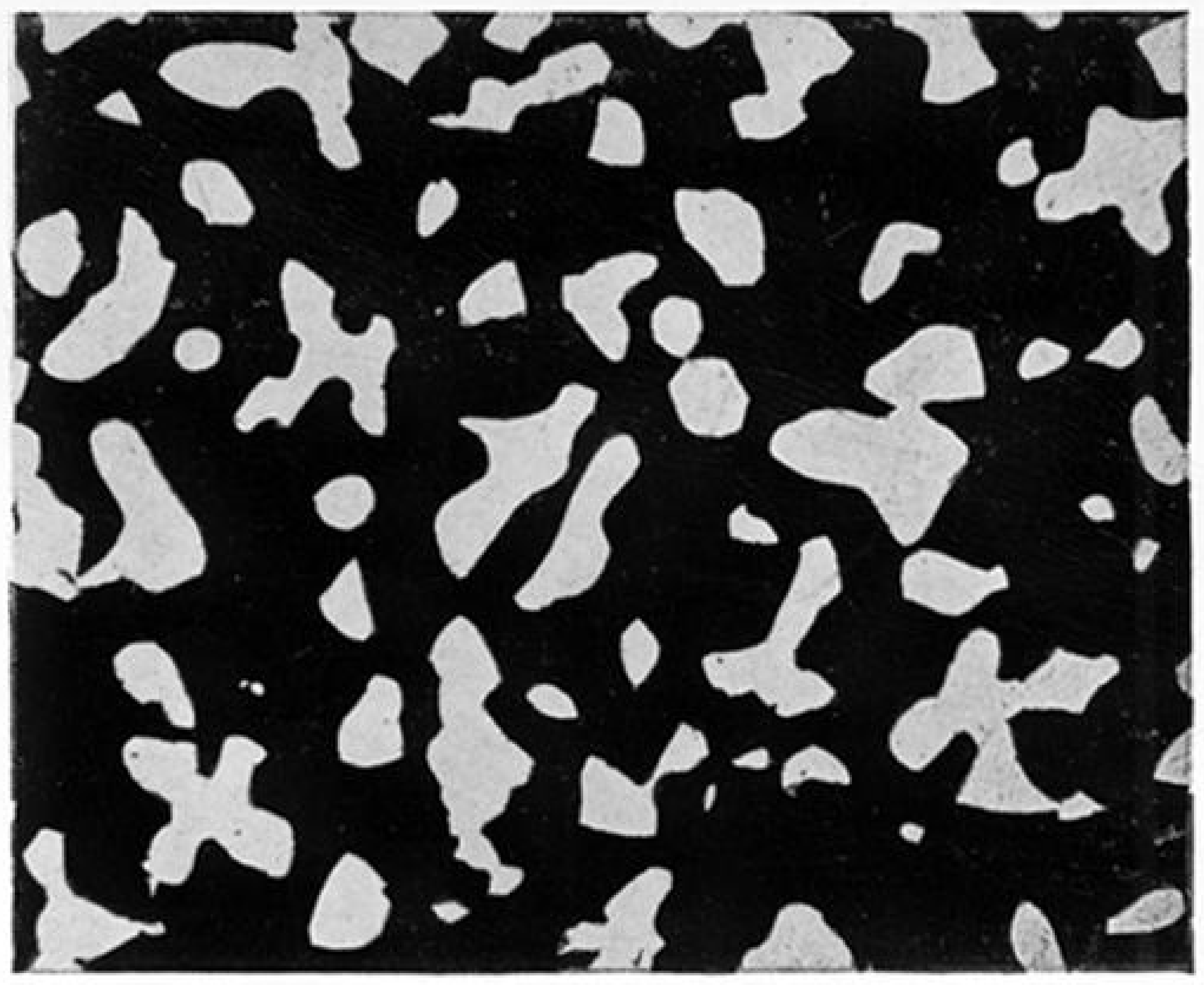

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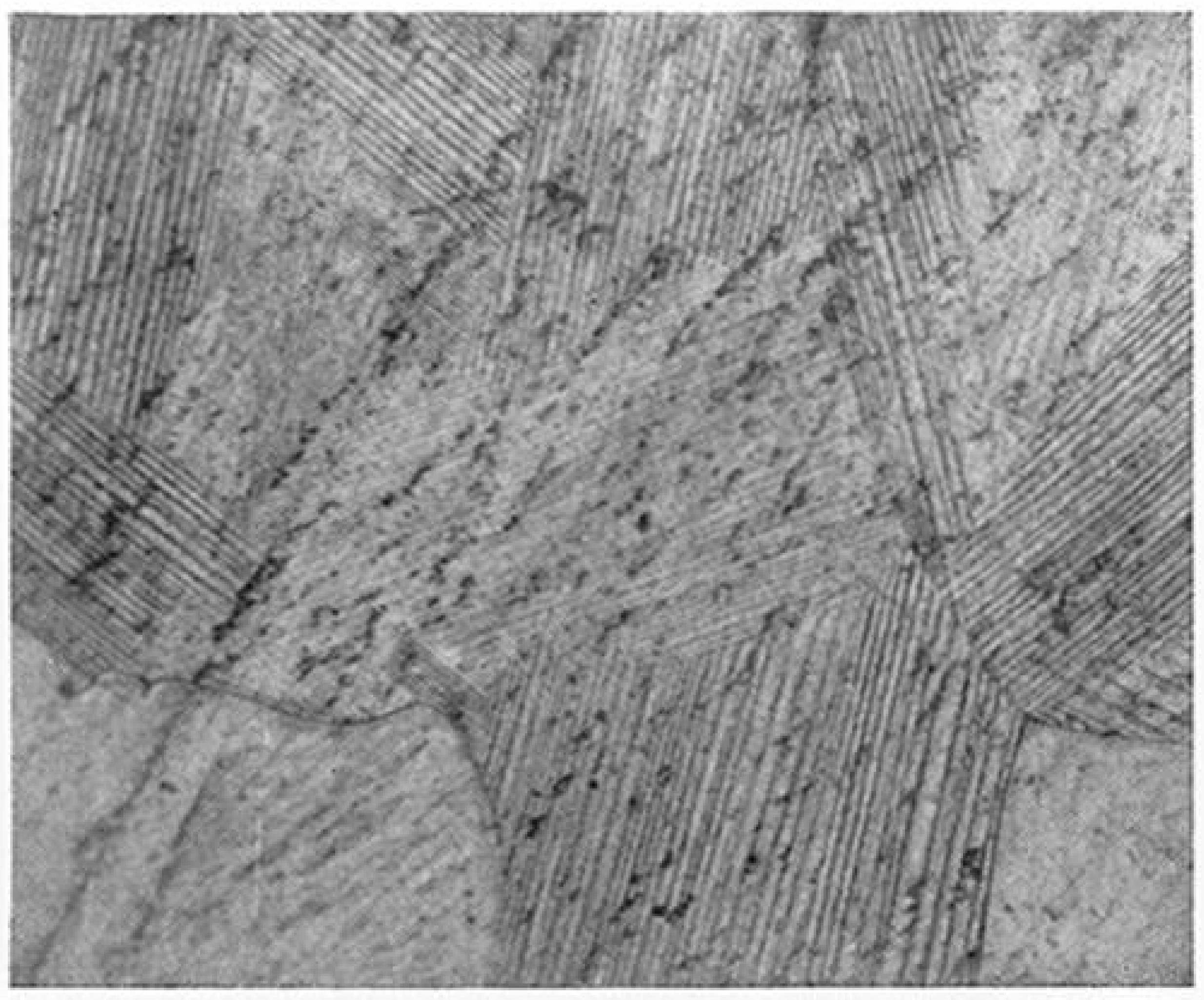

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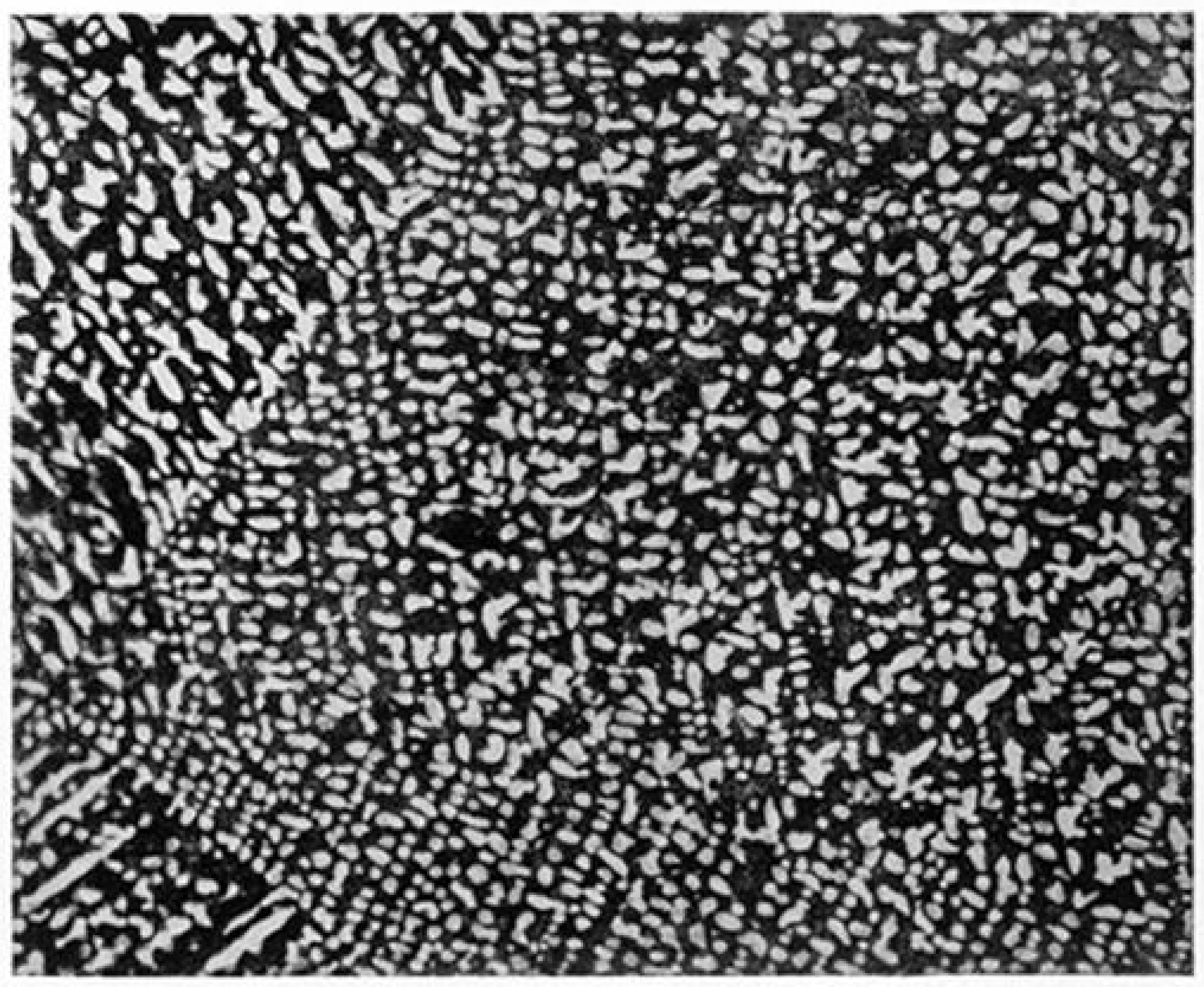

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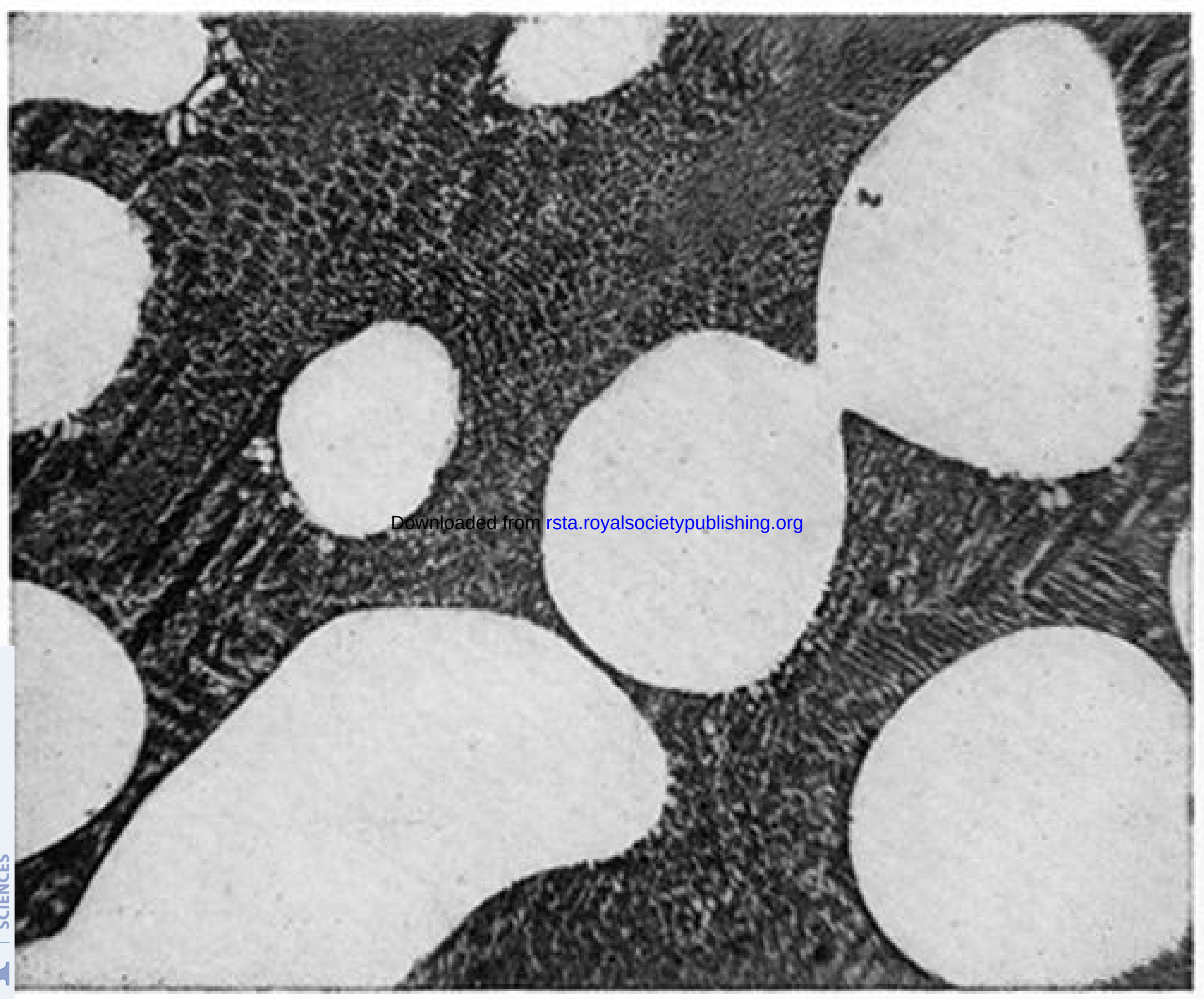

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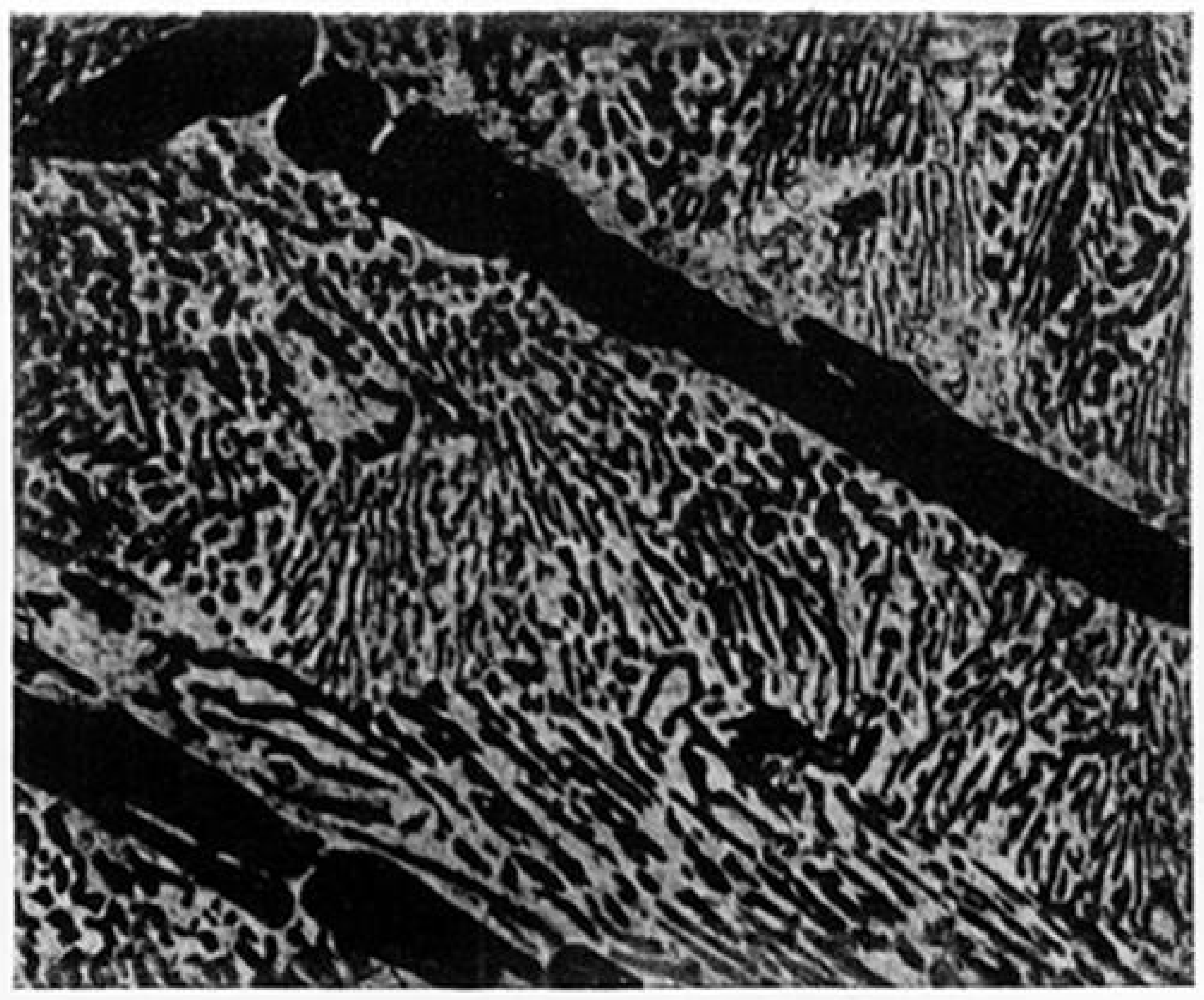

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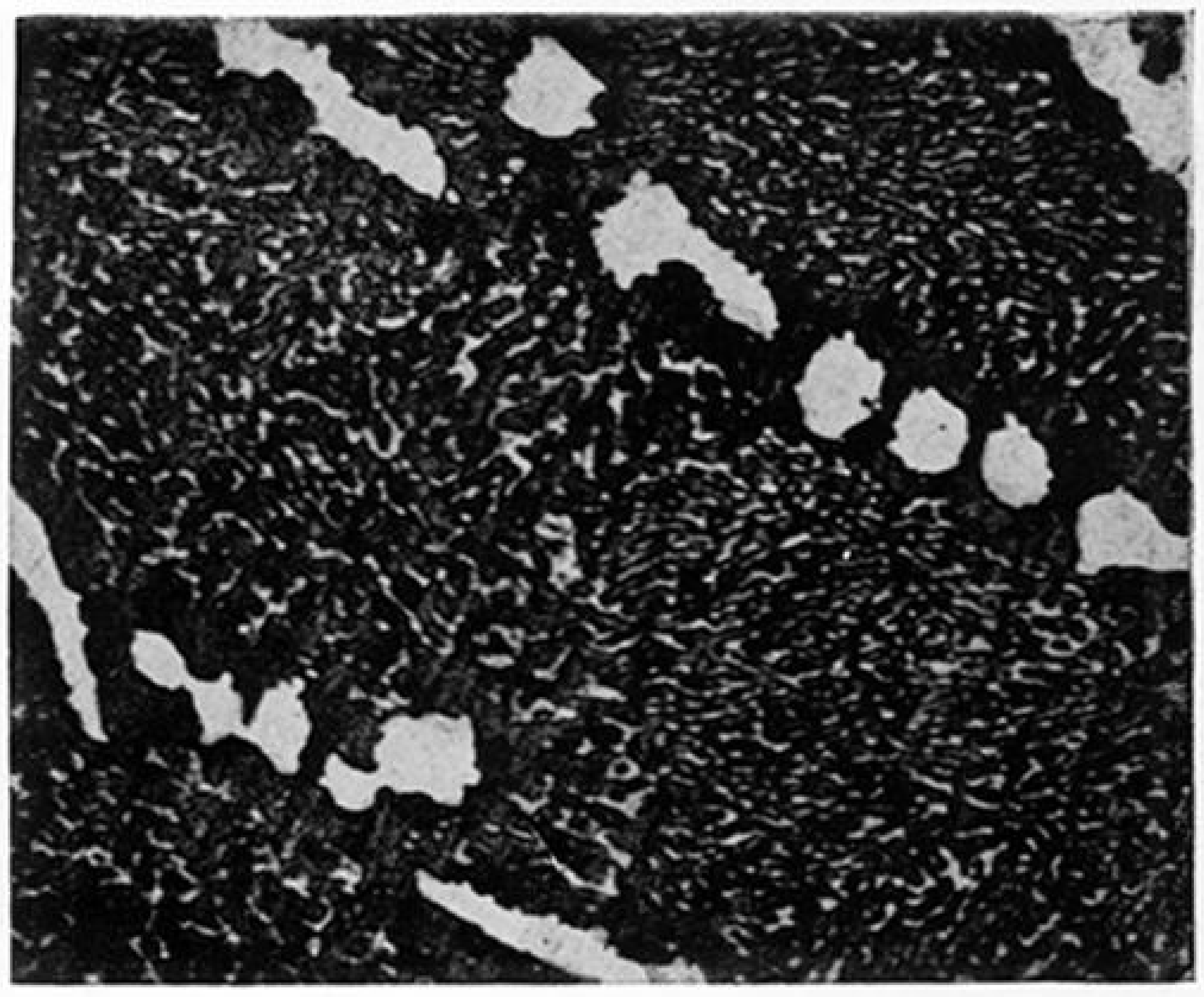

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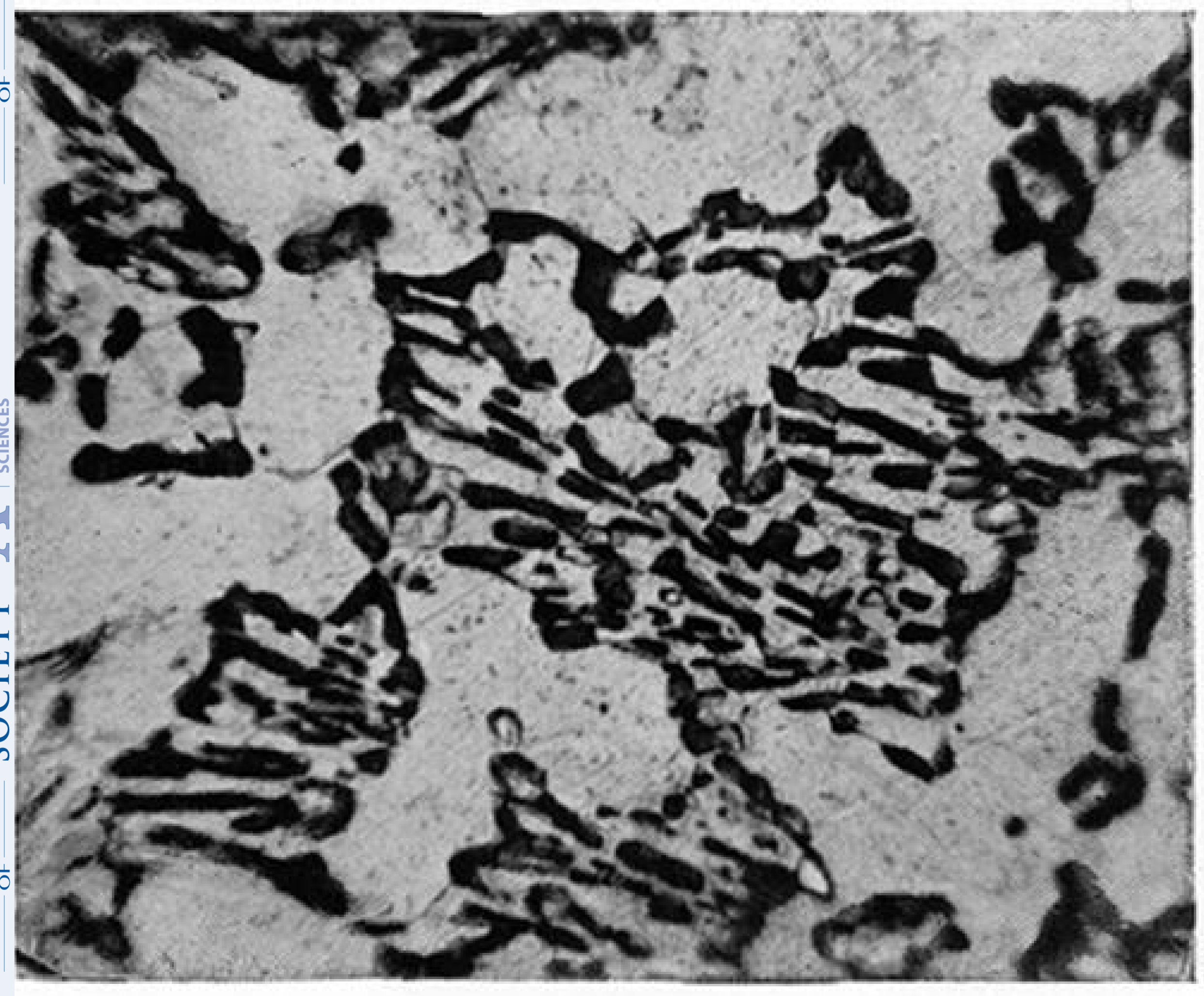

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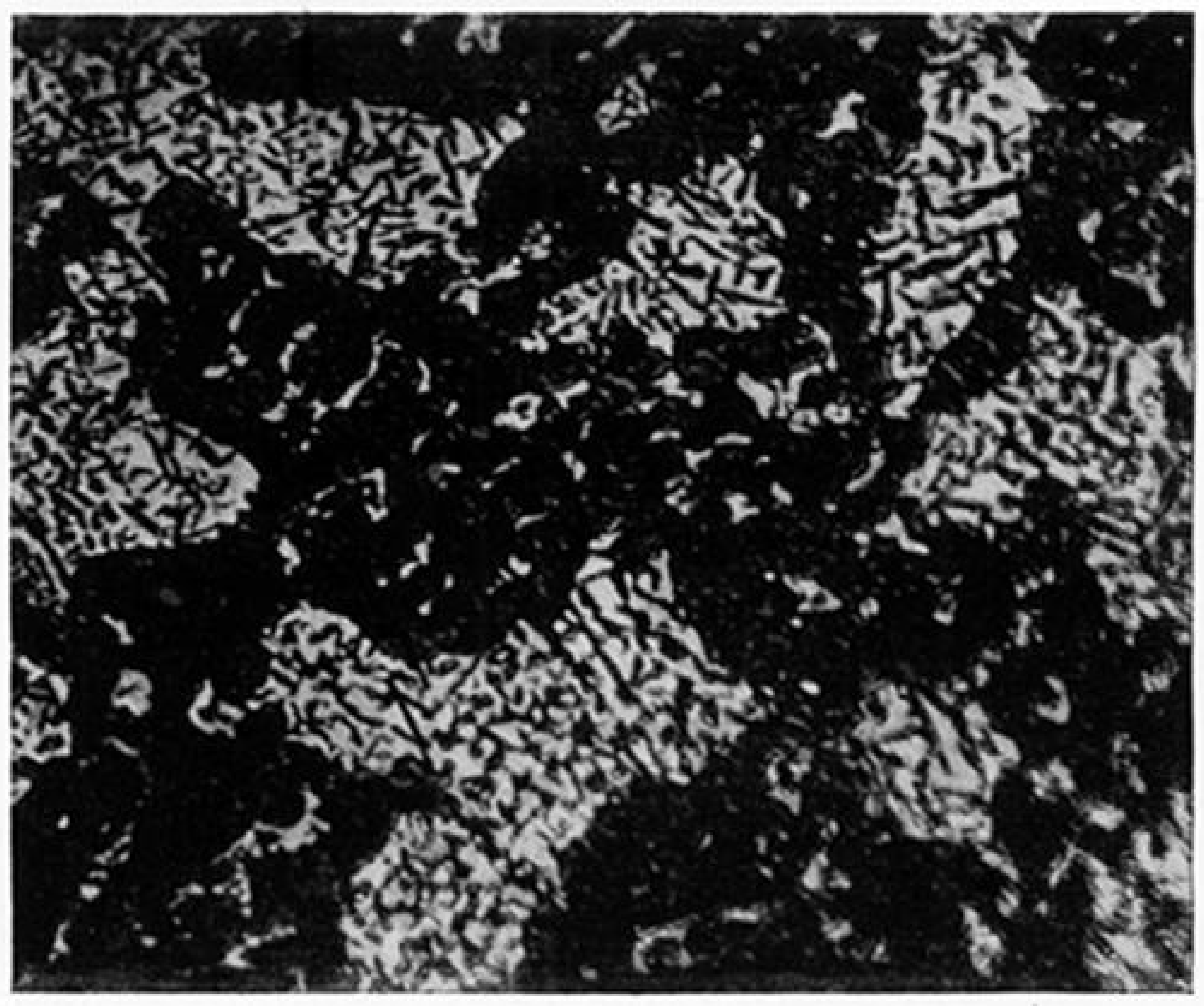

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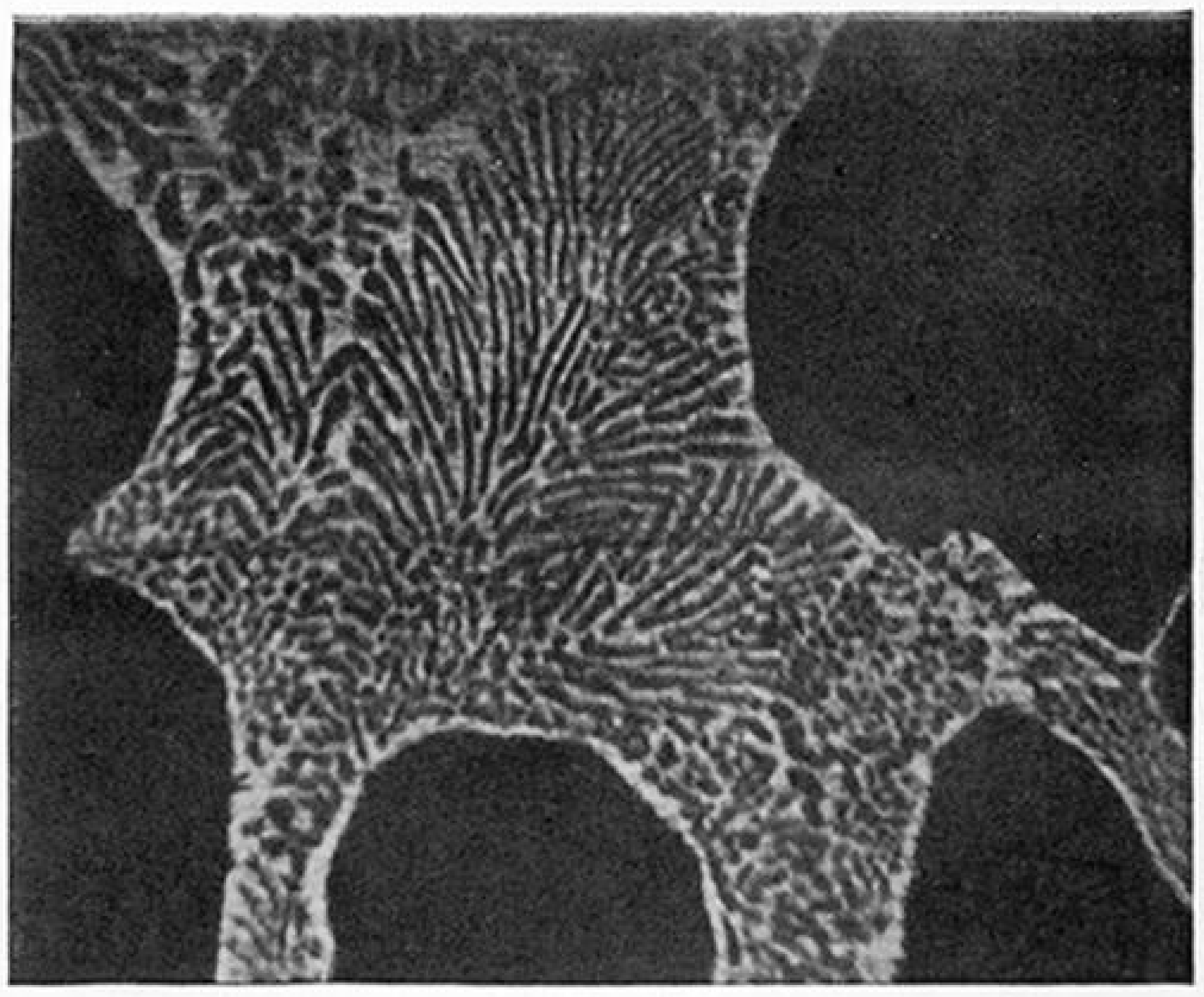

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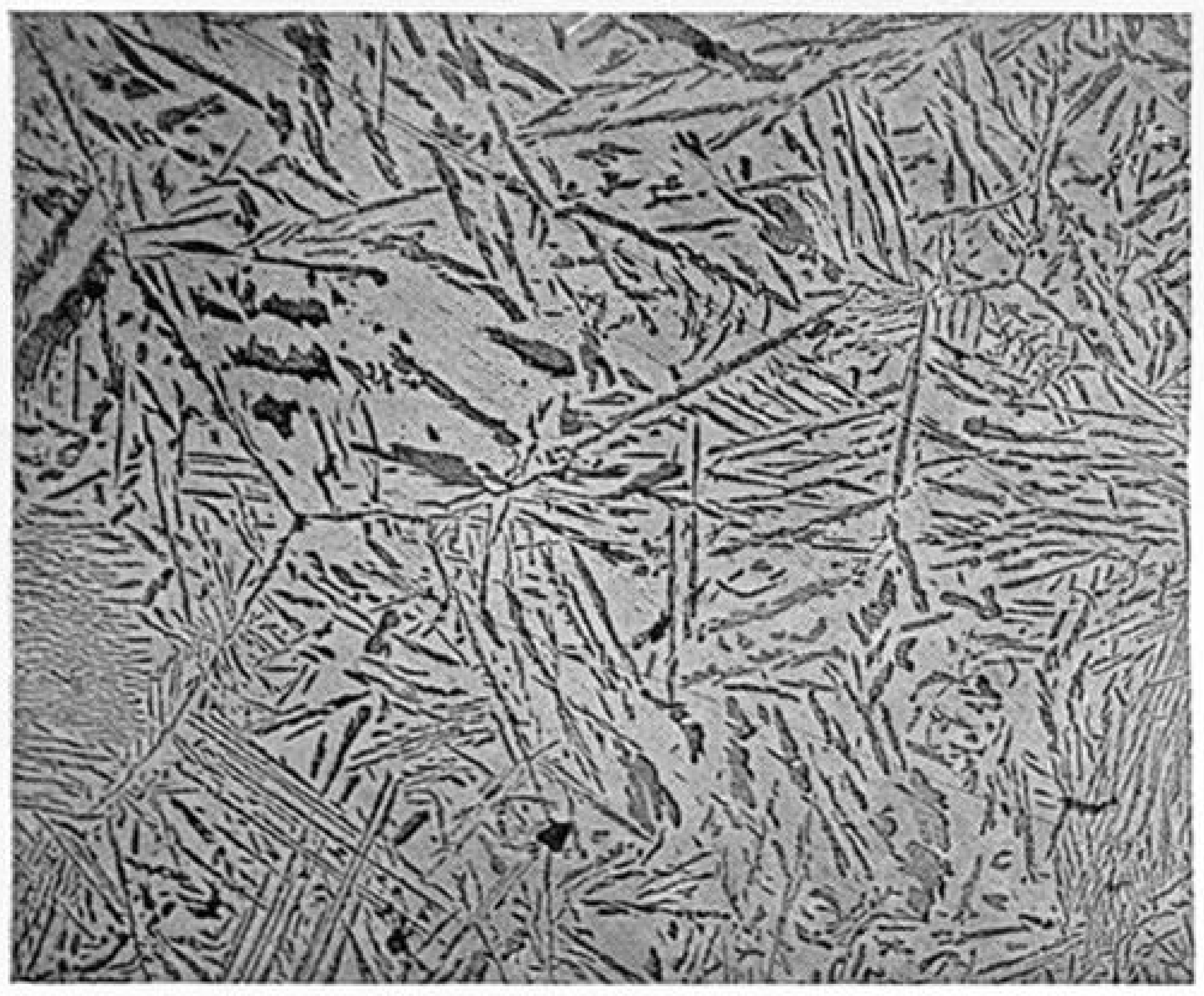

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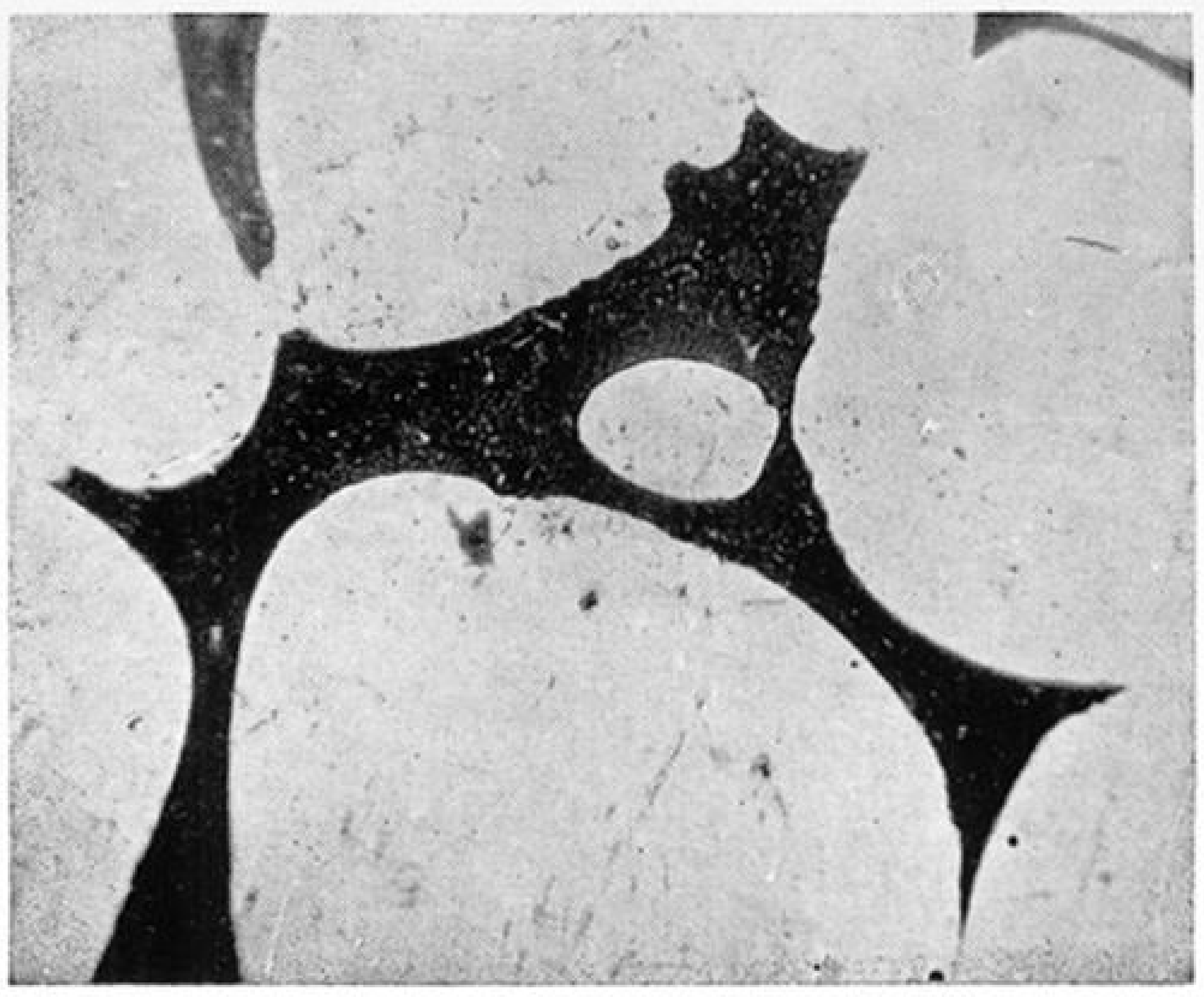

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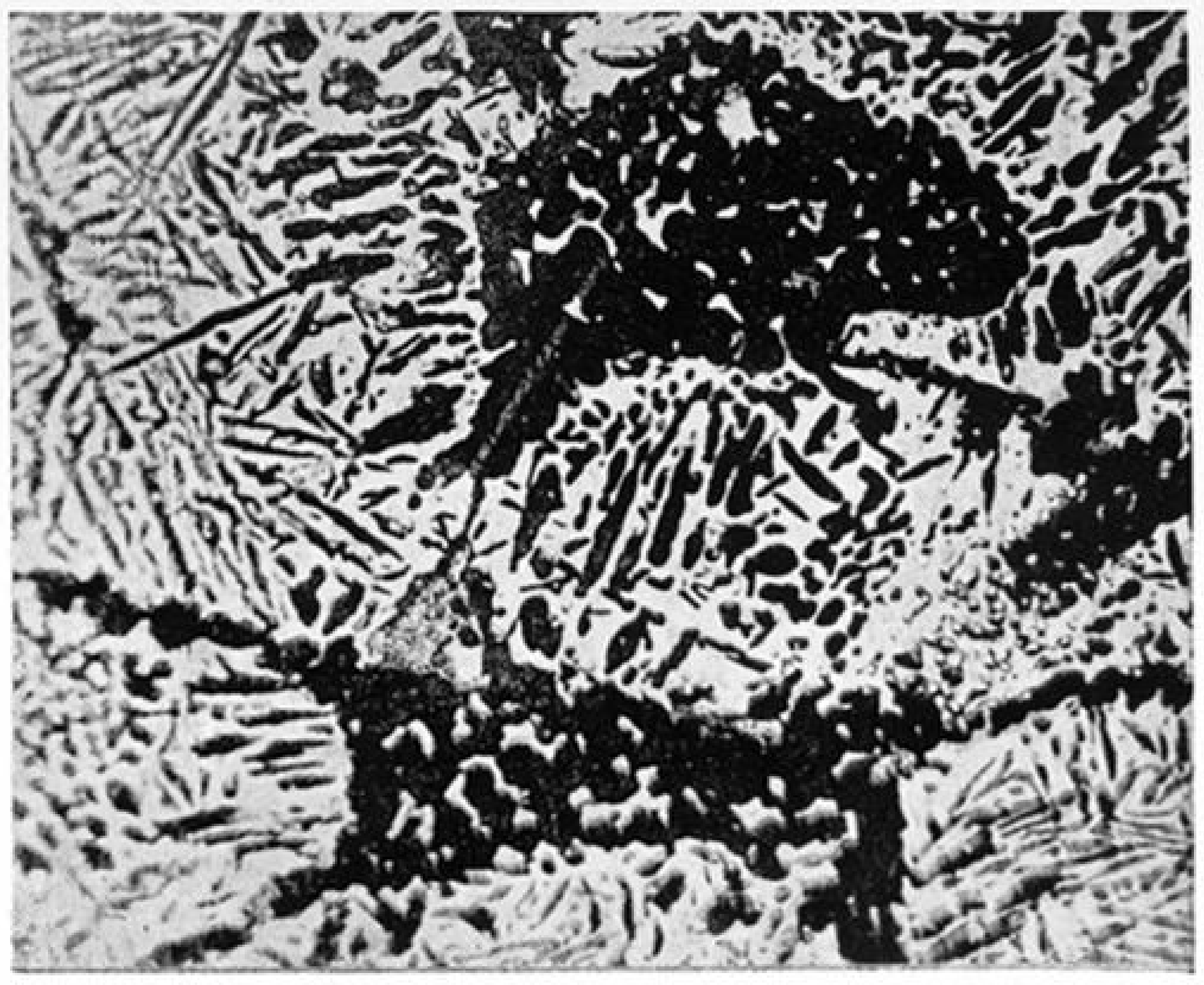

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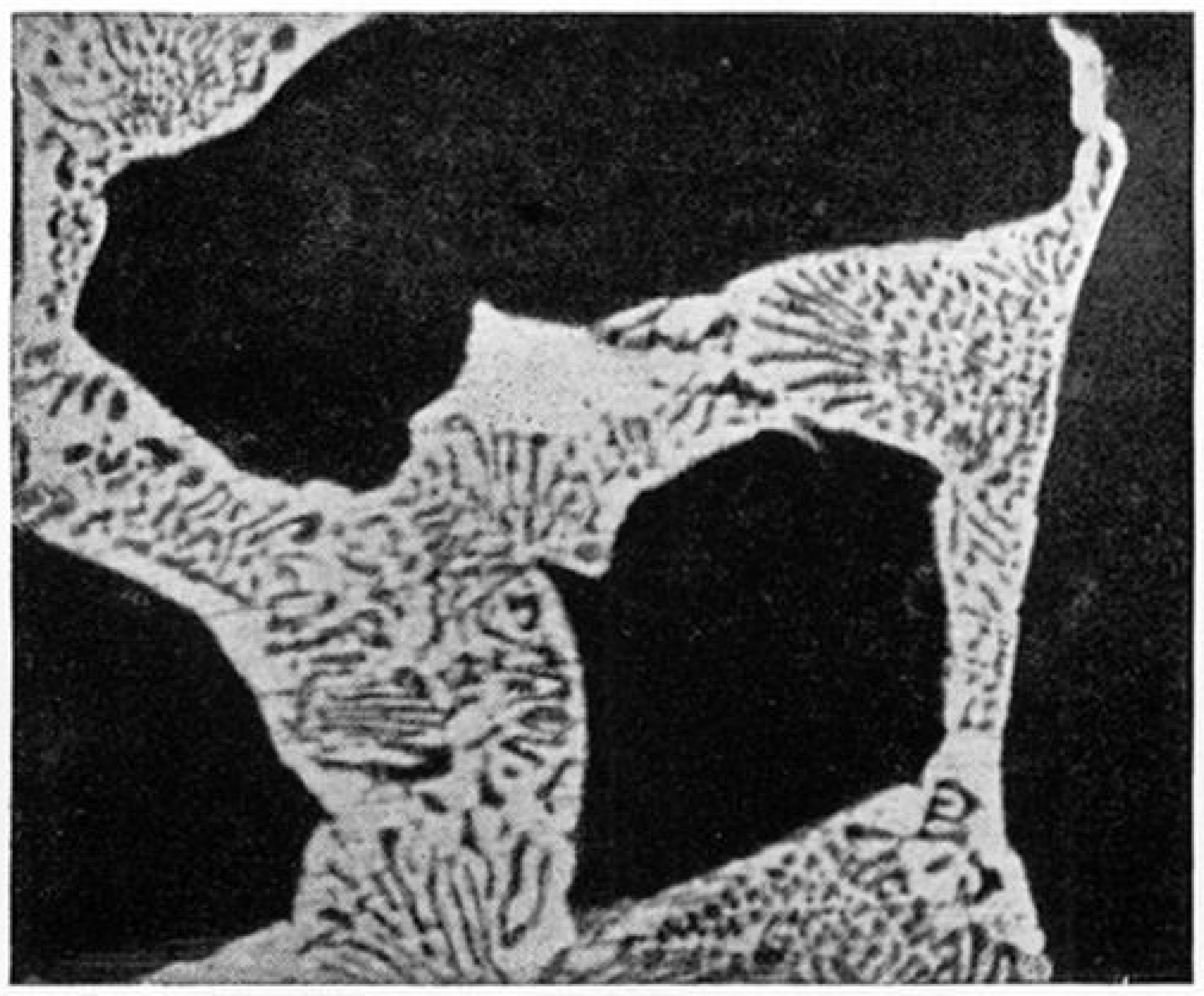

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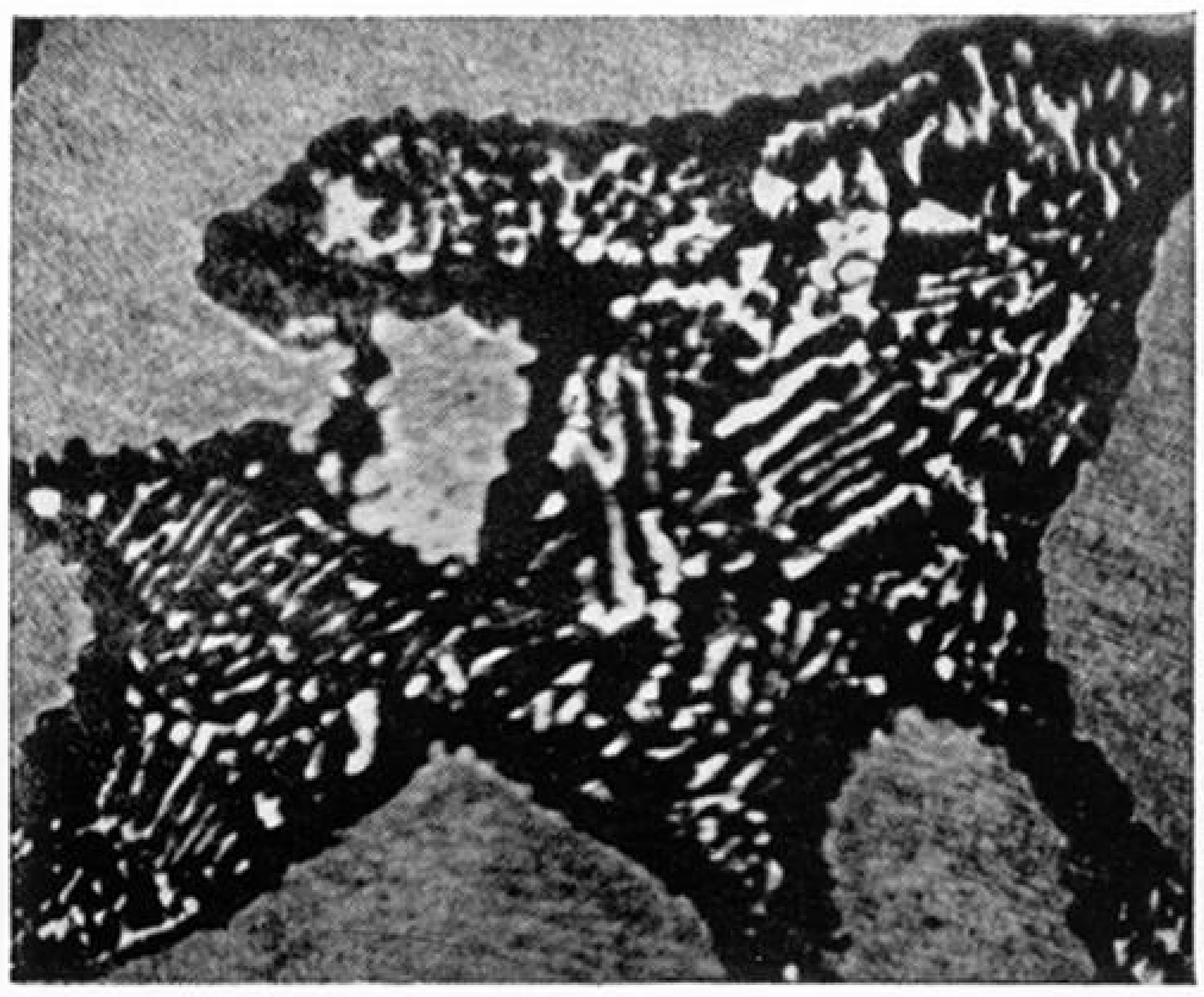

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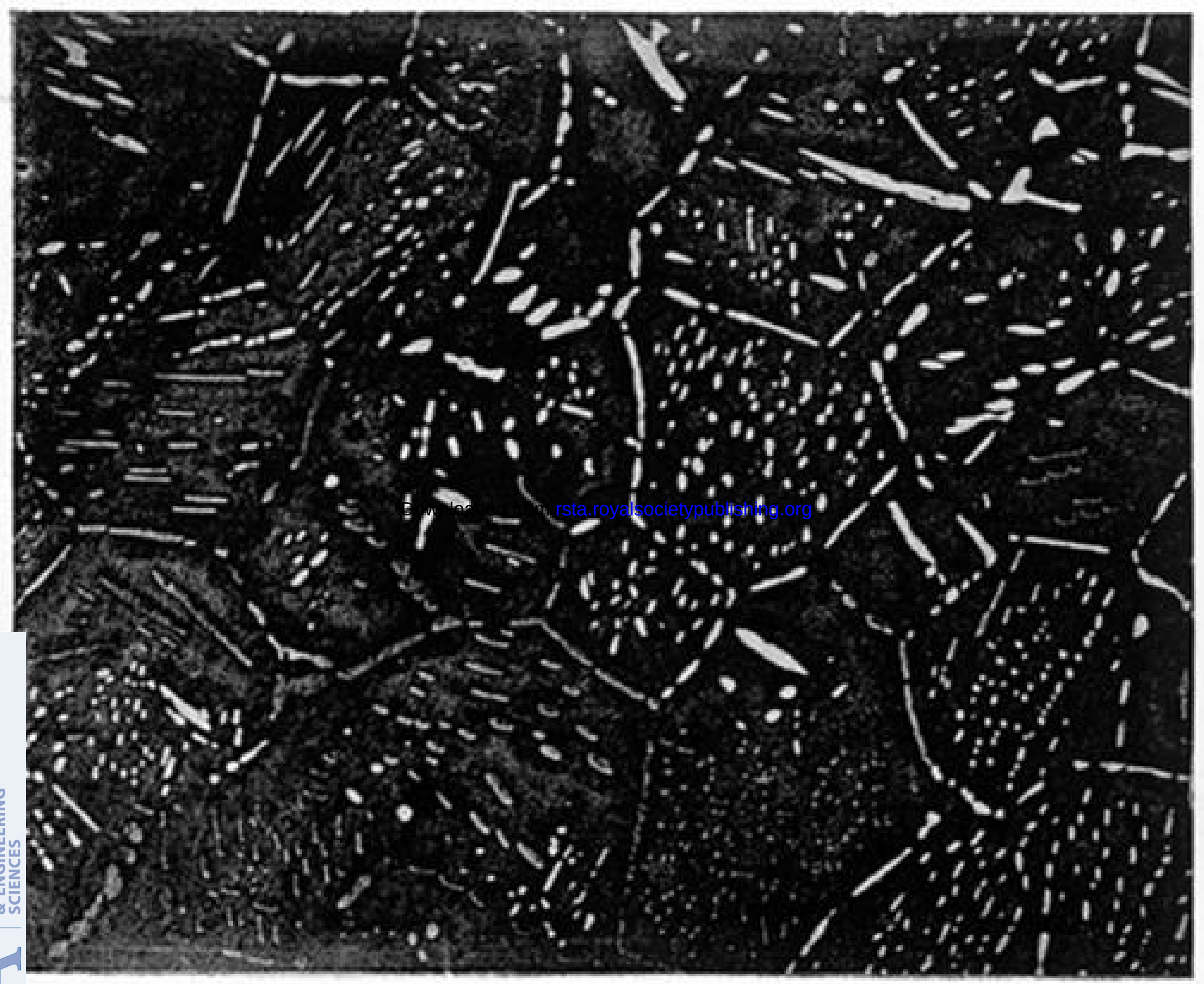

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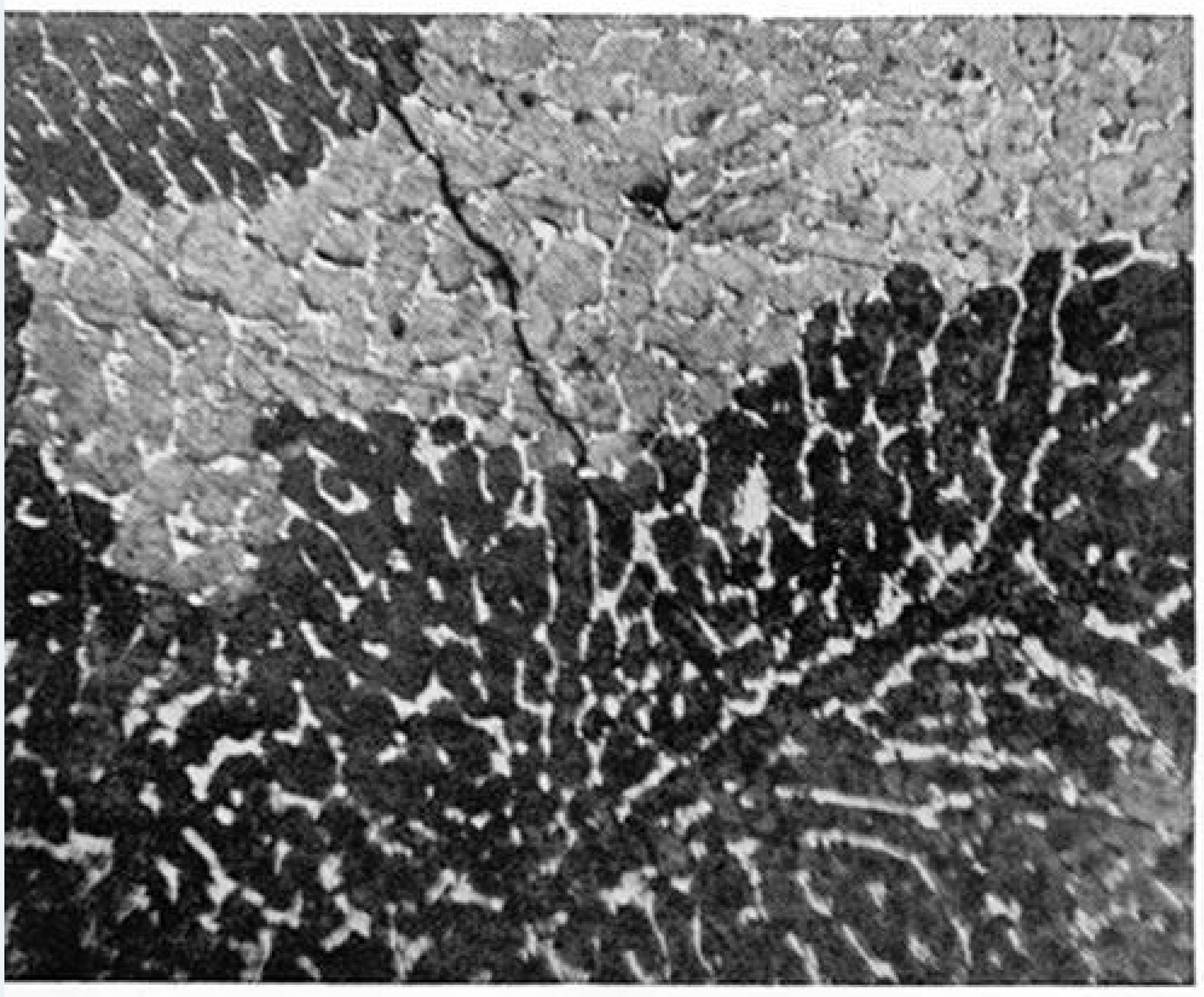

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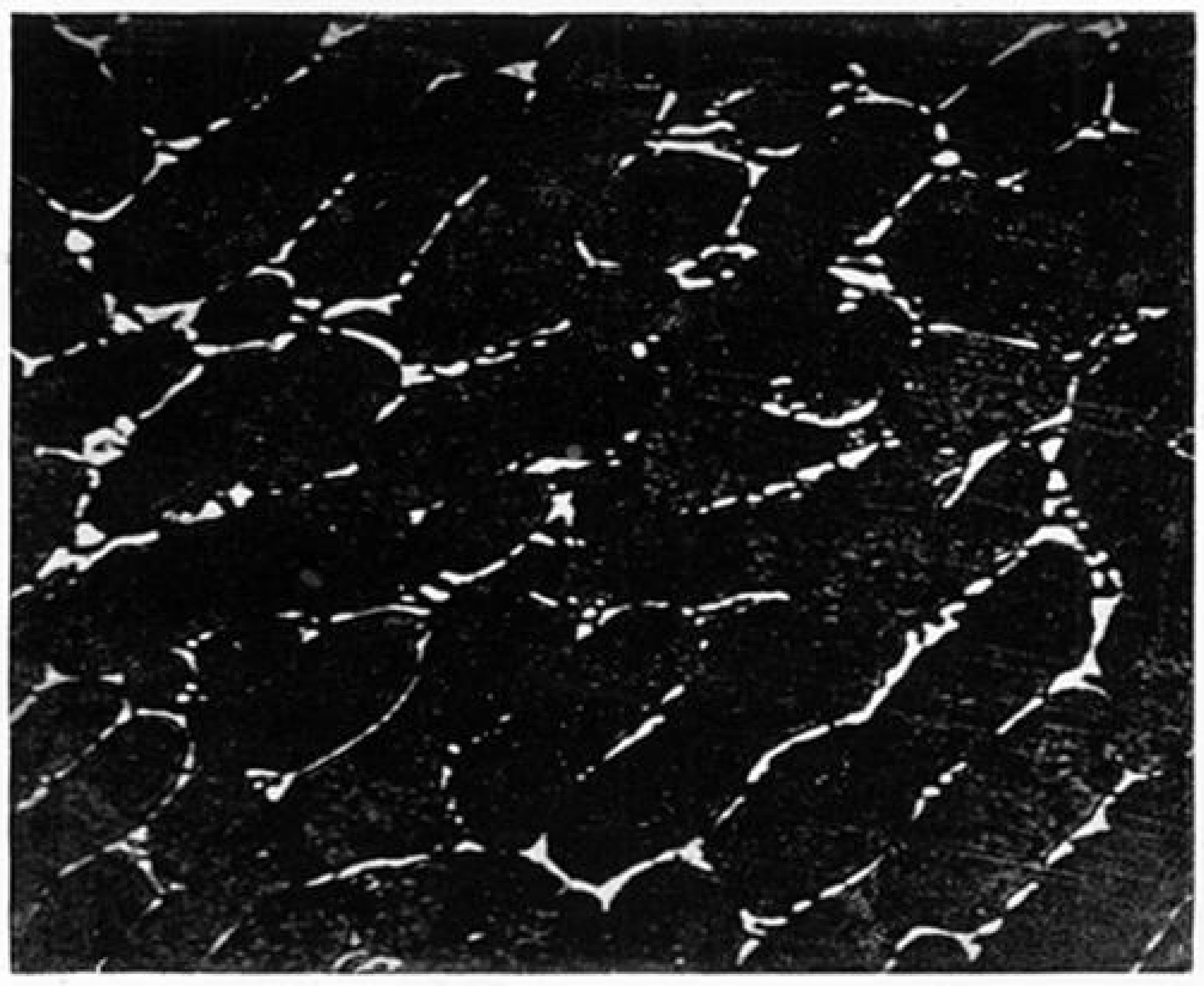

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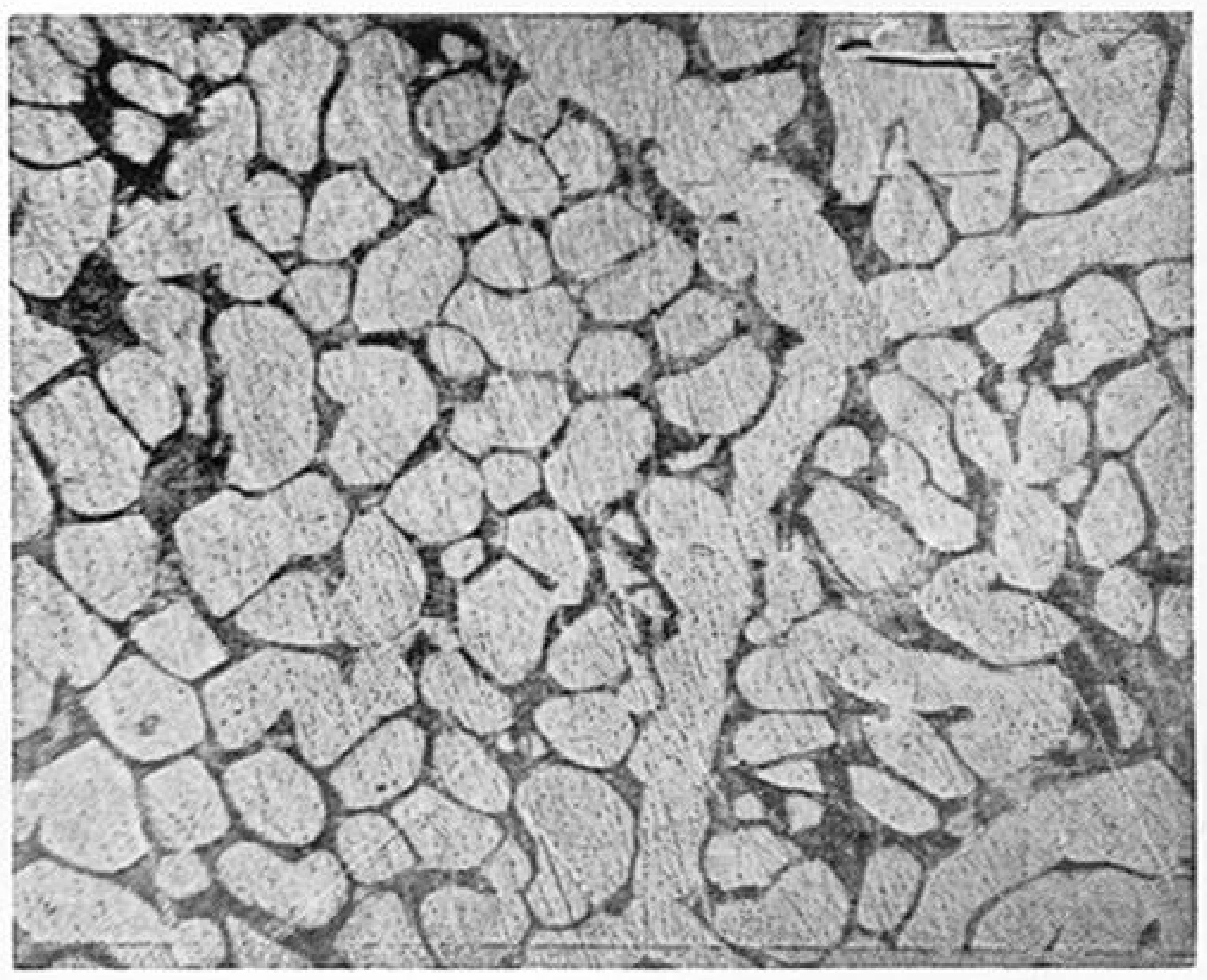

21.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES