VIII. *The Crystalline Structure of Metals.* (Second Paper.)

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[Plates 3—13.]

The investigations described in the present paper deal principally with the phenomena of annealing. They form a continuation of the research described in the Bakerian Lecture for 1899 ('Phil. Trans.,' A, vol. 193, 1900, pp. 353–377). In iron, steel, and brass these phenomena have been studied with the aid of the microscope by various workers, among whom Arnold, Charpy, Stead, and Roberts-Austen should be particularly mentioned. As a result of their labours it is well known that annealing is accompanied by a re-arrangement of the crystalline grains of the metal.

Thus, when a piece of iron is strained in tension its crystalline grains become elongated in the direction of tension; but when the specimen has been subsequently annealed by being heated to a bright red, all signs of such elongation disappear from the crystalline pattern revealed by the microscope. In fact it is not generally possible to find any definite connection between the crystalline pattern seen in the same specimen before and after annealing. In general, the pattern seen after annealing resembles that found in a similar specimen before it has been strained, but the scale and character of the pattern produced depend very much on the details of the annealing process, particularly upon the temperature applied, the time of its application, and the rate of cooling. Arnold and Stead have shown that prolonged annealing tends to produce large crystals in iron and steel. But even short exposure to a suitable temperature is well known to produce complete re-crystallisation, and it has been suggested that these changes occur at critical points corresponding to the "arrest-points" in the cooling of the metal. These arrest-points indicate evolutions of heat, and it is natural to suppose that they are evidences of re-arrangement of the structure of the metal.

At the outset of the present research we hoped to observe this change taking place under the microscope. Although the experimental difficulties of keeping a specimen under microscopic observation while it was being heated were successfully overcome, the attempt to watch the re-crystallisation of iron failed.

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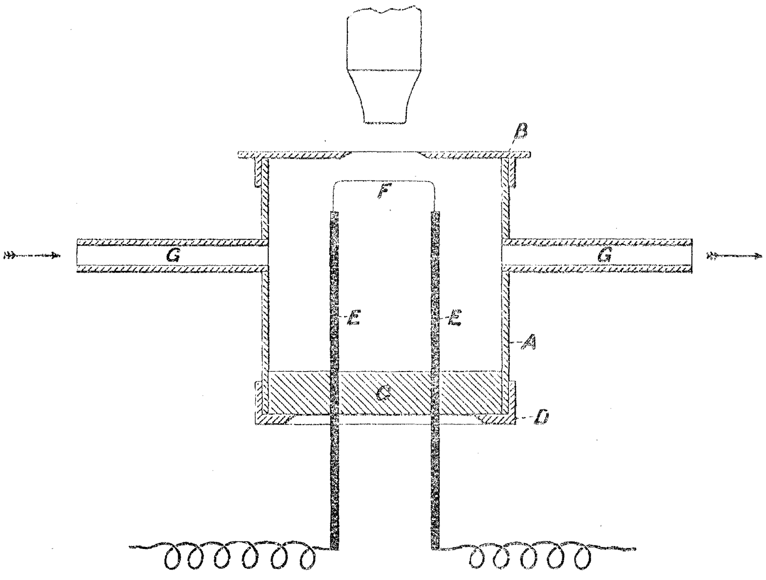
Our first expedient was to surround the specimen with an atmosphere of pure dry hydrogen gas, and to examine the surface through a glass or mica window in the containing vessel. The hydrogen was prepared in the usual way by the action of pure dilute sulphuric acid on pure granulated zinc, and the gas was dried and purified by bubbling through several wash-bottles containing pure sulphuric acid, caustic potash, and permanganate of potash solutions respectively. As a final precaution, it was passed through a long tube of glazed porcelain kept at a red heat and packed with clean pieces of sheet-iron. It was a specimen of similar iron that was to be experimented upon, and we hoped that after passing over this large quantity of hot iron, the hydrogen would be free from any impurities capable of tarnishing the polished surface of our specimen. The specimen itself was a strip of sheet-iron, of the pure kind used for transformer plates, measuring 3 centims. in length and 3 to 4 millims. in width. It was bent to a ⊓ shape, and the upper flat surface was polished and etched. The containing vessel is shown in section in fig. 1. It consisted of a brass cylinder, A, with a screw-cap, B, provided with a window of thin glass or mica. The bottom of the cylinder was formed by a plug of slate, C, fitting against a shoulder, and held in place by a screw-collar, D. Through this slate plug passed two stout copper wires, EE; the upper ends of these rods were split to receive the two legs of the specimen F, whose flat, polished surface thus came immediately beneath the window in the cap. At GG tubes entered the vessel; these allowed the passage of the current of hydrogen.

Fig. 1.



All the joints were very carefully fitted, and made as nearly air-tight as possible; leakage, however, was not an important matter as the hydrogen was kept at a pressure slightly higher than that of the atmosphere. On leaving the apparatus the hydrogen was burnt as a small jet.

The specimens were observed through the window by means of "vertical" illumination coming through the objective itself; as we were content with moderate magnifications (up to 100 diameters) an objective of long focus could be used.

In spite of the precautions taken, we did not succeed in keeping the polished surface untarnished after a red heat had been reached; but in the course of our observations an interesting phenomenon was observed. On beginning an observation, when the specimen was still cold, the "ferrite" grains could be clearly distinguished. If the temperature of the specimen were then slowly raised by gradually turning on an alternating electric current, the first visible change was a dimming of the image, which resulted in its becoming completely blotted out. This we supposed to be due to condensation of moisture on some part of the optical system, but we could not locate it. On raising the temperature further, the image of the crystals reappeared very vividly; at this point, by shutting off the reflected light, the metal could be seen to be just vividly red. On heating still further, the pattern was rapidly and totally obliterated by the tarnishing of the surface; the metal was now dull-red. The red then brightened, but suddenly dark spots appeared, and spread rapidly over the entire field of view. The speed at which they spread could, however, be regulated by suitably adjusting the heating current. The spots appeared well in the middle of the specimen, and the apparent darkening could only be pushed to the extreme edges by using a considerably higher temperature. On allowing the specimen to cool, no change was visible, either on passing through this range of temperature or at any other period; nor could the phenomenon be made to recur until the specimen had been cooled below redness; but, if this was done, the phenomenon would recur indefinitely in the same specimen. It seems probable that the action which causes this appearance occurs in the metal itself and not merely in the surface film of tarnish, as details in this film remain entirely unaffected by it, thus giving the observer the impression that he is looking at an action taking place beneath a thin and partially transparent film. On repeating these observations with the specimen maintained in other atmospheres than hydrogen, no such phenomenon was observed; and this leads us to suppose that the phenomenon is a result of chemical reaction between the hydrogen and the iron. From its occurrence just above redness it would seem to correspond to the arrest-point, about 487° C., discovered by Sir W. ROBERTS-AUSTEN ('Alloys Research Report,' Inst. Mechan. Engin., 1899).

Believing that this action of the hydrogen caused the surface of our specimens to tarnish on heating, we sought to overcome this difficulty by observing the surface of a specimen heated in vacuo. The heating was again done electrically, either by passing the current directly through the specimen, or else by placing the specimen in the centre of a coil of fine platinum wire wound on a piece of terra-cotta. In both cases the specimen was placed in a test-tube, the electrodes passing through a sealed cork at the end; the tube could be exhausted by means of a Fleuss pump. The specimen was placed with its polished and etched surface as near to the top of the tube as possible, and a 22 millims. objective was used. When the specimen became really hot, the radiation would have endangered the objective, and this difficulty was met by keeping a blast of air directed partly upon the lower end of the objective and partly upon the surface of the test-tube. The apparatus was thus kept quite cool without in any way disturbing the distinctness of the image.

We found that with the best vacuum we could obtain, even with the addition of phosphoric anhydride drying tubes, our specimens always tarnished if kept at a red heat for any length of time. We are inclined to ascribe this to the action of gases occluded in the metal and given out on heating. The tarnishing, however, was not very rapid, and a specimen could safely be heated up to bright red once before it became noticeable. This enabled us to make observations which very clearly showed that, even with the greatest experimental refinement, we could not hope to observe the process of re-crystallisation microscopically. We have found that if a strained, polished and etched specimen, showing distinctly elongated crystals, be gradually heated in vacuo no change whatever is visible in the outlines of the crystals; on removing the specimen from the apparatus it is sometimes found coated with a thin blue tarnish, and on examination with the microscope it is seen that this tarnish has not obliterated the original crystals, but in fact differentiates them by various colours on different crystals. If this tarnish be now polished off, as may easily be done by the use of rouge alone, and the specimen be re-etched, an entirely new set of crystals is revealed. This was readily established by drawing the outlines of the original crystals at a marked spot on the specimen before and after the light re-polishing. Simple re-polishing and etching a similar specimen, without annealing, produces only very small changes in the pattern. We may therefore conclude that in the above experiment the iron did re-crystallise when at a red heat, but that this re-crystallisation did not immediately affect the pattern on the surface. The explanation is obvious when we realise that the pattern seen in the microscope is due to the differences of level and texture in the surface of the specimen which have been produced by the action of the acid used in etching. This pattern, although in its origin dependent upon the actual crystalline structure of the metal at the time when the surface was etched, remains as a mere mask, beneath which re-orientation of crystalline elements may go on without affecting its appearance. The etched pattern is in this respect in the same position as a scratch or mechanical marking of the surface, and the persistence of the etched pattern after annealing is simply an extension into more minute detail of the well-known fact that the external shape of a piece of metal is not in general affected by annealing, although the crystalline structure is entirely changed.

These considerations show that we cannot expect to see the process of re-crystallisation in any metal where etching, staining, or relief polishing is needed to differentiate the constituents. We therefore abandoned the attempt to observe this process in iron, but our attention was directed to the study of similar processes of annealing or re-crystallisation as seen in more fusible metals, particularly lead.

The question, What is the temperature required to produced re-crystallisation in lead? was raised by the appearance we observed in specimens of plumbers' sheet-lead that had been etched with dilute nitric acid. When thus treated, ordinary sheet-lead exhibits a remarkably brilliant crystalline structure on such a large scale that no previous polishing is required. The etched surface shows all the appearances due to the selective effect of oblique light on etched crystalline surfaces; when the specimen is turned the light catches the various crystalline grains in turn, the colour and brightness being uniform over each grain, but different on different grains. Fig. 2, Plate 3, is a photograph of such a surface magnified two diameters: these surfaces tarnish immediately on drying, and must therefore be observed and photographed while wet with the acid solution.

An examination of this etched surface reveals a peculiarity in the configuration of the crystalline grains; these are seen to have many remarkably straight boundaries meeting at sharp angles, several sets of parallel boundaries being frequently observed. These features, which strongly resemble what we had previously observed in wrought copper, are to be ascribed to the frequent occurrence of twin crystals. In our earlier observations on twin crystals their presence had always been readily detected by the configuration of slip-bands produced in them by slightly straining the specimen after polishing. An instance of twinning observed in sheet lead by this method has been given by us in a previous paper ('Phil. Trans.,' A, vol. 193, 1900, Plate 26, fig. 40). In the present instance this method of detecting twins is not available, as the roughness of the surface and the great depth of etching employed make it impossible to study the slip-bands. But the presence of twin lamellæ nevertheless becomes evident under slightly higher magnification with oblique light. Fig. 3, Plate 3, is a photograph of crystals with twin lamellæ magnified 40 diameters. The figure illustrates the selective effect of oblique illumination, which has picked out a few isolated crystals, lighting these brilliantly while neighbouring ones remain almost dark. Within the area of the brightly-illuminated grains, a number of dark patches are seen, and these show the straight boundaries occurring in parallel sets which are characteristic of twinning. In this instance there are three distinct parallel sets of dark bands, and the fact that they are twin lamellæ becomes apparent when the stage carrying the specimen is rotated, thus altering the incidence of the light. As the specimen is turned, the grains that were bright become dark, but presently some of the patches that were previously dark shine out brilliantly, all the bands which are parallel to one another flashing out simultaneously. Fig. 4 is a photograph of the same field as fig. 3 after a rotation of about 30°, and illustrates this appearance. But those parallel bands which catch the light simultaneously are evidently portions of the crystal in all of which the orientation of the elements has been changed by the same amount; in other words, they are twin lamellæ.

Further evidence of the crystalline structure of sheet-lead is found when a slightly higher magnification (100 diameters) is applied. Many of the crystals are then seen to be marked with geometrical figures, most frequently hexagons, but sometimes triangles and rectangles. These figures are similar, and similarly oriented, over the entire area of any one crystal, but they are generally different in shape and orientation on adjacent crystals. In this respect they resemble the geometrical etched pits in iron and geometrical air-bubbles in cadmium described in our previous paper cited above. Their occurrence in *cast* lead that has been exposed to dilute nitric acid has been described by Professor MIERS and Mr. A. DICK in the 'Journal of the Mineralogical Society,' April, 1899. Professor MIERS measured their crystallographic angles, but does not connect them definitely with the crystallisation of the solid metal —and Mr. DICK'S view is that they are promiscuously deposited crystals due to electrolytic transfer of lead from the upper to the lower surface of the specimen. Careful microscopic examination shows that in some instances this is the case in sheet lead. Some of the geometrical figures can be seen to be the outlines of deposited, or at all events, projecting crystals; but the remarkable fact remains that even here these crystals are deposited with their elements in the same orientation as those of the crystal upon which they are being deposited. In many cases, however, geometrical markings are found which form the outlines of pits instead of projections. Sometimes these pits occur on the same grain as the deposited crystals, and both then have similar outline and orientation.

Fig. 5, Plate 4, is a photograph of such geometrical markings on etched sheet-lead, seen under oblique light and magnified 100 diameters.

The observations here described form a full demonstration of the marked crystalline structure of sheet-lead, but the origin of this structure is not immediately apparent. Sheet-lead is produced by rolling out cast ingots of the metal without the aid of heat. In the sheets we have, therefore, metal which has been subjected to a very great amount of plastic deformation. The view of plastic strain enunciated in our former paper ('Phil. Trans.,' 1900, Series A, vol. 193, pp. 353-375) would lead us to suppose that the structure of such violently deformed metal would still be entirely crystalline, but its crystals would show peculiarities of shape corresponding with the nature of the plastic deformation imposed upon the mass of the metal. Thus, in a specimen which had been rolled from a solid lump into a sheet, we should expect to find the crystals thin and flat, but of considerable area parallel to the surface of the sheet. Sheet-lead, however, shows no such feature; on a transverse section of the sheet no flattening of the crystals is seen. This led us to suppose that some process of annealing or re-crystallisation had been at work in the metal subsequent to its manufacture, and, as the lead had not been subjected to any thermal treatment, it seemed that re-crystallisation must have occurred in it at ordinary atmospheric temperatures. We therefore directed our experiments to test this supposition, and generally to investigate the phenomena of annealing or re-crystallisation in lead.

The first step was to determine the effect of very severe strain on the crystalline structure of lead. In such a soft, ductile metal, plastic deformation may be carried to so great an extent that the adaptability of the individual crystals to change their shape by means of slips on cleavage planes may be insufficient. Careful observation of the crystalline structure of a piece of lead under severe compression confirms this view. Up to a certain point the crystals are gradually flattened out in proportion to the flattening of the whole specimen, but when the "flow" becomes considerable it is found that the crystals, already very thin and flat, are driven into and through one another, this process resulting in a grain or structure which is small, but still entirely crystalline. The action is analogous to what occurs in the fracture of a more brittle metal, with this difference, that in a more brittle metal, when "slip" has gone so far as to extend right across a crystal, the new surfaces thereby brought into contact do not unite or "weld," and fracture results; in lead the freshly exposed surfaces do weld or re-unite under the pressure, a fact which is associated with the possession, on the part of the metal, of great ductility. Fig. 6 is a micro-photograph showing the crystalline structure of ordinary cast lead magnified 12 diameters, while fig. 7 shows the much more minute structure of freshly and severely-strained lead magnified 30 diameters. In this and in the following experiments with lead, the process of straining was carried out by squeezing a cast block of the metal in a compression-testing machine, letting it expand laterally until the block, originally about 1 inch high and $\frac{5}{8}$ inch diameter was flattened into a plate about $\frac{1}{8}$ inch thick.

In order to investigate the changes in the crystalline structure of such strained lead, we adopted the method of taking a series of photographs of a marked area of each specimen at intervals of time during which the metal was exposed either to the ordinary temperature of the room or was subjected to special thermal treatment. Before each photograph was taken the surface was thoroughly re-etched; our experiments on the annealing of iron had convinced us of the necessity of this proceeding, and our observations on lead specimens have confirmed the previous experience. In no case did thermal treatment in any way produce a visible change in the surface pattern until further etching had been resorted to, and fairly deep etching is required to obliterate the old pattern entirely. This applies more particularly to the channels which are etched out at the inter-crystalline boundaries—these may often be seen forming a network on the newly-formed pattern, but quite independent of the new structure.

The method of etching consisted of alternate applications of concentrated and very dilute nitric acid. In some cases, where very deep etching was required, an electrolytic method was used. One of the great advantages of dealing with a metal like lead arises from the large size of its crystals; by enabling us to use deep etching it allows all fine polishing to be dispensed with, and it becomes possible to obtain micro-photographs at low magnifications, and under oblique light, which exhibit clearly the various changes in crystalline structure.

The low power required is a further advantage in view of the fact that an etched lead surface must be kept wet with an acid solution while it is being examined and photographed, as such a surface becomes dull and useless as soon as it dries.

To identify the areas which were to be kept under observation, we marked them by scratches or furrows made with a steel point. Unsymmetrical patterns of marking were used for this purpose to facilitate replacing the specimen in its former position and orientation. It is an essential precaution in taking micro-photographs under oblique illumination which are to serve for purposes of comparison, that the orientation of the specimen and the angle of incidence of the light should be constant throughout the entire series. Our micro-photographic arrangements enabled us to comply with these conditions to a considerable degree of accuracy.

The first series of these micro-photographs (figs. 8 to 13 inclusive, Plates 5 and 6) was taken from a specimen of lead which, after being severely strained, was simply kept during six months at the temperature of an ordinary room without any special thermal treatment whatever, being carefully re-etched and photographed at intervals. The first of the series (fig. 8) was taken immediately after the specimen had been strained. The magnification (12 diameters) is too low to clearly resolve the minute crystalline structure which existed at this stage. The identification marks are very clear at this stage, but they become less clear after each successive etching.

Fig. 9 represents the same surface, re-etched after six days; a small amount of change is visible, and this becomes more marked in figs. 10, 11, 12, and 13, which represent the state of the specimen after one, two, four, and six months respectively. Comparing figs. 8 and 13, the great change in the crystalline structure is strikingly evident.

Measurement of the largest crystals seen in fig. 13 gives some rough idea of the rate at which these crystals have grown. In one case the dimensions are as follows :—

Length of crystal in freshly-strained specimen = ·0025″
,, ,, specimen after 1 month = ·0083″
,, ,, ,, ,, 4 months = ·0100″
,, ,, ,, ,, 6 ,, = ·0115″

From this it would appear that the rate of growth is greatest in the first month after the specimen has been strained; but a close examination of such specimens reveals a feature which considerably affects this question. It is seen that the crystals do not grow by the steady accretion of layers all over their surface, but that they throw out arms or branches, which invade neighbouring crystals, thus forming a skeleton crystal somewhat similar to those that are often noticed in the crystallisation of fused substances. The more or less dim and mottled appearance of the larger crystals in figs. 8 and 9, and the much greater brightness and uniformity shown by the same crystals in figs. 10, 11, and 12, is undoubtedly due to the formation of these skeletons, and their subsequent filling in.

The figures given above must therefore be taken as no more than an extremely rough indication of the order of magnitude with which we are concerned in these questions of growth at ordinary temperatures.

Taking a specimen of plumbers' sheet-lead showing fairly large crystals as an example of metal in which air-temperature annealing has continued for a long time, we next tried the experiment of applying a higher temperature, so as to determine whether any further change would occur. Our observations show that the metal in this state is very sensitive to moderately high temperatures, three minutes' exposure of ordinary sheet lead to a temperature of 200° C. being sufficient to produce a great change in the crystalline pattern. If the specimen be kept at 200° C. for a long time there is a continued change, but it becomes very slow, and ultimately a state is reached when further change is imperceptible.

Figs. 14 to 19, Plates 6 and 7, inclusive are a series of micro-photographs of a specimen treated in this way. Fig. 14 shows the appearance of a typical specimen of sheet-lead, and fig. 15 shows the change produced by 30 minutes at 200° C. Except in one or two isolated instances it is very difficult to trace any connection between the pattern now seen and the original. Fig. 16 shows the same surface, re-etched after a further 30 minutes at 200° C. There has been further change, but not to anything like the same extent as in the first half-hour. The change is most marked in a large crystal on the left-hand side of the figure; in fig. 15 it shows a mottled or skeleton appearance, and this becomes filled in in fig. 16, while there is a considerable increase in the length and thickness of the two tongue-like projections that start on the right-hand side of the twin band.

A further development of this crystal is seen in fig. 17, which was taken after 48 hours' further annealing at 200° C. Here another twin band has become evident, and a further filling in and straightening of the boundaries has taken place. This process has gone slightly further in fig. 18, taken after four days' further annealing. This photograph may be taken as representing the final state of this specimen, as very prolonged annealing produced no further considerable change. This specimen, however, showed another interesting feature, which we have often observed in other cases. The marked area chosen for photography occupied the centre of the surface of the specimen, which measured approximately $\frac{3}{4}$ inch square by $\frac{1}{8}$ inch thick. Somewhat to our annoyance, this marked area did not show by any means the best development of crystalline growth. In this case, as in many others, we found that the largest and most rapidly growing crystals were formed at or near the edges of the specimen. Fig. 19, taken at the same stage as fig. 18, and with the same magnification, but outside the marked area, shows the remarkable development of crystals in some parts of the specimen.

In comparing the members of such a series of photographs, one consideration must be borne in mind, the great difference produced in the appearance of the surface by a minute change in the angle of incidence of the light. In spite of the utmost precaution to keep the incidence constant, a small change will sometimes cause the entire disappearance of a crystal whose facets happen to be near the critical angle. But, provided any portion of a crystal is shown bright in the photograph, any changes in its outline or surface are certainly genuine, for light that catches the facets on one part of the crystal must necessarily catch all similarly oriented facets also. Where, therefore, the same crystal appears in successive members of a series, the photographs may be taken to represent its life-history accurately.

Another feature of these photographs requires explanation. In figs. 18 and 19, and more or less in most of the others, an irregular network of dark lines or channels is seen to cover the surface, and these lines obviously have little or no relation to the crystals. As a matter of fact, these lines are only found in specimens that have been etched, and then annealed and re-etched. In such a case as figs. 3 and 4, where only one etching has been applied, similar lines are seen to follow the inter-crystalline boundaries. In that case they are simply "corrosion channels" caused by the action of the acid at the crystalline junctions. These channels are of comparatively great depth, and when such a specimen is allowed to re-crystallise, and is then re-etched to develop the new crystalline structure, this second etching is rarely carried deep enough to remove the old etched corrosion channels, and these remain as a network over the surface, simply indicating the positions in which crystalline boundaries formerly existed before the structure became changed. This view is borne out by the observation that deeper etching will eventually remove all trace of this network. In many instances these traces of the former crystalline boundaries are very useful as indicating the nature and extent of the growth that has taken place. On the other hand, the deep etching that would be required to remove these lines was considered undesirable, as very deep etching might of itself alter the apparent shape of the crystals. By observing the effect of successive deep etchings on the pattern of a stable specimen we satisfied ourselves that it would require exceedingly vigorous and prolonged etching to cause any visible change of pattern, and that, in the specimens illustrated in this paper, the changes cannot possibly be ascribed to that cause.

Our next experiment was to expose a freshly-crushed specimen of lead to a temperature of 200° C. for a long time, and to watch the changes produced in its crystalline structure. The annealing ovens* used for this purpose consisted of wooden boxes, lined with asbestos cloth, and heated by means of one or more incandescent electric lamps. The temperature could be regulated by regulating the current in the lamps, and, more conveniently, by adjusting the lids of the boxes so as to admit more or less air. Variations of 10° C. in the temperature were rare.

Figs. 20 to 27 inclusive, Plates 8, 9, and 10, illustrate our observations on one specimen treated in this way. Fig. 20 represents a marked area on the etched surface

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* These annealing ovens were devised and used by Mr. S. R. ROGET in his researches on effects of prolonged heating on the magnetic qualities of iron. 'Proc. Roy. Soc.,' May 12 and Dec. 8, 1898.

of a freshly-squeezed specimen; the following photographs were taken after the specimen had been exposed to 200° C. for the time shown in the table:—

Number.	Days.	Hours.
Fig. 21 . . .	—	17·5
„ 22 . . .	1	17·5
„ 23 . . .	2	17·5
„ 24 . . .	5	16
„ 25 . . .	39	20
„ 26 . . .	39	20

Fig. 20 shows the small structure characteristic of freshly-strained lead, with one or two larger crystals that have persisted from the original crystallisation. In fig. 21 these are seen to have grown considerably, and a general change of pattern is observed; the most striking feature is the large skeleton crystal that has developed in the lower left-hand corner of the marked area. This skeleton is seen to grow and fill in continuously in figs. 22 and 23. Figs. 24 and 25 were taken under a different angle of illumination in order to show another large crystal which gave signs of vigorous growth. In fig. 24 it is still somewhat skeletal, but in fig. 25, while it has become much more consolidated, all its outlying arms have disappeared, having been absorbed by a well-defined crystal, part of which is seen as a dark arm in fig. 25. Fig. 26 is a photograph of the specimen at the same stage as fig. 25, but at a lower magnification (8 diameters), and so illuminated as to bring the new crystal, whose dark arm is seen in fig. 25, into brightness. This new crystal is seen to be enormously larger than its neighbours, and from its position relatively to the marked area it can be recognised as the same crystal whose early stages are seen in figs. 22 and 23. This large crystal is an excellent example of what may be called an aggressive individual crystal. Another example, also at 8 diameters, is shown in fig. 27, Plate 10. In both figures the edge of the specimen can be seen, and the photographs illustrate the observation that the largest crystals are generally near the edges of the specimen. It should be added that these large crystals are not mere surface layers, but extend well into and across the thickness of the specimen, and can be readily identified on the opposite surface when, as in this case, the specimen is a plate about one-eighth of an inch thick.

The occurrence of such large crystals in the annealed metal is apparently in no way dependent upon the size of the crystals in the original state before straining; the large crystal in fig. 27 was developed in a specimen whose original crystals were very small.

A remarkable feature, well illustrated by the photographs (figs. 26 and 27) of these large crystals, is the frequent occurrence of twin crystals, both as inclusions in the body of the crystal and at the boundaries. In fig. 26 three distinct sets of straight parallel boundaries are visible, and their "twin" character is evident when they are examined in the manner described above.

In our previous paper we have already given the observation that twin crystals are rarely, if ever, found in a *cast* metal, but that they are frequently developed by strain, and that they are very commonly found in metal that has been annealed after severe straining. Our present observations on lead entirely agree with these statements; but it may now be possible to suggest an explanation for the frequent occurrence of twins in annealed lead. When the metal solidifies from the liquid state, it does so by the formation of skeleton crystals, starting from a great number of centres, and the arms of these skeletons continue to grow until arrested by meeting with other growths.

From these arms other arms again shoot out, and so on until the entire metal is solidified; but each crystalline element as it settles into place on any of these arms must assume the proper orientation to enable it to fit in, and in the process of filling space by means of such a system of many meeting and interlacing arms, the formation of a twin would be almost impossible. But when the metal re-crystallises after severe strain, it does so by the growth of skeleton arms that must often start from a cleavage plane of an actual solid crystal, and probably the new elements deposited upon such a plane would find it as easy to assume the twin orientation as the normal. The idea that twin crystals are formed in annealed metal by growth starting from cleavage planes which have been sheared across in the process of compression is suggested by the very straight boundaries observed as a characteristic feature of twin lamellæ.

Having observed the comparatively rapid growth of crystals in strained lead at 200° C., we extended our experiments to both higher and lower temperatures. Our observations were recorded photographically as before, but the general character of the results is so similar to those already illustrated that it is unnecessary to reproduce these photographs. Experiments were made at temperatures of 100° C., 150° C., 250° C., and 300° C.

In the absence of a reliable method of measuring the rate of growth of crystals, the following statements must be taken as based upon a rough general estimate. With this reservation, our observations over this range of temperatures may be summed up as follows:—

(1) In lead which has been severely strained, re-crystallisation goes on at all temperatures from that of an ordinary room up to the melting-point.

(2) The higher the temperature the more rapid are the changes in the crystalline structure.

(3) The rate of change varies with different specimens, probably depending upon the nature and quantity of impurities present, and upon the severity of the strain to which the metal has been subjected.

(4) The size of the crystals ultimately produced does not vary appreciably between 100° C. and 300° C. In lead annealed at the temperature of the air, very large crystals have not yet been obtained, but this is probably only a question of time.

(5) The phenomena of growth of crystals occur in lead only when the metal has previously been subjected to severe plastic strain. The structure of a cast specimen remains unaltered at temperatures which cause a strained specimen to show rapid change. By casting in a mould arranged to cause rapid cooling, specimens of lead can be obtained having a minute crystalline structure, whose scale is not very different from that of severely crushed lead; such a specimen was exposed to 200° C. for nearly seven days, but no visible change of structure occurred. A piece of this specimen was then strained by severe crushing, and on further exposure to 200° C. vigorous growth took place.

(6) The rate at which a lead specimen is cooled from temperatures of 200° C. to 300° C. down to the ordinary air-temperature has no visible effect on the structure. Even "quenching" in liquid air has no visible effect; quenching in water, cooling in air, and slow cooling in the oven, were all tried on a number of specimens without in any way affecting them.

(7) Lead is mechanically hardened to a small extent by severe strain, and the subsequent effect of annealing in restoring softness is correspondingly small. In one of the experiments a specimen of lead was crushed under a given load in the testing-machine, and the load was left on until no further creeping occurred. The specimen was then annealed and again placed under the same load, when a distinct amount of further crushing was seen to take place.

Some of the experiments described above as having been made with lead were extended to certain other metals that lend themselves to similar treatment; those used were tin, cadmium and zinc.

The crystalline structure of tin is well shown when a surface of a cast ingot of the metal is etched with strong hydrochloric acid. These crystals are generally large, but a much more striking display is obtained on etching the surface of commercial tin-plate. Even before etching, the inter-crystalline boundaries may be seen on the surface, where they are marked by fine grooves or channels. The presence of these channels is readily accounted for by the method of manufacture, during which these plates are drawn out of a bath of melted tin, and allowed to drain. As the plate is drawn out, the layer of tin adhering to it crystallises, but any fusible impurity present in the tin would remain fluid slightly longer, and, being forced by the crystallising tin into the inter-crystalline junctions, the still fluid impurities will drain off, thus leaving a minute channel.

The appearance of the etched surface of commercial tin-plate is shown in fig. 28, Plate 10, which is a photograph at one-half the natural size. In this photograph the outlines of the large crystals can be clearly seen, but it also illustrates another and peculiar feature of etched tin-plate. In all cases of an etched crystalline metal viewed by oblique light we have always observed that, under a given incidence of light, certain crystals were bright while others were dark, and that the illumination was uniform over the entire area of each crystal. In the etched tin-plate this is not the case, the brightness shades off across individual crystals, sometimes uniformly, so as to give the crystal a concave appearance; at other times in patches, giving a mottled effect. On closer inspection, it appears that such variations in brightness occur only in one direction in each crystal; in that direction the brightness may be made to move across the crystal by a slight oscillation of the plate, but another direction can generally be found where the crystal appears uniformly bright and is quite free from the concave appearance.

It is well known that the usual selective effect of oblique illumination on etched crystalline surfaces is due to the fact that etching develops on the surfaces of crystals a great number of minute but similarly oriented facets or pits, and the uniformity of illumination over any area is a direct result of the constancy of orientation of these pits over that area. In the specimens of tin-plate here described we would therefore expect to find that the orientation of the etched pits or facets was not strictly constant over the entire area of each grain.

By examining the etched surface of tin-plate under the higher powers of the microscope the etched pits or facets can be clearly resolved. Their appearance is illustrated at a magnification of 100 diameters in figs. 29 and 30. Under this power their orientation is apparently quite constant, and even under a power of 1000 diameters the departure from strict constancy is only very slight. That it does exist could only be seen by comparing the outlines of apparently similar pits at opposite ends of a large crystal; even there the change in the angles of the figure or of the orientation of one of the sides, as compared by means of a cross wire in the eyepiece, was too small to be measured, but in certain cases the character of one of the outlines of the pit altered slightly, being a fine line at one end of the crystal, and a narrow wedge-shaped dark area at the other. This appearance indicates a change in the slope of that side of the pit, and thus a change of orientation of the internal facets of the pit. This change of orientation seems therefore to occur principally—if not entirely—in the vertical plane, *i.e.*, in the plane of least thickness of the layer of tin.

Under these circumstances it seems that the term "crystal" should only be used with some qualification in speaking of the patches developed by etching the surface of commercial tin-plate. In a crystal which is undistorted by elastic strain constancy of orientation of the elements is an essential characteristic of a true crystal. Some light is thrown on this matter by the fact that we have not observed this "concave" appearance in samples of solid tin, but only on commercial tin-plate where we are dealing with a very thin layer of tin adhering to sheet-iron. Even in tin-plate this effect may be made to disappear by re-melting the tin over a flame and allowing it to cool slowly and at rest. The appearance produced on re-etching such a specimen is shown in fig. 31 (to the same scale as fig. 28). Here, although the crystals are marked with a multitude of straight lines, suggesting a great number of twin crystals, there is little or no trace of the "concave" effect seen in fig. 28.

In view of these observations we are inclined to attribute the "concave" appearance to a distortion or bending of true crystalline plates; such distortion would probably arise from differences in the coefficients of expansion of iron and tin brought into action by a suitable rate of cooling. Considering the extreme thinness of the layer of tin, the amount of distortion might well be purely elastic and insufficient to produce slip in the crystals of tin.

Fig. 32, taken from a different specimen, but to the same scale as fig. 31, illustrates the change in the dimensions and arrangements of the tin crystals that can be effected by changing the rate of solidification; the crystals in fig. 31 were formed in a slowly cooled specimen; those in fig. 32 by quenching the specimen in water while the surface layer of tin was still melted. By means of local quenching and re-melting a great variety of patterns can be obtained; such processes have long been in commercial use in the manufacture of what is called "*moirée metallique.*"

It is important to notice that the small crystals of tin which are obtained by quenching the melted metal in water do not show any growth when the metal is exposed for long periods to temperatures short of the melting-point. Even a temperature just short of fusion does not make them grow or re-arrange themselves. A solid block of tin may, however, be reduced to a minutely crystalline structure by severe compression, and in specimens so treated we have observed re-crystallisation to occur at 150° C.

We also made some experiments on the re-crystallisation of cadmium at moderate temperatures. This metal also can be strained by compression until its crystalline structure becomes minute through interpenetration of the original larger crystals. Fig. 33, Plate 12, is a low-power (12 diameters) photograph of an etched and marked area on the surface of a freshly-strained piece of cadmium. Fig. 34 shows the same area, re-etched, after 24 hours' exposure to 200° C. It now shows a well-defined crystalline structure. Fig. 35 shows the same area again, after six days' further exposure to 200° C., and a very considerable increase in the size of the crystals is visible. In this case, although the gradual growth of some of the crystals is very strikingly shown, many of the features that we have observed in the case of lead are entirely absent. In the cadmium we can see no invading branches and no aggressive individuals, nor does there seem to be any considerable amount of twinning.

Experiments similar to those just described were also made on specimens of zinc, with the result that specimens of zinc strained by compression at ordinary temperatures were found to re-crystallise on exposure to 200° C. Some results obtained with sheet-zinc, such as that used for electric batteries, were particularly interesting. It is a well known fact that the mechanical properties of zinc are widely different at different temperatures, particularly that the metal is soft and ductile at temperatures slightly above 100° C., and that it is generally worked at that temperature, while it is known to become very brittle at and above 200° C. Commercial sheet-zinc, rolled at temperatures above 100° C., remains fairly soft and flexible at ordinary temperatures, and its crystalline structure is too minute to be seen in specimens etched without previous polishing.

If a specimen of such sheet-zinc be exposed to a temperature of 200° C. for about half-an-hour, it shows on etching with strong hydrochloric acid a brilliantly crystalline texture as illustrated in fig. 36, Plate 13, magnified 8 diameters. The metal is then much harder, but at the same time brittle; when bent it emits a "cry" like that of tin, and finally breaks with a crystalline fracture which zig-zags along the cleavage-planes of the various crystals through which it passes.

Many of the phenomena described above as occurring in such metals as lead, tin, zinc, and cadmium, have close and well-known analogues in iron and steel. In those metals, however, the temperatures involved are much higher, and the experimental difficulties are consequently greater; we have consequently been able to make many observations on the re-crystallisation of lead which it has not yet been possible to make in the case of iron or steel. The question, therefore, suggests itself, how far the analogy between the various metals holds true. One view which is held by many persons—perhaps unconsciously—may be called the theory of "corresponding temperatures"; the central idea of this view is that the properties and behaviour of metals are to a great extent a function of their distance from their own melting points. Thus a phenomenon seen in lead at 200° C. is strictly analogous to a similar phenomenon seen in iron at 800° C. To a certain extent this view is justified, but it may easily be carried too far. Thus, while lead at 10° C. is soft and ductile like iron at 800° C., yet gold at 10° C. is also soft and ductile, while it is further from its melting-point than iron at the same temperature. Again, one of the most characteristic features of lead is the extreme straightness of its "slip-bands," while those of iron are characteristically curved and irregular. We have not had an opportunity of examining the slip-bands produced by straining red-hot iron, but we have made the converse experiment of straining lead at the temperature of liquid air, with the result that the slip-bands developed were as characteristically straight and regular as ever, thus showing that the straightness of the slip-bands, which is so closely associated with softness and ductility, is a characteristic of the metal rather than a function of the temperature. In order to thoroughly test the same question in relation to annealing, a long series of experiments to determine whether or not gradual re-crystallisation goes on in strained iron at ordinary temperatures and a similar series on lead at much lower temperatures would be required. In the case of glass-hard steels it is well known that a certain amount of annealing takes place at 100° C., and even at atmospheric temperatures; but in the case of steel, where a distinct chemical change is involved, the nature of the annealing action may differ very considerably from that in an approximately pure metal. Certain phenomena in the recovery of elasticity after over-strain in both iron and steel (Muir, J., "Recovery of Iron and Steel from Over-strain," 'Phil. Trans.,' 1899) also point to the fact that changes of internal structure may occur in iron at very moderate temperatures; further evidence in the same direction is afforded by the effect produced (Roget, S. R., 'Proc. Roy. Soc.,' 1898) on the magnetic properties of soft iron by roasting at moderate temperatures. On the other hand, it has been very widely believed that annealing or re-crystallisation, particularly in iron and steel, are "critical" phenomena which can only occur at or above certain definite temperatures. ARNOLD has gone so far as to make a careful determination of such an "annealing point." Various of the "arrest-points" in the cooling of iron and steel have also been regarded as representing critical points in respect to annealing, but the connection between the two is by no means fully proved. Having found phenomena of annealing or re-crystallisation in other metals, it therefore became interesting to inquire whether any corresponding arrest-points could be found in the cooling of these metals. We investigated the matter by means of a pyrometric arrangement consisting of two thermo-electric junctions, a very sensitive D'Arsonval galvanometer, and a potentiometer somewhat similar to that used by Sir W. ROBERTS-AUSTEN; the deflections of the galvanometer were, however, observed by means of a telescope and scale, instead of being photographically recorded. It may be, therefore, that either from this cause, or from insufficient sensitiveness of the whole arrangement, some minute arrest-points were overlooked; but between the melting-points and the ordinary temperature of the air no trace of an arrest-point was observed in the three metals tried, *i.e.*, lead, tin and cadmium. Such arrest-points, if they exist at all, may be found at much lower temperatures than those to which our experiments were carried.

Having thus failed to correlate the phenomena of re-crystallisation in lead, &c., with any definite point at which heat is evolved during the cooling of the metal, and having reason to believe that even in iron the arrest-points are not necessarily intimately connected with annealing, we look for a theoretical explanation of these actions in another direction. The theory of re-crystallisation which we shall now advance as a working hypothesis for the explanation of the phenomena described in this paper ascribes an important part in the action to the impurities present even in "pure" metals. The impurities which we believe to be of importance are those which are capable of forming eutectic alloys, or fusible compounds, with the metal itself; they would therefore be mainly metals, particularly the more fusible metals, such as bismuth, tin, cadmium, mercury, sodium, or even rarer metals, such as gallium. It is well known that when a metal containing a small proportion of such impurities crystallises, the impurities are, for the most part, segregated in the inter-crystalline boundaries. The crystals themselves form at a temperature when the eutectic alloys are still quite fluid, and the growing crystals gradually push the remaining eutectic into the boundaries. Where the quantity of impurities present is sufficiently great, this eutectic can be seen under the microscope forming an inter-crystalline cement. Mild steel, where the "pearlite" plays the part of a eutectic, is a good example of such a structure; other examples can be found in the gold-aluminium alloys illustrated by Messrs. HEYCOCK and NEVILLE.* Where the quantity of eutectics present is very small, the meshes of inter-crystalline cement

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* "Gold-Aluminium Alloys," HEYCOCK and NEVILLE, 'Phil. Trans.,' A, vol. 194, plates 4, 5.

cease to be visible, but the presence of the impurity makes itself felt by the formation of deep grooves or channels along the inter-crystalline boundaries on etching. Even a very minute amount of impurity would suffice to form a thin but practically continuous film of eutectic in the crystalline boundaries.

The close analogy between alloys and salt solutions has been so fully worked out that it is barely an assumption to say that a eutectic alloy in contact with crystals of one of its constituents will behave in much the same way as a saturated solution of a salt in contact with crystals of that salt would do. Our view, then, is that there is constant diffusion from the surface of the crystal into the eutectic film and equally constant re-deposition of metal upon the crystal from the eutectic film. If there are several crystals in contact with the same eutectic, then there will be, under some conditions, a state of dynamic equilibrium between them, the amount dissolved from each being exactly counterbalanced by the amount deposited upon it; if, however, there is any difference in the solubility of various crystals, in other words, if there is any difference in their "solution pressure" in respect to the eutectic, then the less soluble will grow at the expense of the more soluble. In the case of salt crystals in an ordinary solution it is well known that the large crystals gradually absorb the small ones, a transformation generally explained on the ground that a system tends to assume a position of minimum potential energy. In the case of metallic crystals in a solid metal we have, however, this special condition, that the eutectic (or solution) exists as a mere thin film in contact with only one face of one crystal on either side. If, therefore, these two crystal faces differ in solubility or "solution pressure" in the eutectic, gradual transfer of the metal by diffusion through the eutectic film from one crystal to the other would result, and the one crystal would grow at the expense of the other. This action might go on while the eutectic was solid—Sir W. C. ROBERTS-AUSTEN has demonstrated that diffusion does occur in solid metals,* but at extremely slow rates, unless the metals are near their melting-points. The metal constituting the eutectic films, being much nearer its melting-point than the rest of the mass, would thus be favourable to comparatively rapid diffusion, but the rate of such diffusion and, consequently, the rate of growth of crystals, would be enormously increased by heating the metal to a temperature above the melting-point of the eutectic in question.

The theory† which we suggest to explain crystal growth in a solid metal depends upon the existence of a difference in the solubility of the two crystal faces in contact with a eutectic film. The only difference between these two faces is, apparently, in the orientation of the crystalline elements; but this very difference is sufficient to produce a difference in the rate of solution of such surfaces in an acid. A polished surface of metal when attacked by an acid is not attacked at a uniform

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* Bakerian Lecture, "Diffusion of Metals," by W. C. ROBERTS-AUSTEN, 'Phil. Trans.,' A, 1896, vol. 187, pp. 383–416; "Diffusion of Gold into Lead," 'Proc Roy. Soc.,' May 5th, 1900.

† It is proper to say that the credit for this theory belongs to Mr. ROSENHAIN.—J. A. E.

rate all over, but at different rates over different crystals, in such a way as to produce marked differences of level between adjacent crystals. Another phenomenon, seen best in etching lead in dilute nitric acid, is also of interest in this connection; it has already been described in the present paper (see p. 284). We there have a case of lead dissolved from one crystal and deposited upon another crystal in its proper orientation.

In view of these facts, we think it must be admitted that different crystal faces, having a different orientation of their elements, differ in solubility in the same solvent. To inquire into the cause of this difference is a further step in speculation which is, perhaps, hardly necessary in this connection. Such differential actions may, however, most probably be attributed to differences of electrical potential in the surfaces involved. If we accept this view of the matter, then the diffusion across films of eutectic becomes a case of electrolysis. Now, while diffusion in metals and alloys is a proved fact, the possibility of electrolysis in an alloy has not yet been demonstrated experimentally.* On the other hand, the close analogy with salt solutions leads one to expect that alloys could be electrolysed, and those who have experimented in the matter are not by any means certain that greater experimental resources will not enable them to electrolyse alloys.

There is at least one fact in the phenomena of re-crystallisation which the solution theory, apart from electrolysis, does not cover, while the electrolytic theory explains it very readily. We refer to the fact that only strained crystals will grow, while unstrained crystals show no tendency to change even at higher temperatures. The explanation, on the electrolytic theory, is that in the unstrained state the crystals are surrounded by practically continuous films of eutectic, and that electrolysis only becomes possible when severe distortion has broken through these films in places, allowing the actual crystals to come into contact; the electrolytic circuit would then be for each pair of crystals, from one crystal to the other by direct contact and back through the eutectic film.

Our view of the phenomena of re-crystallisation in solid metals may be summed up thus:—We believe that the action is one of solution and diffusion of the pure metal constituting the crystals into the fusible and mobile eutectic forming the inter-crystalline cement. This diffusion results in the growth of one crystal at the expense of the other, owing to differences in solubility of the crystal faces on opposite sides of the eutectic film, and it seems probable that this phenomenon of directed diffusion is really a form of electrolysis.

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* It has, however, been shown by GARNIER ('Comptes Rendus de l'Académie des Sciences,' vol. 116, 1893, pp. 144–9), that the diffusion of carbon into iron is affected by the action of an electric current. He interposed a layer of carbon between two iron electrodes enclosed in a fire-clay tube; the whole was heated to 1000° C., and a current of 55 ampères was passed for three hours, when the anode was found to be unchanged, while the cathode had undergone considerable cementation. This action in the interior of the iron is practically electrolysis of the carbon-iron eutectic.

There is one deduction from this solution theory of re-crystallisation that lends itself to experimental investigation. If eutectics play an essential part in re-crystallisation, these phenomena should disappear in the total absence of impurities capable of forming eutectics. In a perfectly pure metal, re-crystallisation by annealing after severe strain should not occur; but it is almost hopeless to obtain a specimen of such purity as to justify the conclusion experimentally in this form. The degree of purity required can be roughly gauged from the fact that 0·1 per cent. of carbon in iron is easily visible as "pearlite" under the microscope; so that, probably, an impurity of one part in one million would vitiate the experiment.

But our conclusion can be narrowed down to more practicable limits by putting it in this way :—That if the presence of a eutectic is essential to crystalline growth, then a crystalline boundary free from eutectic should be a barrier to all such growth. This condition can be approximately realised by means of a weld between two clean-cut surfaces of a metal. Lead lends itself particularly well to such experiments, as it welds readily under pressure without the aid of heat. In this way we have obtained a striking experimental verification of the conclusion deduced from the above theory.

The welds were made in various ways; generally two lead discs about $1\frac{1}{2}$ inch in diameter had their surfaces scraped clean with a clean, sharp knife, the two surfaces being put into contact immediately after scraping. They were then subjected to a pressure of 5 tons steadily applied in a testing-machine; in some cases pressures up to 50 tons were used. The behaviour of the specimens under pressure depended upon the previous preparation of the lead discs; as a rule, and in order to obtain the metal in a condition where its crystals would grow rapidly, these discs were prepared by crushing a cast cylinder an inch long by $\frac{5}{8}$ inch diameter. In other cases the discs were obtained by casting, and were then only strained when the welding pressure came upon them; in these cases there was considerable "flow" while the two discs were in contact, but their ultimate behaviour was the same in all cases.

The welded discs so obtained were found to be firmly united and could be sawn into sections as desired; they were cut up into sections suitable for microscopic examination, sometimes before, but generally after "annealing." The annealing was done by exposing the specimens to a temperature of 200° C. for a considerable time—varying from 24 hours to over a month, and the crystals in all cases grew vigorously. Sections at right angles to the plane of the weld were then cut smooth and etched for examination. On the freshly-cut surface the line of the weld could never be distinguished. The etching had to be carried to a considerable depth, because we found that the cut surface was covered by a thin layer of very minute crystals—evidently the result of the violent strains set up by the cutting-tool.

Microscopic examination, generally at 80 diameters, of these etched sections showed that, although the crystals on either side of the weld had grown vigorously, none of them crossed the line of the weld, which was clearly visible as an inter-crystalline boundary continuous along the whole specimen; in many cases aggressive individual crystals had grown up to the line of the weld and there ended quite abruptly. It must not, however, be supposed that this weld line was mechanically weak; it proved on trial to be quite as difficult to cut or tear the metal along the weld as in any other direction. The weld therefore behaved as a true inter-crystalline boundary, differing only in the absence of eutectic, and therefore forming a barrier to crystalline growth. Fig. 37 shows the appearance of such a weld in section after annealing and etching, at a magnification of 30 diameters. The line AB is the weld. As these experiments were made on commercial lead, we were prepared to find that, as a mere matter of probability, some eutectic would have occasionally found its way into the welding surfaces, but this seems to have happened only very rarely. We examined some forty specimens, and only in two instances did we see a slight amount of crystalline growth crossing the line of the weld. We think that we are justified in attributing these rare exceptions to the accidental presence of impurity.

We then went a step further. If we have in a welding surface an inter-crystalline junction which acts as a barrier to crystalline growth owing to the absence of eutectic, then if a suitable eutectic be supplied, growth should occur there as elsewhere.

Our first experiment was to interpose a thin but continuous layer of lead-bismuth eutectic between the lead discs in welding; the specimen was then annealed for several days at 200° C.—well above the melting-point of the eutectic—but on examination it was found that the layer of eutectic had persisted as such, and allowed no growth to cross it. But in this case the film of eutectic introduced at the weld was continuous, and the conditions were therefore analogous to those which hold at the boundaries of unstrained crystals, where, as we have pointed out, growth does not occur. To make the experiment conclusive it was necessary to have a discontinuous film of eutectic at the weld. We accordingly tried another experiment, introducing only a few small flakes of the same alloy, and after annealing we found that crystalline growths had crossed the line of the weld in many places. This experiment was repeated many times, various impurities being used, such as the lead-tin-cadmium-bismuth eutectic, pure tin, cadmium, bismuth, and mercury. All these gave the same result, showing considerable growth across the weld after prolonged annealing at 200° C., but the amount of growth observed varied very much.

Fig. 38 shows a typical example of crystals that have grown across the weld; the line of the weld is still faintly indicated by a discontinuous line, CD, probably representing an included impurity of a non-metallic character, around which the crystals have grown much as they grow around the slag in wrought-iron.

In order to remove all doubt as to the action of the impurities which were introduced, and particularly to obviate the possible contention that their action was either purely mechanical or else of the nature of that of the "dirt" more or less requisite in many chemical actions, certain further experiments on welds in lead were made. In these, the matter introduced at the weld was—

(1) Flakes of lead.
(2) Clean iron filings.
(3) Clean sand.

In all three cases no growth across the weld took place, which confirms the view that the presence of a more fusible eutectic in an inter-crystalline boundary is essential to crystalline growth across that boundary. We think, therefore, that we are justified in regarding the results of these experiments as strong confirmation of the solution theory of crystalline growth in annealing.

INDEX OF PLATES.

Fig. 2. A general view of an etched surface of sheet-lead, under oblique light, magnified 2 diameters. (Plate 3.)

Figs. 3 and 4. Two photographs of the same area of etched sheet-lead under different incidence of oblique light. Magnification 40 diameters. These photographs illustrate the appearance of twin lamellæ. (Plate 3.)

Fig. 5. Geometrical markings on etched sheet-lead seen under oblique light and magnified 100 diameters. (Plate 4.)

Fig. 6. A typical view of the structure seen in etched cast-lead under oblique light and magnified 12 diameters. (Plate 4.)

Fig. 7. A typical view of the structure of freshly crushed lead seen under oblique light and magnified 30 diameters. (Plate 4.)

Figs. 8 to 13. Series of views of a single specimen of crushed lead taken at intervals during six months, showing the growth of crystals at the temperature of the air, seen under oblique light and magnified 12 diameters. (Plates 5 and 6.)

Figs. 14 to 19. Series of views of a single specimen of sheet-lead showing the effect of continued exposure to a temperature of 200° C., seen under oblique light and magnified 12 diameters. (Plates 6 and 7.)

Figs. 20 to 26. Series of views of a single specimen of freshly crushed lead showing the effects of continued exposure to 200° C. seen under oblique light; Nos. 20 to 25 magnified 12 diameters, No. 26 magnified 8 diameters. (Plates 8 and 9.)

Fig. 27. An aggressive crystal developed in crushed lead by annealing, seen under oblique light, magnified 8 diameters. (Plate 10.)

Figs. 29 and 30. Geometrical etched pits seen in tin-plate under vertical light and magnified 100 diameters. (Plates 10 and 11.)

Figs. 28, 31 and 32. Photographs of etched tin-plate as seen by daylight at half the natural size. (Plates 10 and 11.)

Figs. 33 to 35. Series of views of a single specimen of freshly crushed cadmium, showing the effects of continued exposure to 200° C., under oblique light, with a magnification of 12 diameters. (Plate 12.)

Fig. 36. Crystals developed in sheet-zinc by exposure to 200° C., oblique light, magnification 8 diameters. (Plate 13.)

Fig. 37. Section through a cold weld in lead, using clean surfaces, after prolonged annealing; the line of the weld is seen at AB. Oblique light, magnification 30 diameters. (Plate 13.)

Fig. 38. Section through a cold weld, using eutectic in the weld, after prolonged annealing. The line of the weld is at CD. Oblique light, magnification 30 diameters. (Plate 13.)

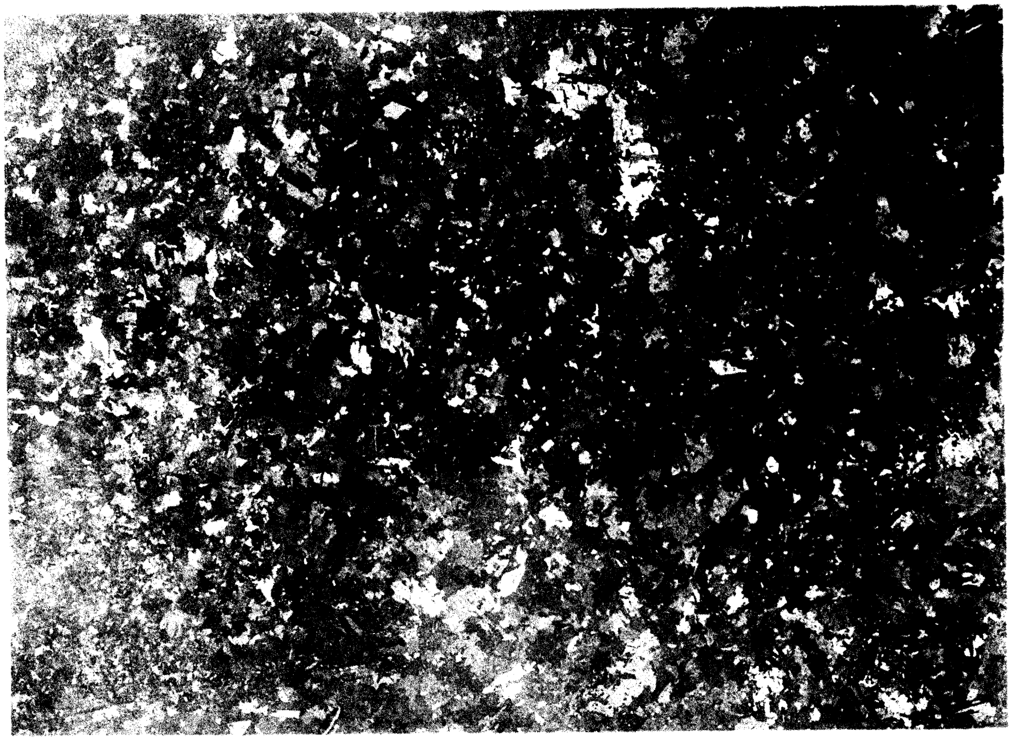

Fig. 2.—Etched Sheet lead. Two diameters.

Fig. 3.—Crystals in sheet-lead showing twins, oblique light. × 40.

Fig. 4.—Same field as Fig. 3 with direction of illumination rotated through 30°. × 40.

Fig. 5.—Etched sheet-lead. × 100.

Fig. 6.—Cast lead. × 12.

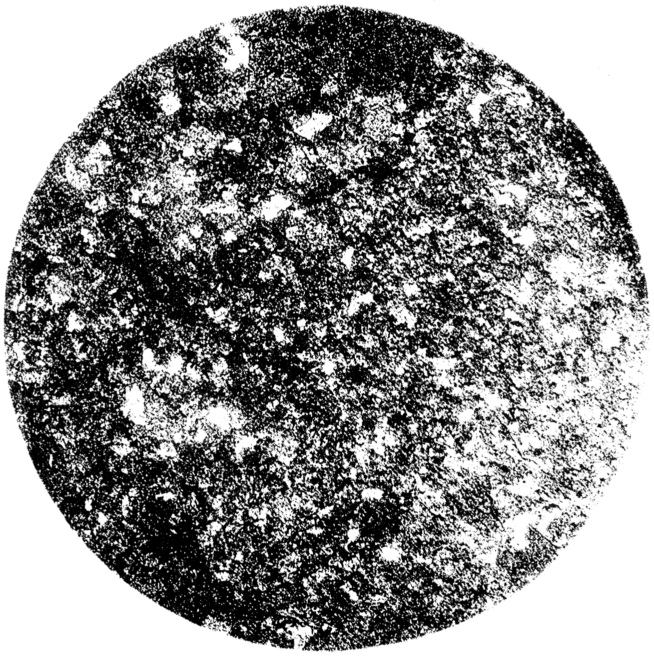

Fig. 7.—Freshly crushed lead. × 30.

Fig. 8.—Lead. × 12. Freshly crushed.

Fig. 9.—Same after six days.

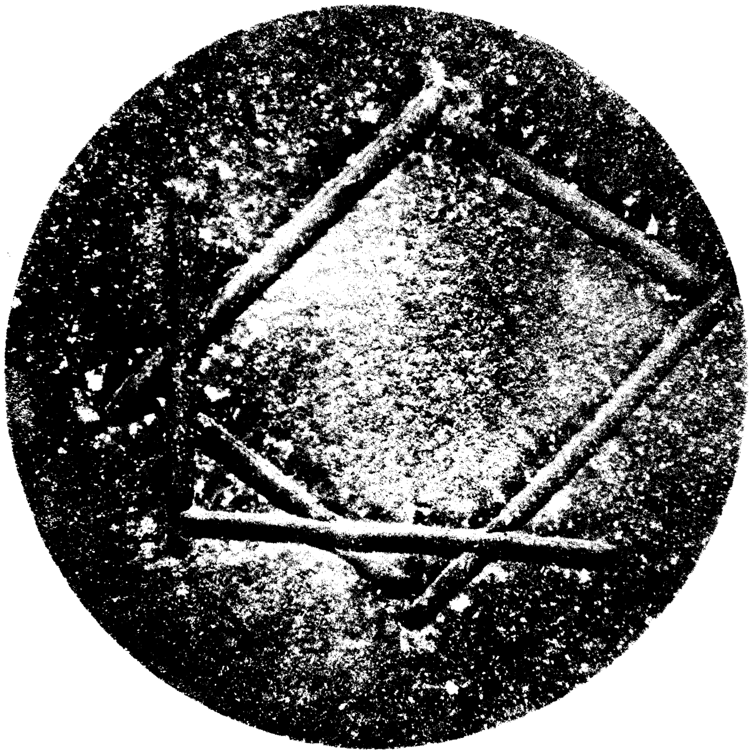

Fig. 10.—Same after one month.

Fig. 11.—Same after two months.

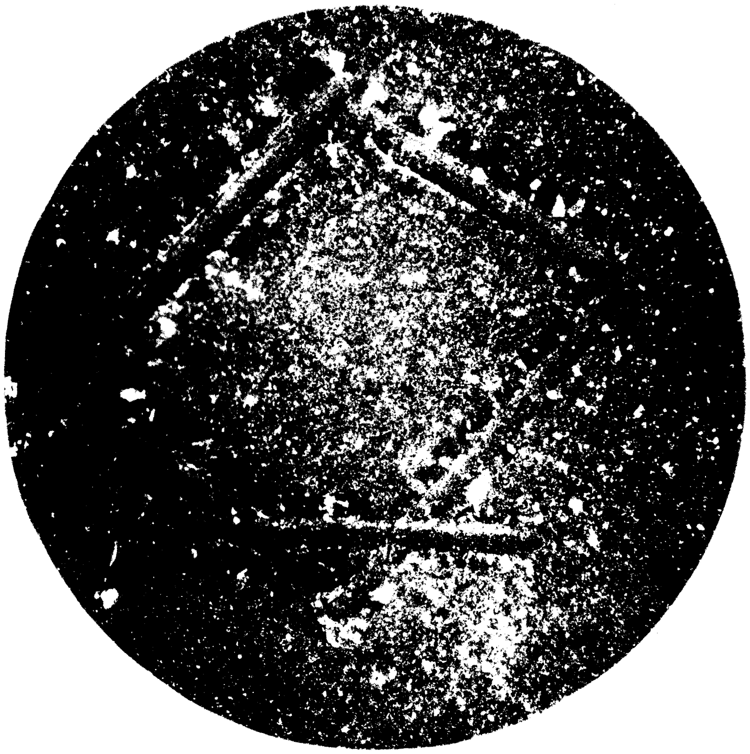

Fig. 12.—Same after four months.

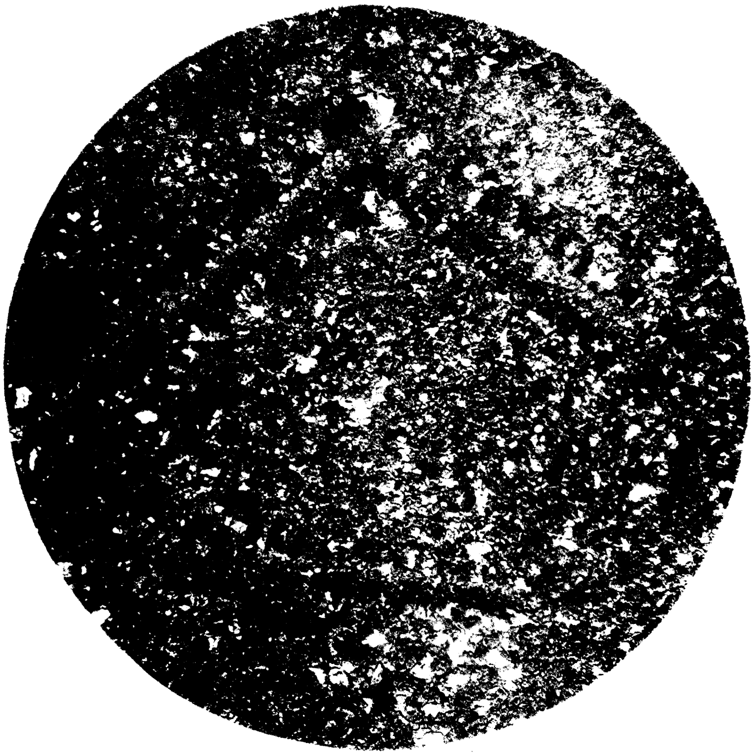

Fig 13.—Same after six months.

Fig. 14.—Sheet lead. × 12.

Fig. 15.—Same sheet lead. × 12. After 30 minutes at 200° C.

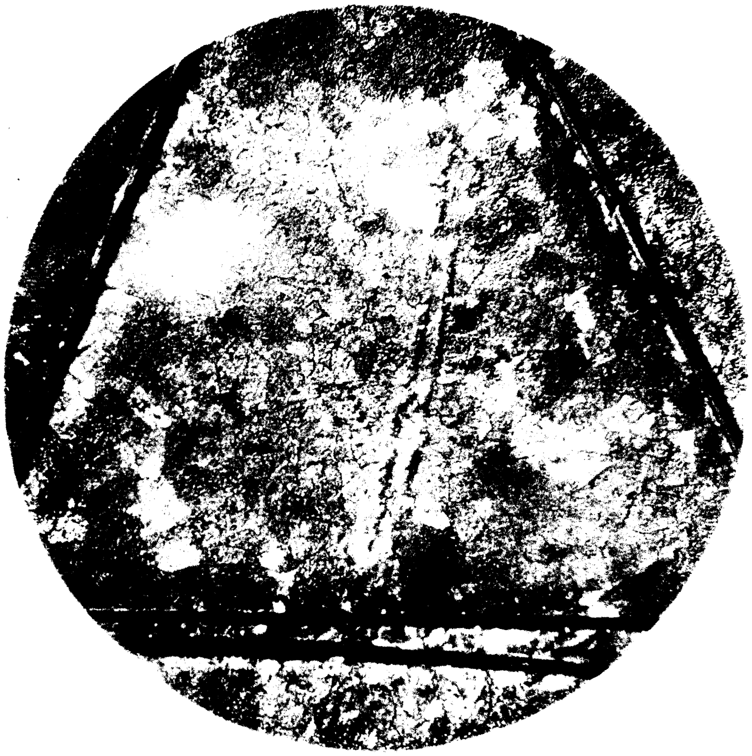

Fig 16.—Same after 30 minutes further at 200° C.

Fig. 17.—Same after 48 hours further at 200° C.

Fig 18.—Same after 4 days further at 200° C.

Fig. 19.—Sheet lead. × 12. Another part of the same specimen as Fig. 18.

Fig. 20.—Freshly crushed lead. × 12.

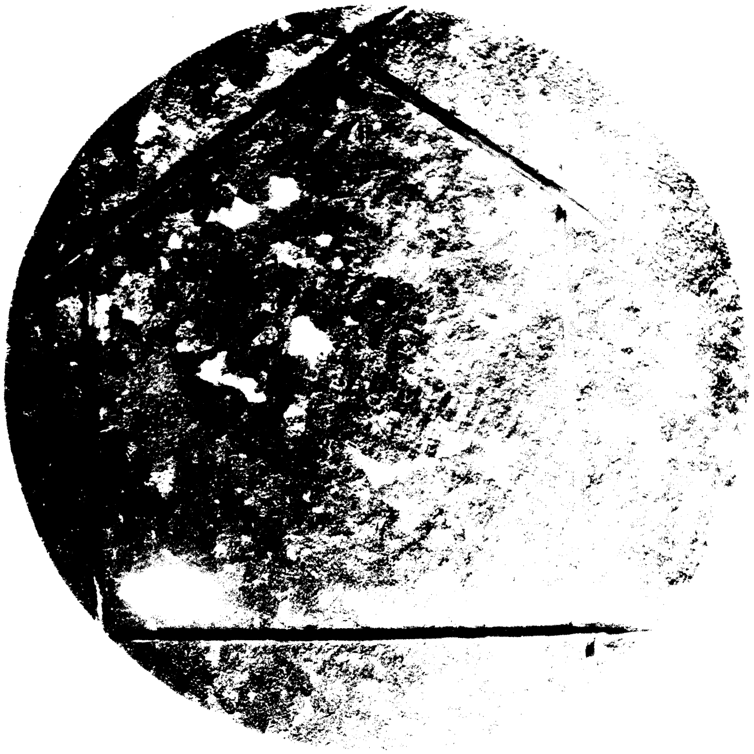

Fig. 21.—Same after 17½ hours at 200° C.

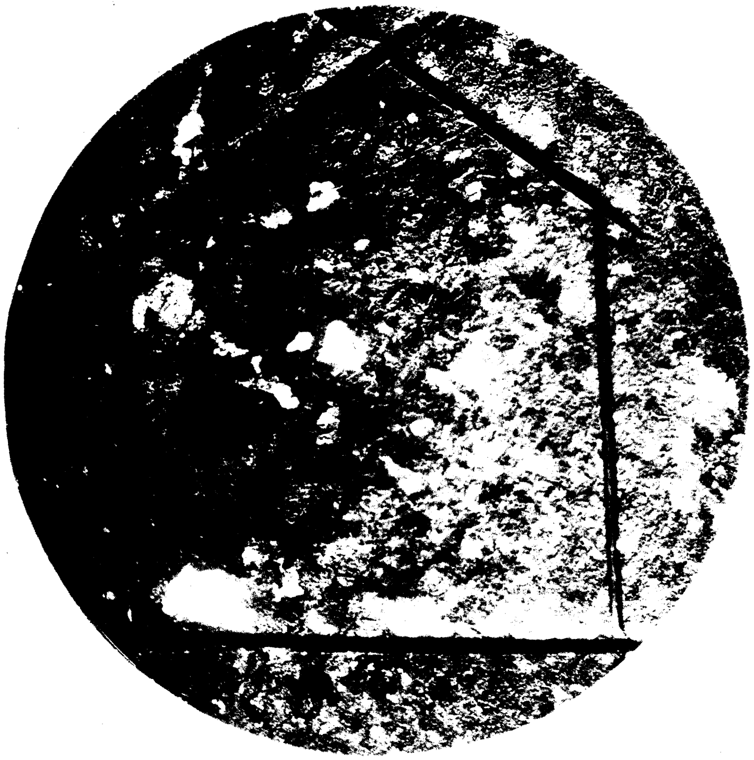

Fig. 22.—Same after 1 day 17½ hours at 200° C.

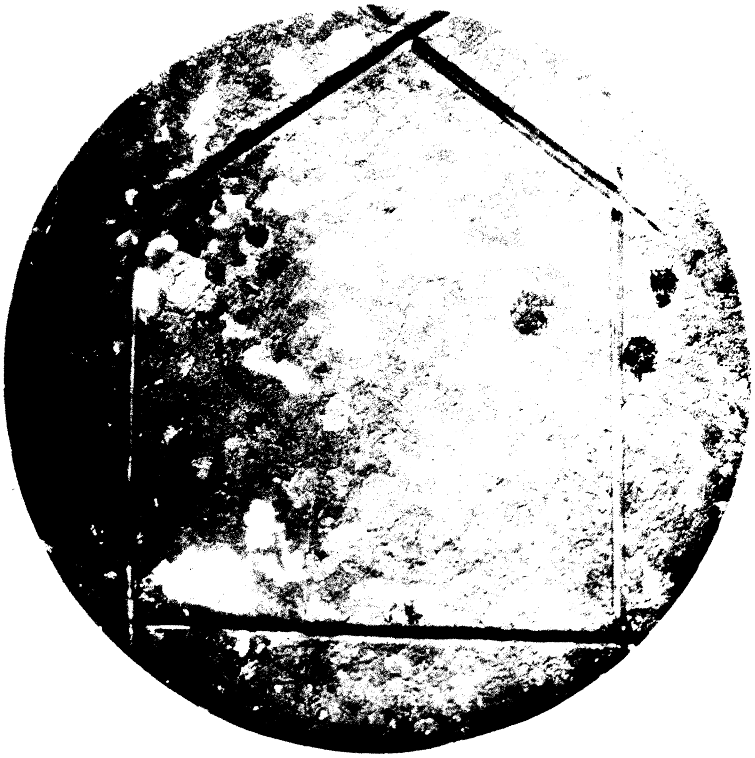

Fig. 23.—Same after 2 days 17½ hours at 200° C.

Fig. 24.—Same after 5 days 16 hours at 200° C. with incidence of light altered.

Fig. 25.—Same after 40 days at 200° C.

Fig. 26.—Same specimen as Fig. 25 (after 40 days at 200° C.) with incidence of light altered. × 8.

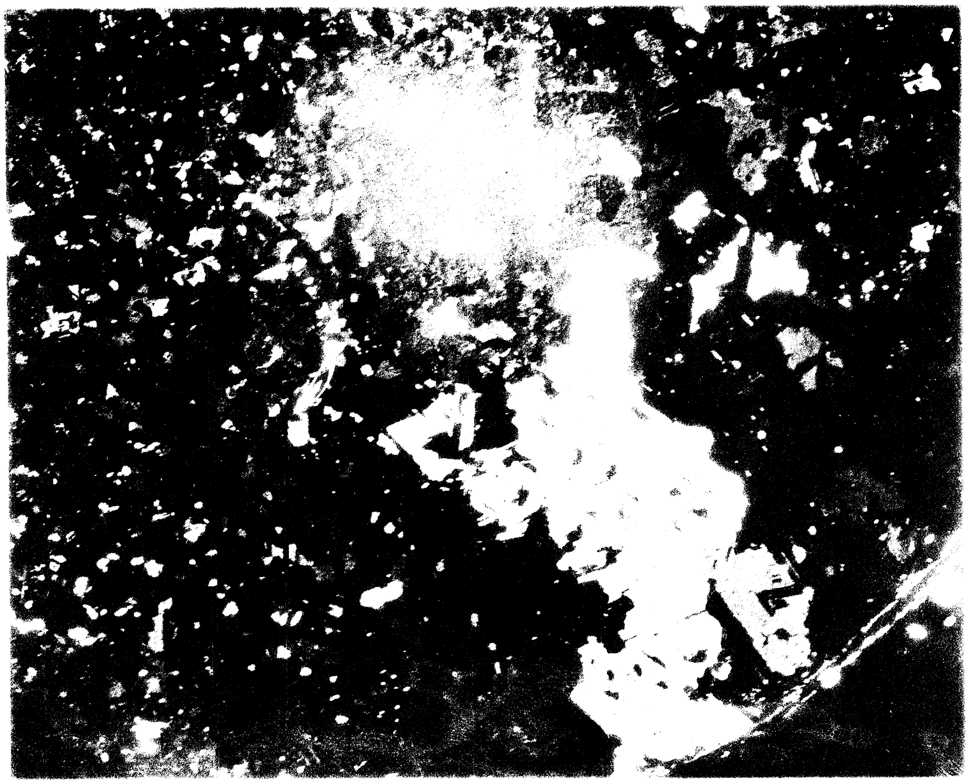

Fig. 27.—Crushed lead, after prolonged annealing. × 8.

Fig. 28.—Tin-plate, etched. × $\frac{1}{2}$.

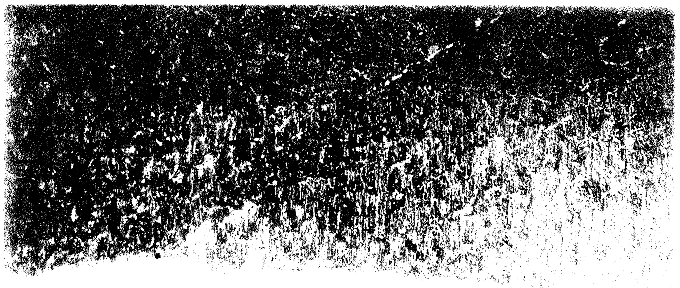

Fig. 29.—Tin-plate, etched. × 100.

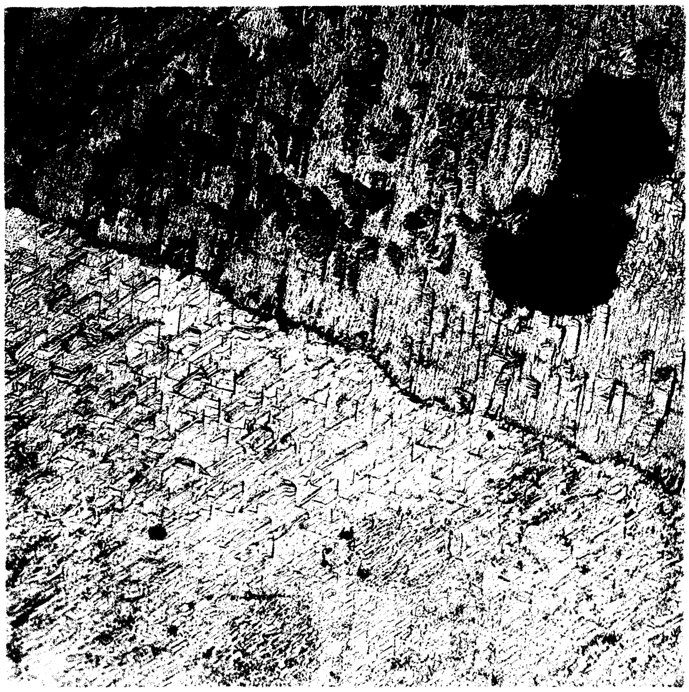

Fig. 30.—Tin-plate, etched. × 100.

Fig 31.—Tin-plate, after re-melting the tin. × ½.

Fig. 32.—Tin-plate, after re-melting the tin and cooling quickly. × ½.

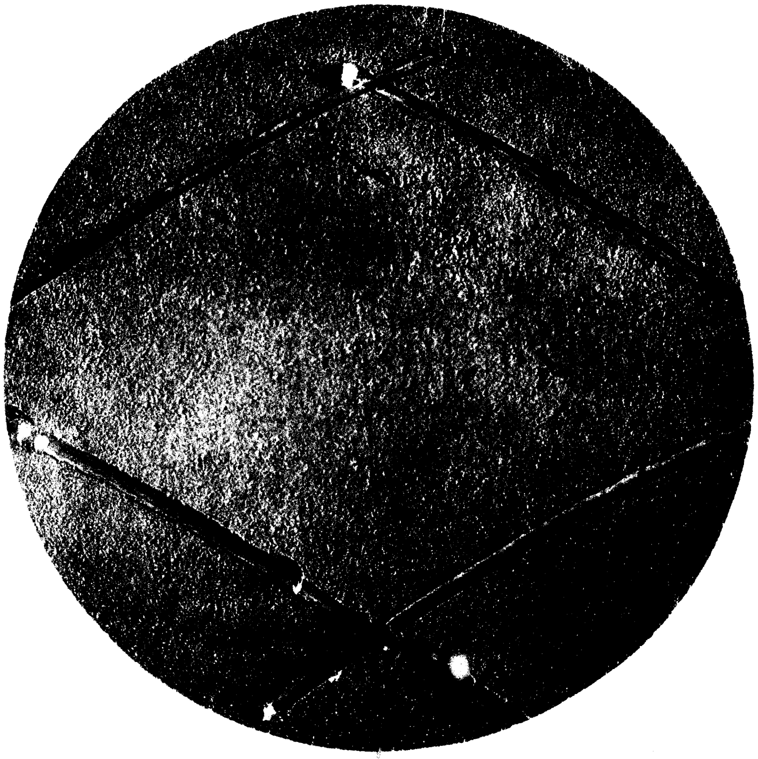

Fig. 33.—Cadmium, freshly strained. × 12.

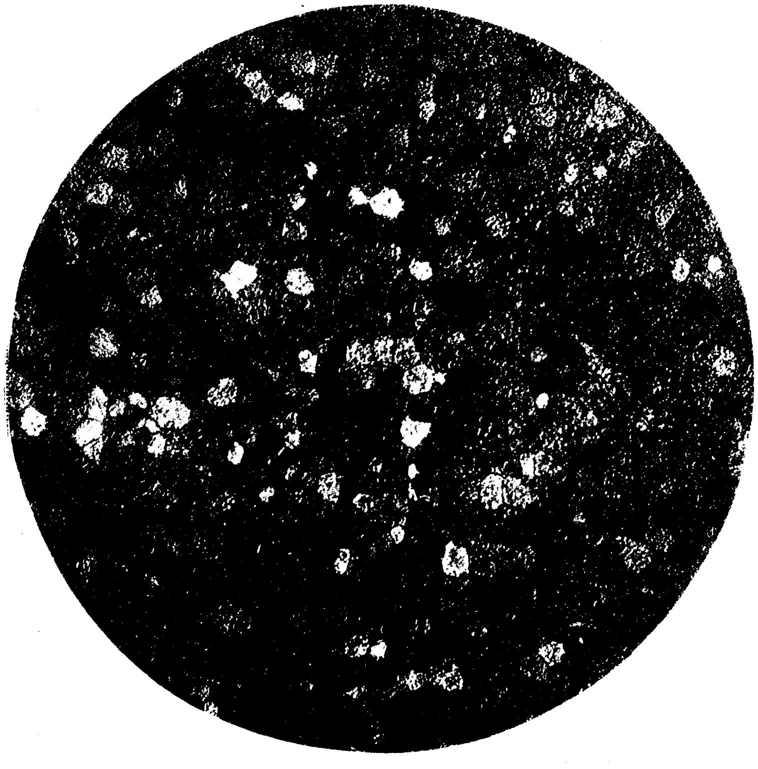

Fig. 34.—Same after 24 hours at 200° C.

Fig. 35.—Same after seven days at 200° C.

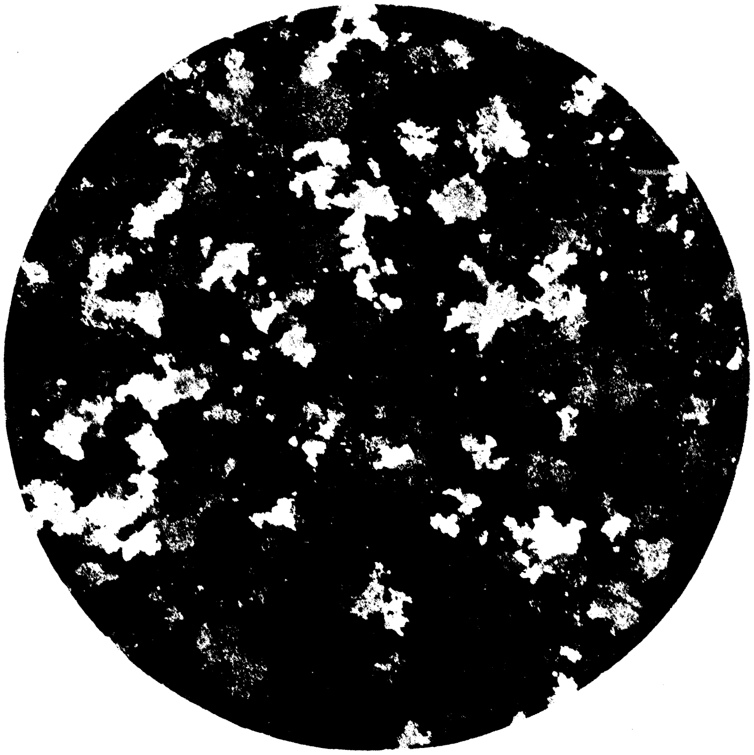

Fig. 36.—Zinc, after heating at 200° C. × 8.

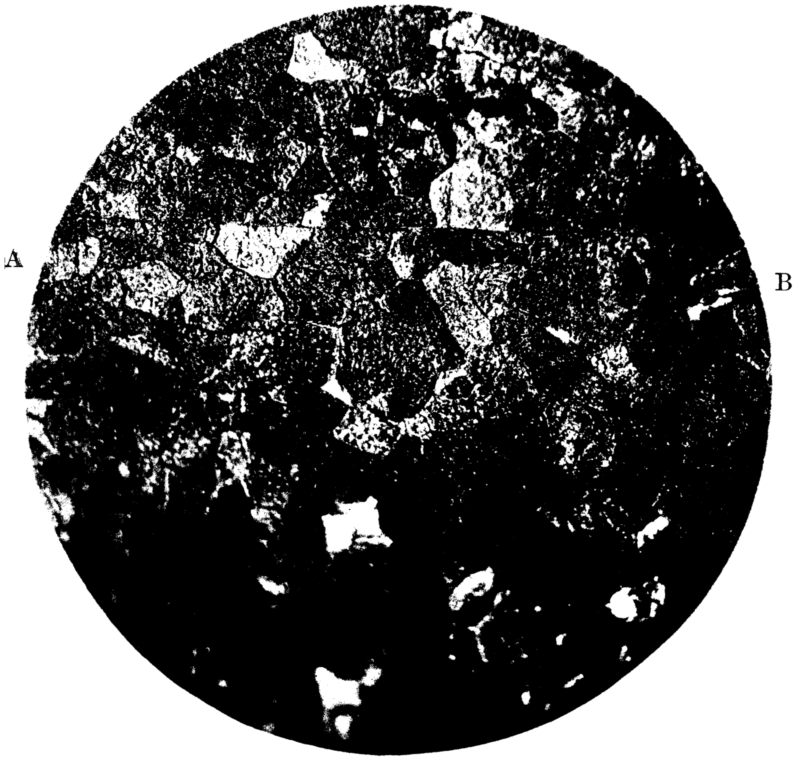

Fig. 37.—Weld in Lead. × 30.

Fig. 38.—Weld in Lead, with eutectic. × 30.

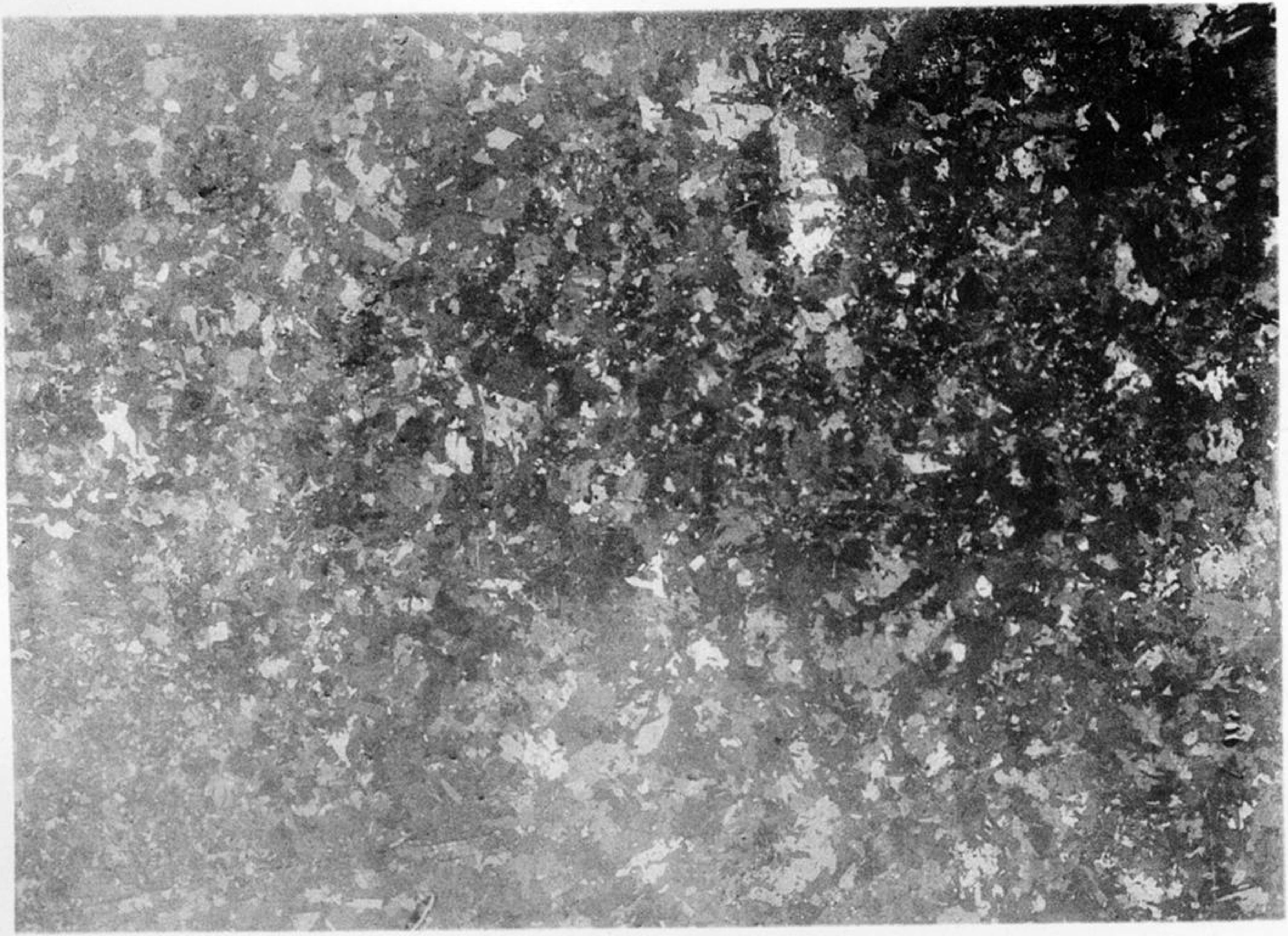

Fig. 2.—Etched Sheet lead. Two diameters.

Fig. 3.—Crystals in sheet-lead showing twins, oblique light. × 40.

Fig. 4.—Same field as Fig. 3 with direction of illumination rotated through 30°. × 40.

Fig. 5.—Etched sheet-lead. × 100.

Fig. 6.—Cast lead. × 12.

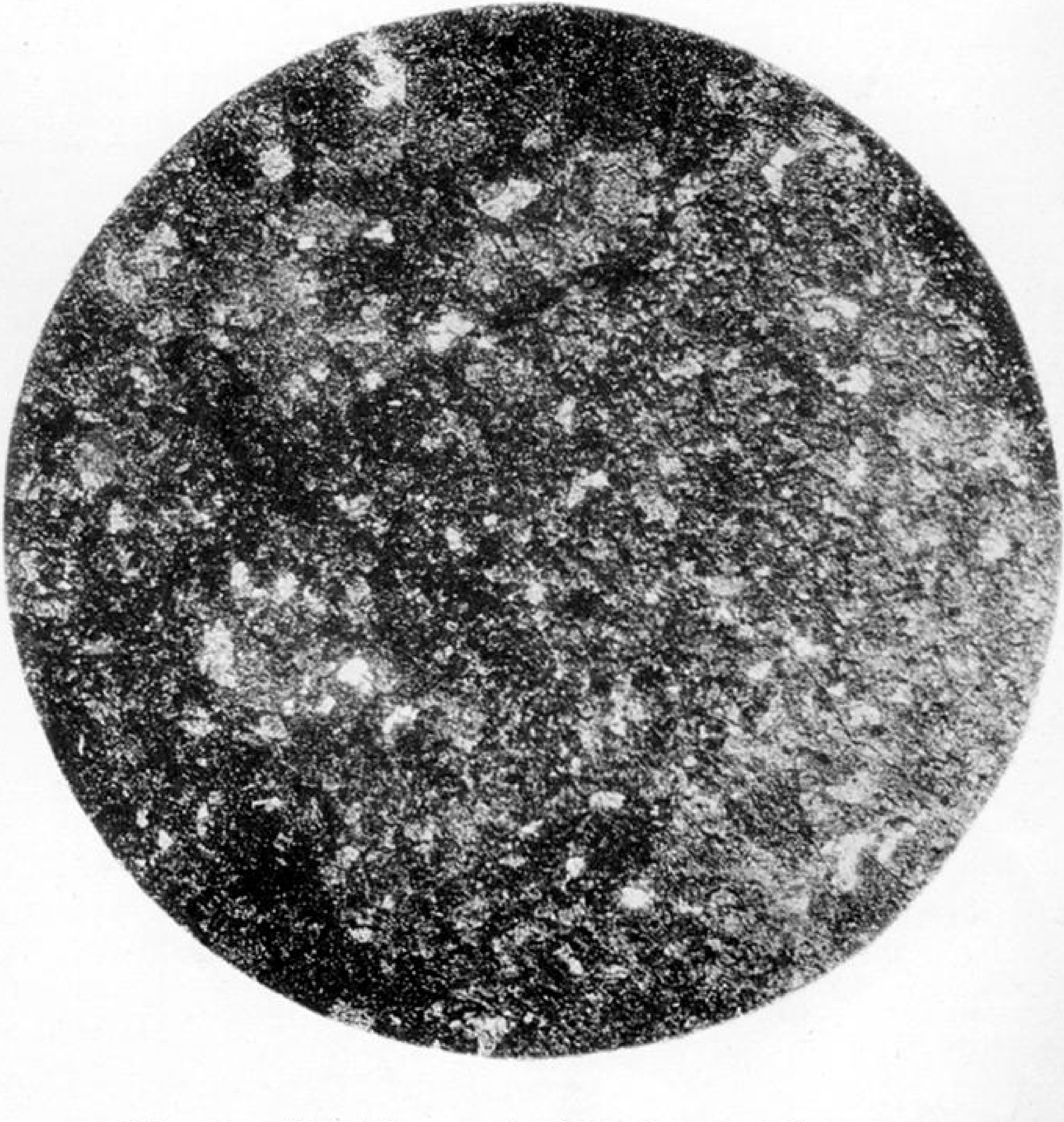

Fig. 7.—Freshly crushed lead. × 30.

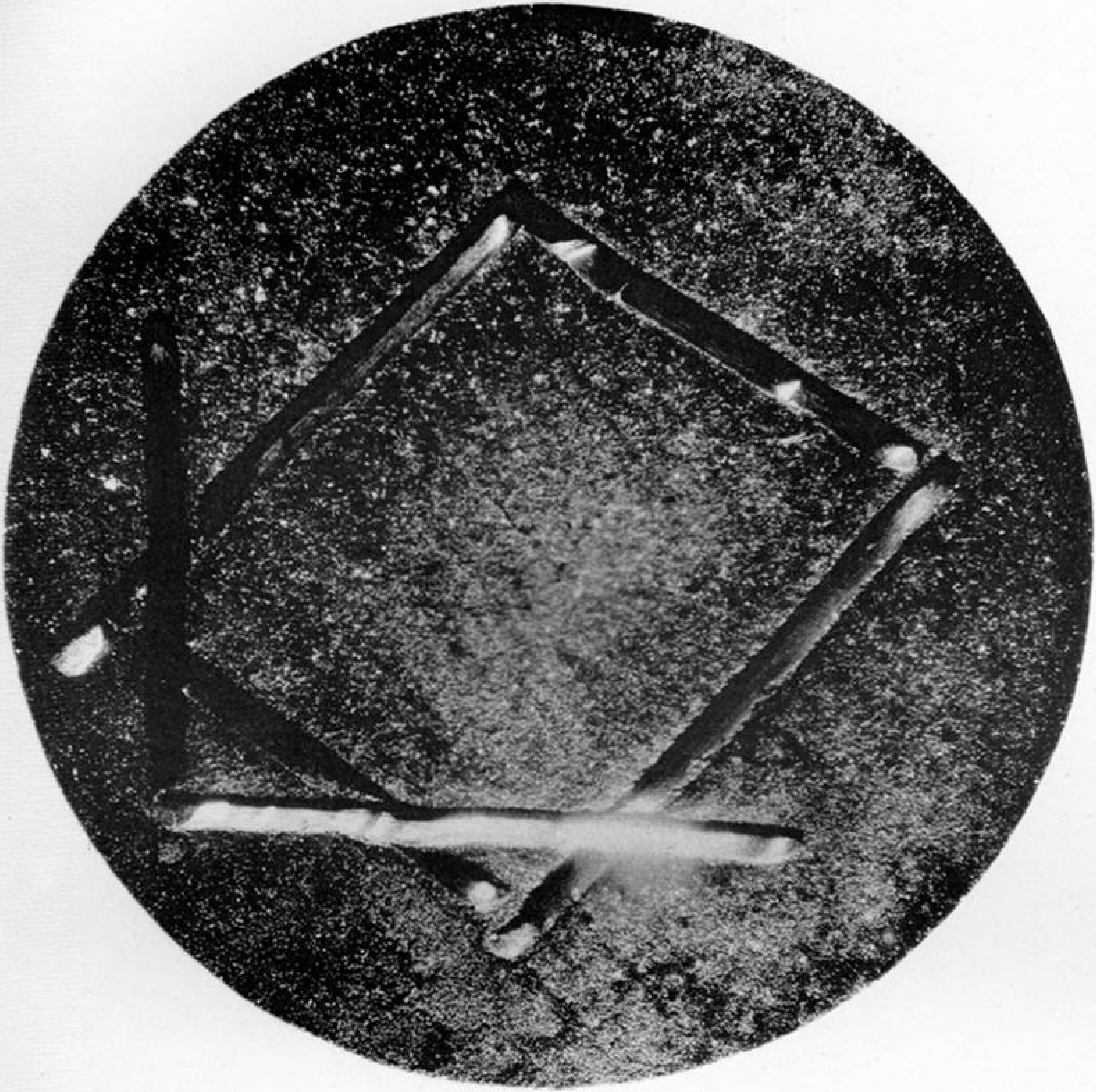

Fig. 8.—Lead. × 12. Freshly crushed.

Fig. 9.—Same after six days.

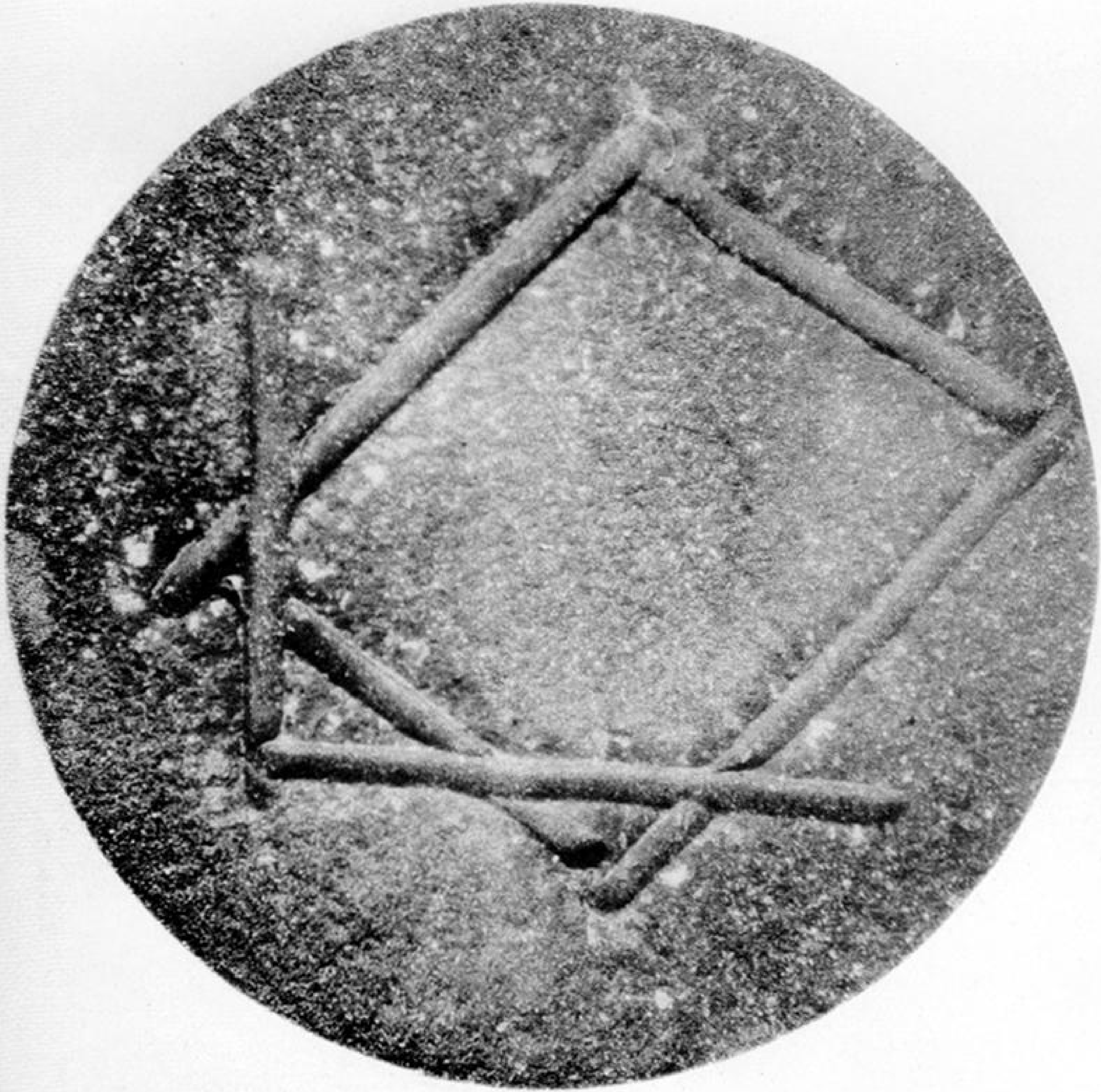

Fig. 10.—Same after one month.

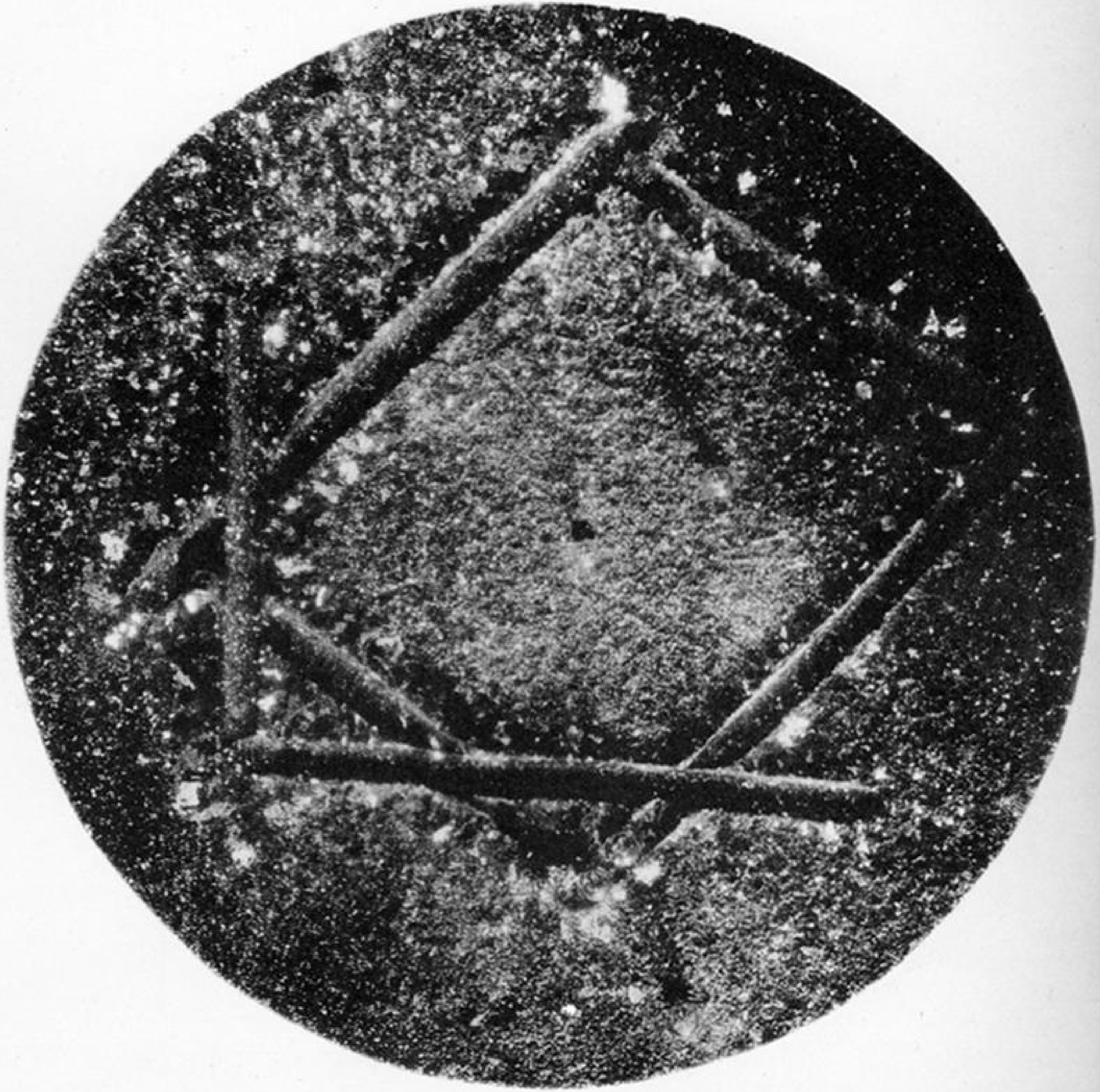

Fig. 11.—Same after two months.

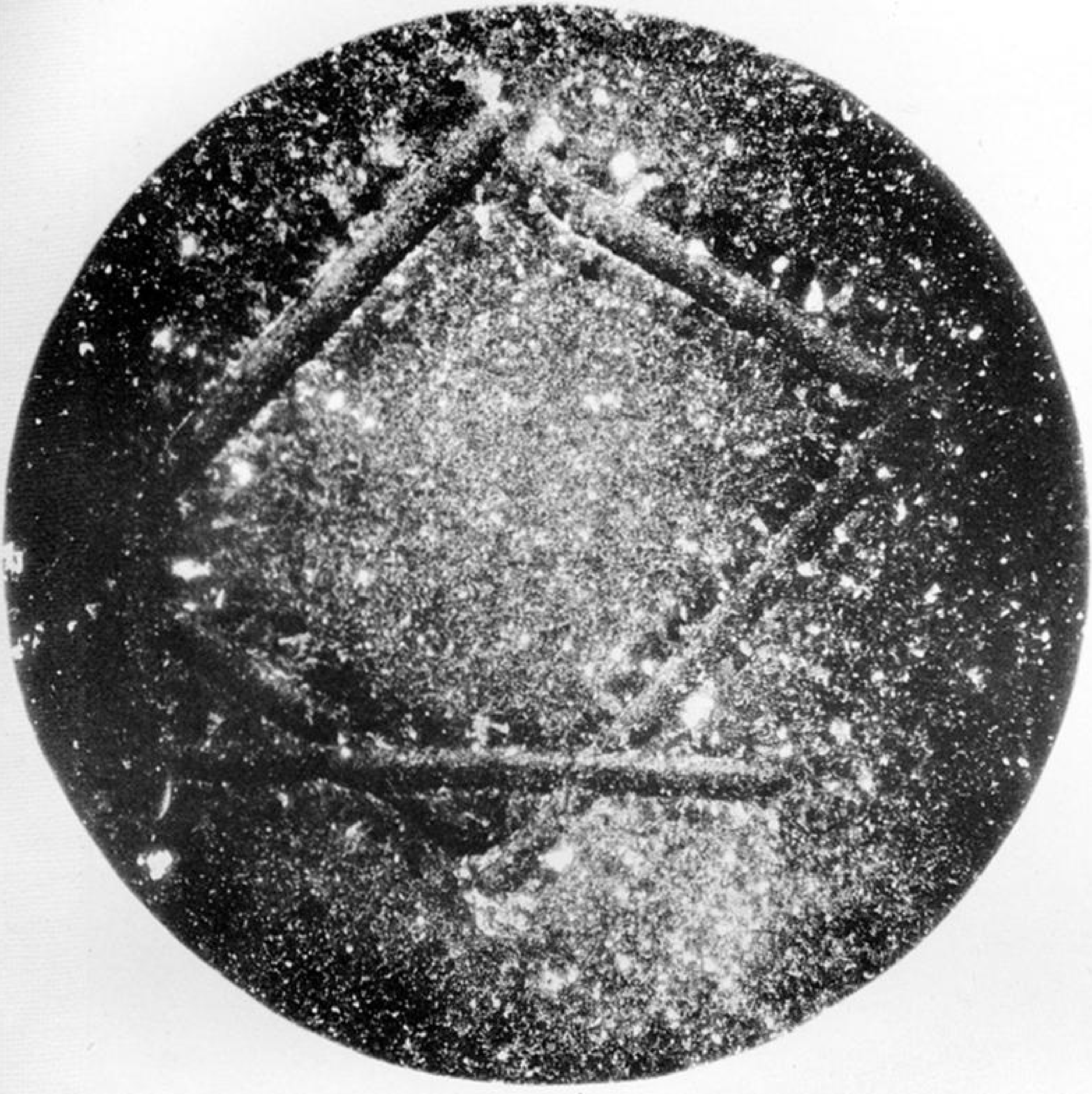

Fig. 12.—Same after four months.

Fig 13.—Same after six months.

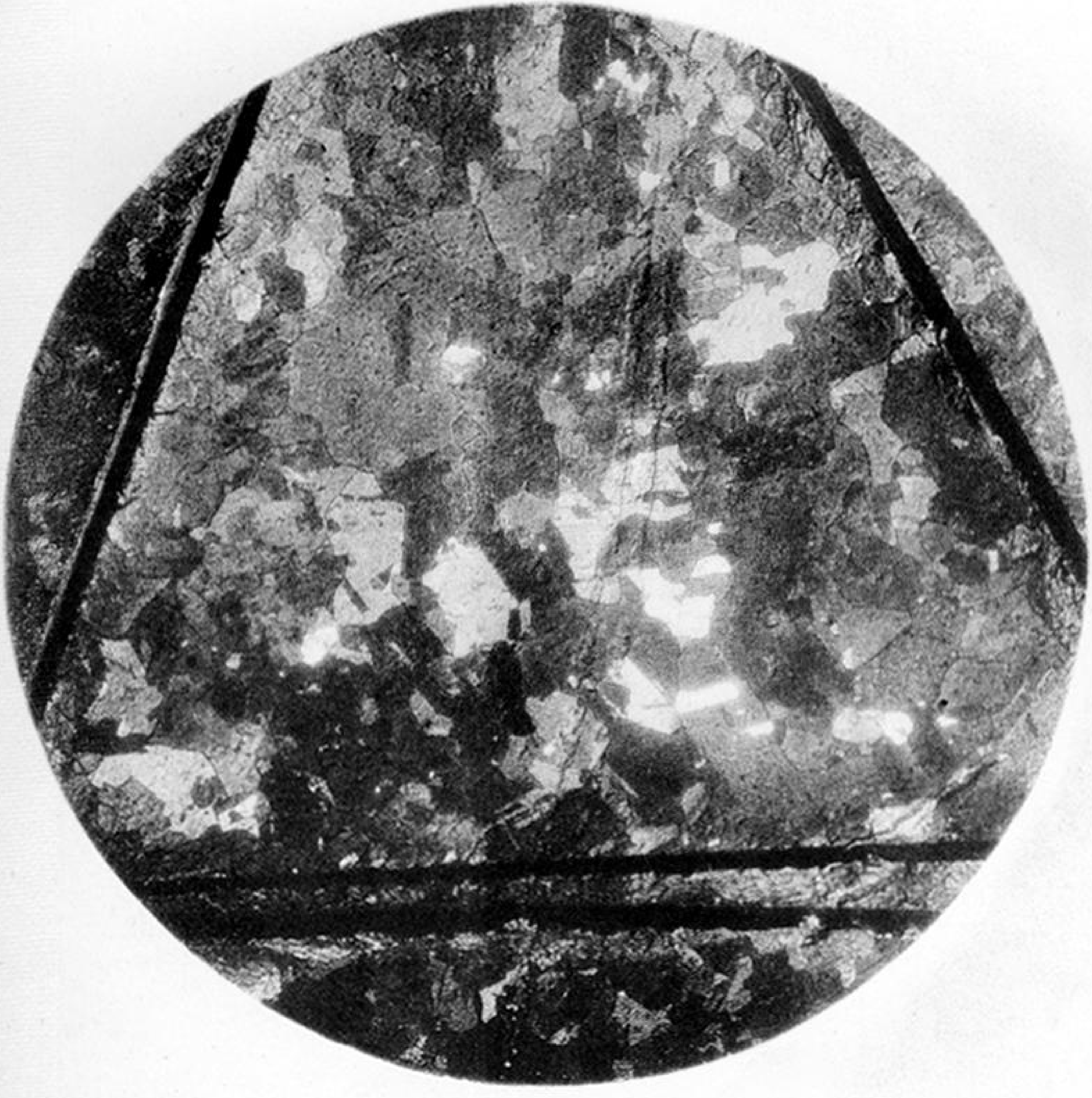

Fig. 14.—Sheet lead. × 12.

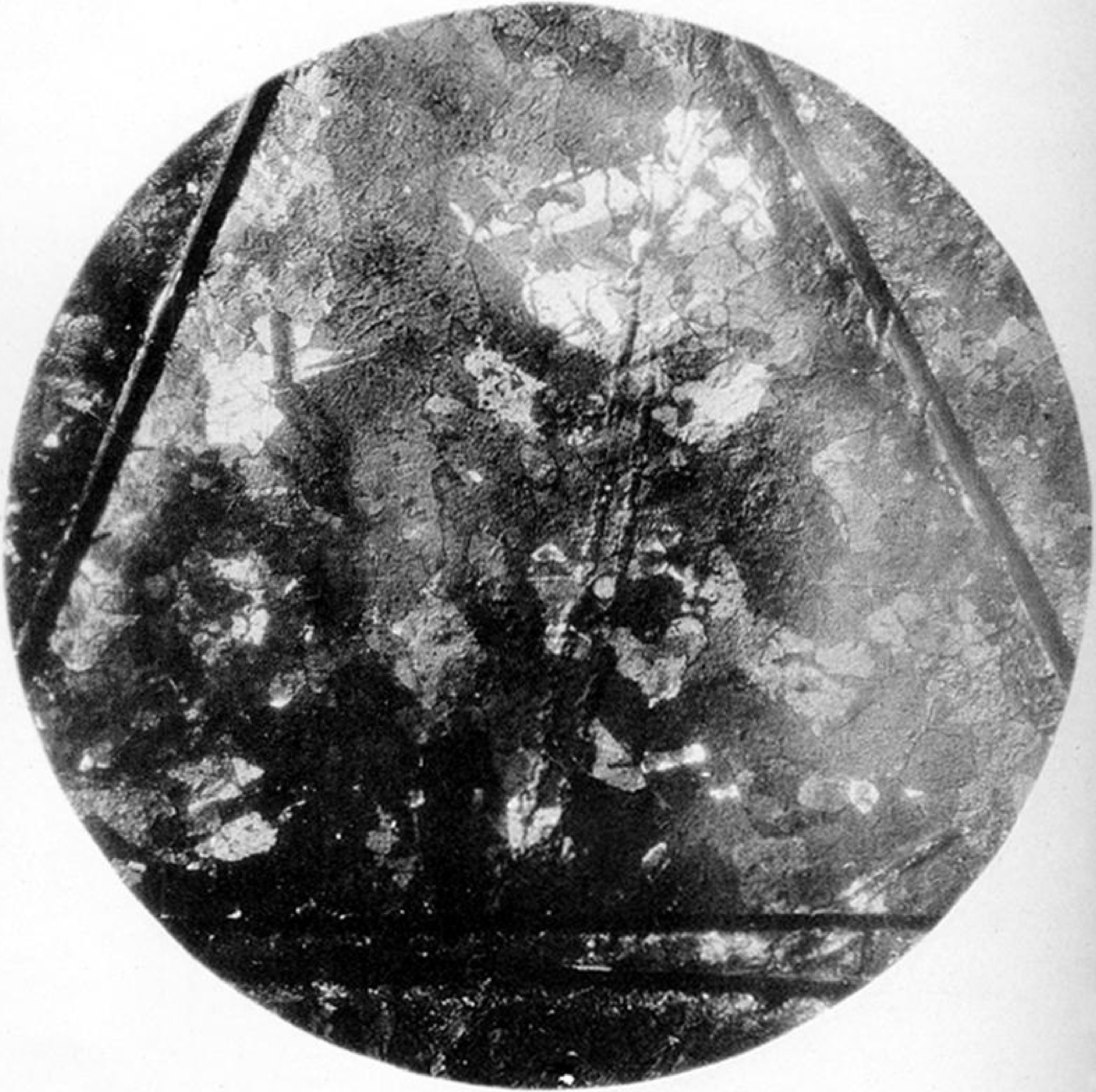

Fig. 15.—Same sheet lead. × 12. After 30 minutes at 200° C.

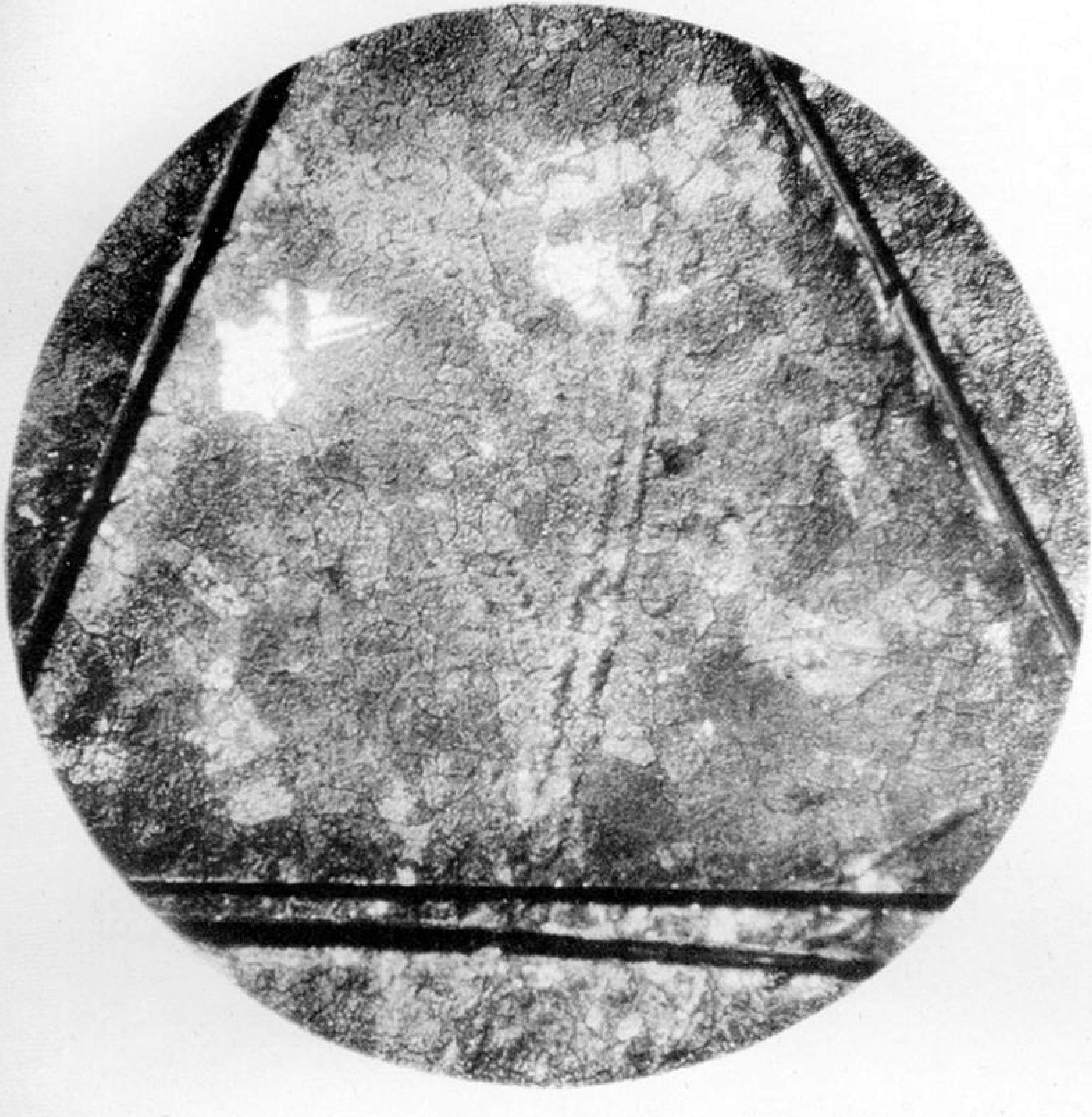

Fig 16.—Same after 30 minutes further at 200° C.

Fig. 17.—Same after 48 hours further at 200° C.

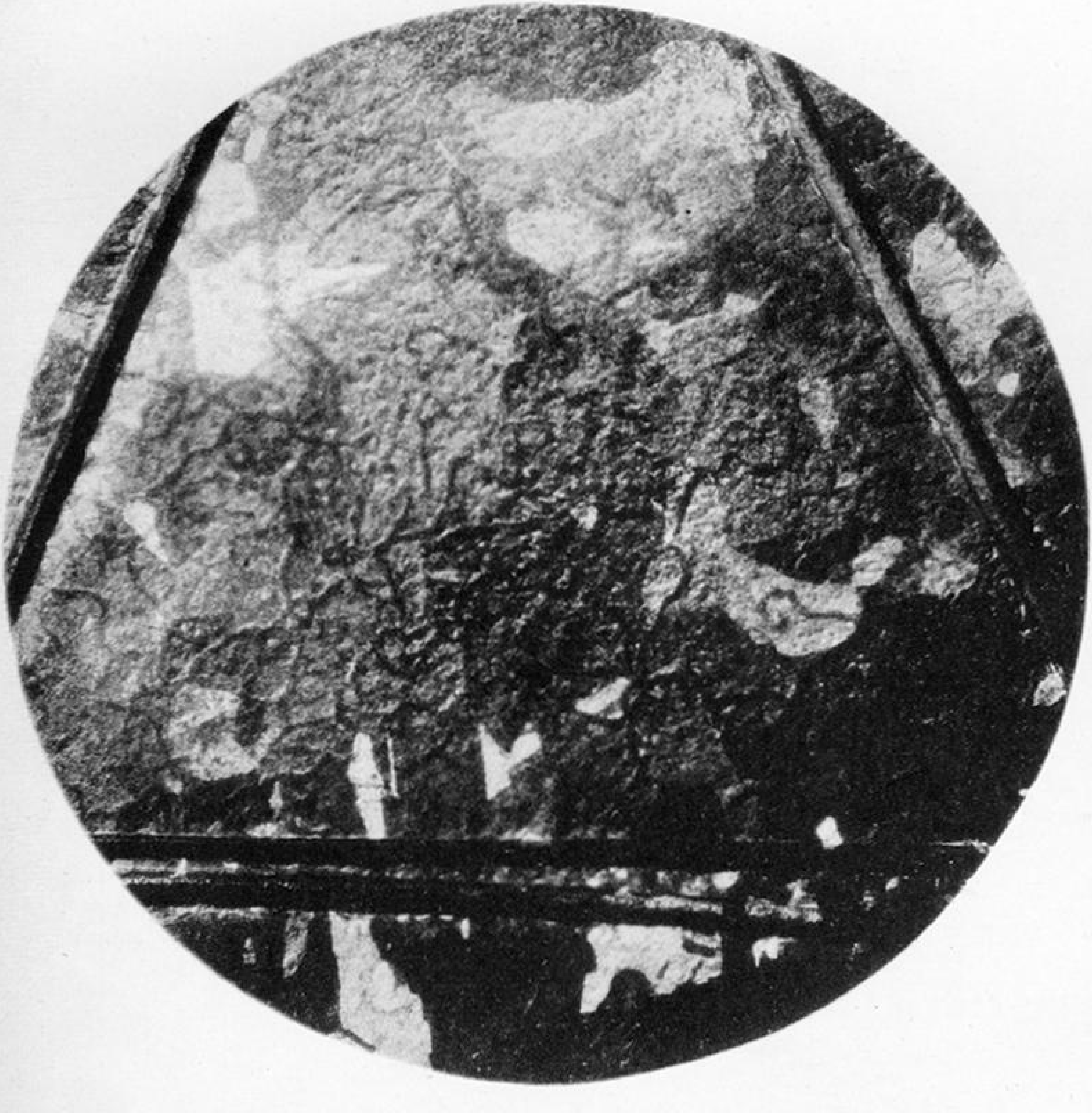

Fig 18.—Same after 4 days further at 200° C.

Fig. 19.—Sheet lead. × 12. Another part of the same specimen as Fig. 18.

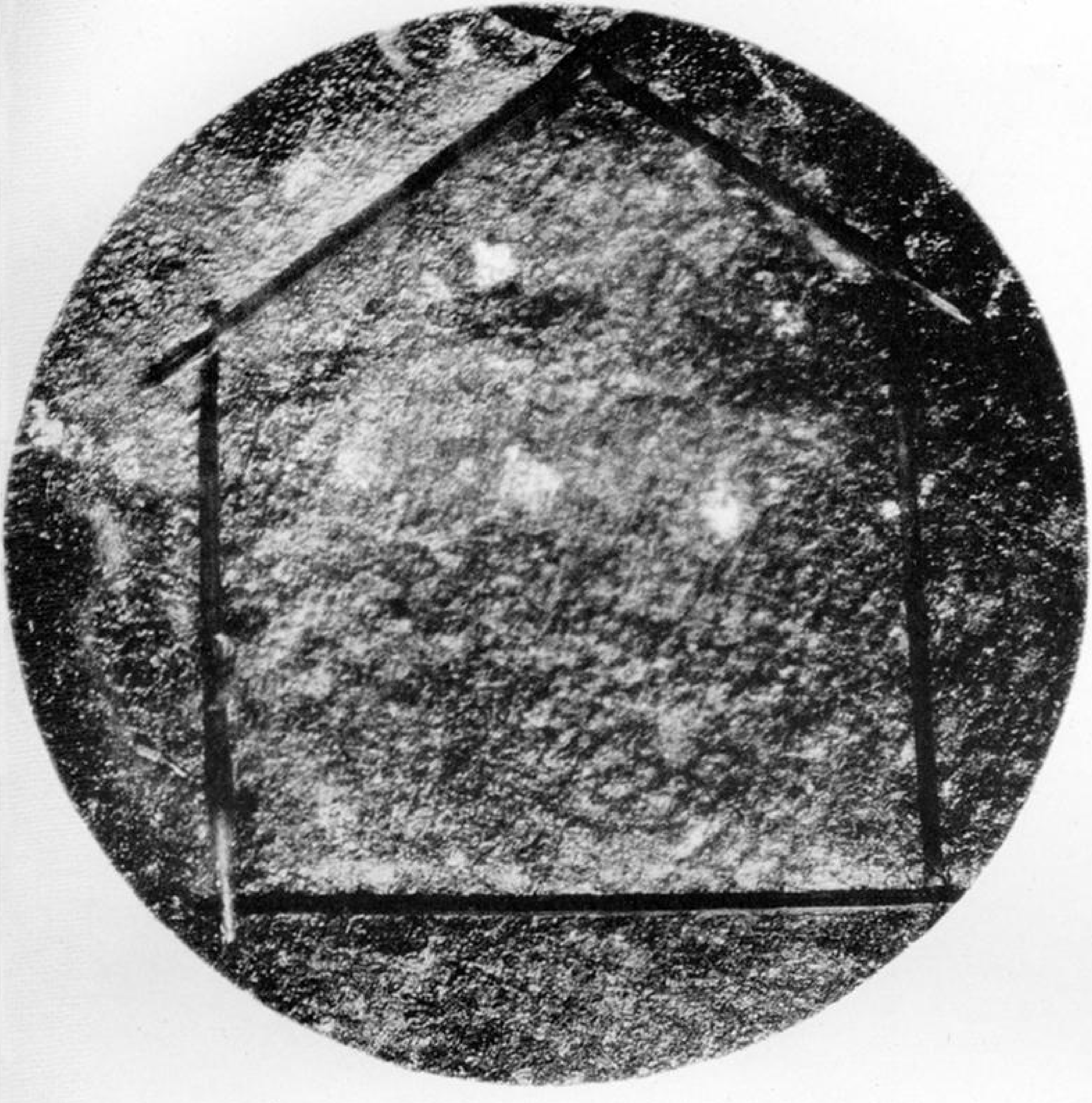

Fig. 20.—Freshly crushed lead. × 12.

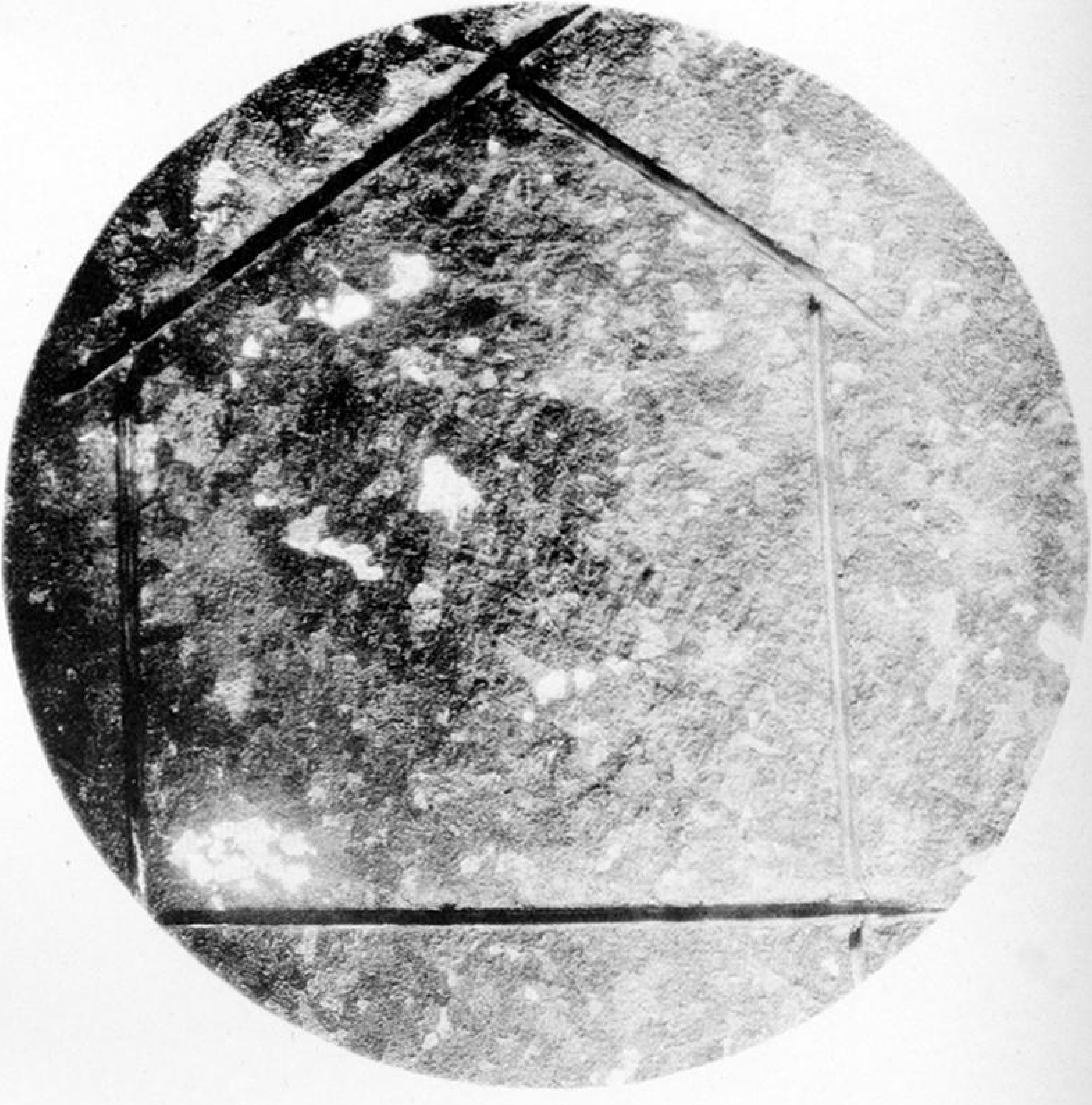

Fig. 21.—Same after $17\frac{1}{2}$ hours at 200° C.

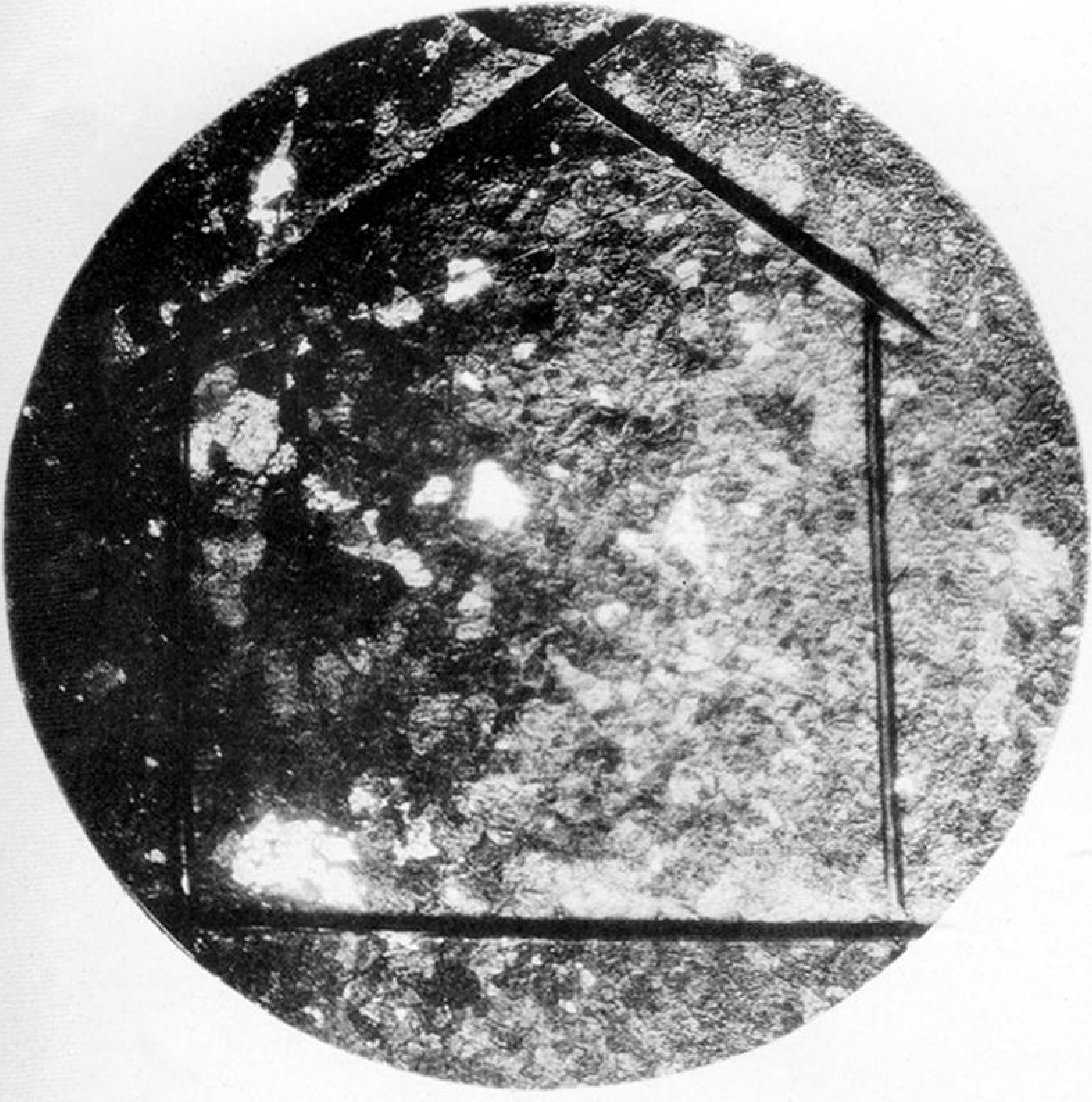

Fig. 22.—Same after 1 day 17½ hours at 200° C.

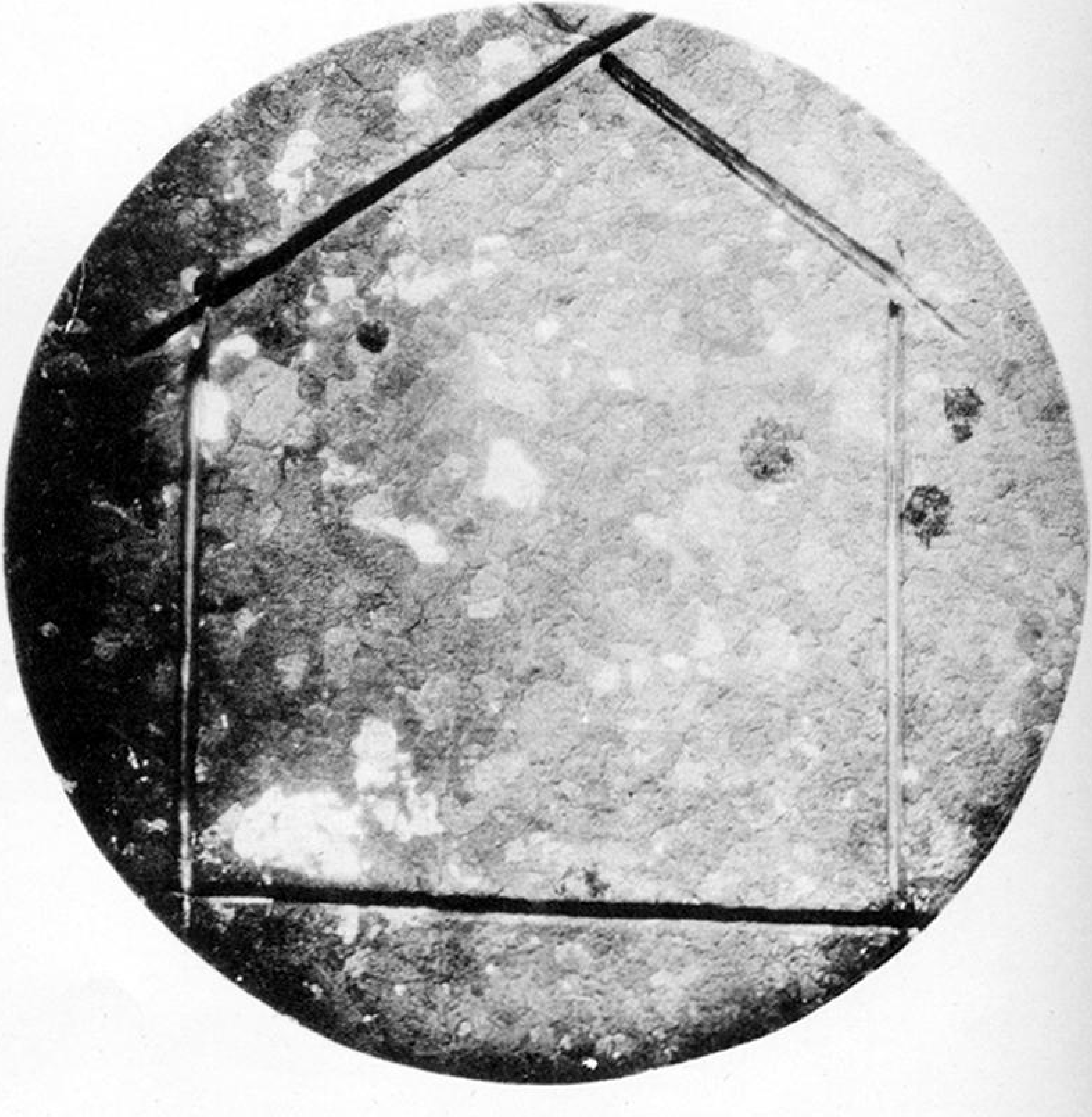

Fig. 23.—Same after 2 days 17½ hours at 200° C.

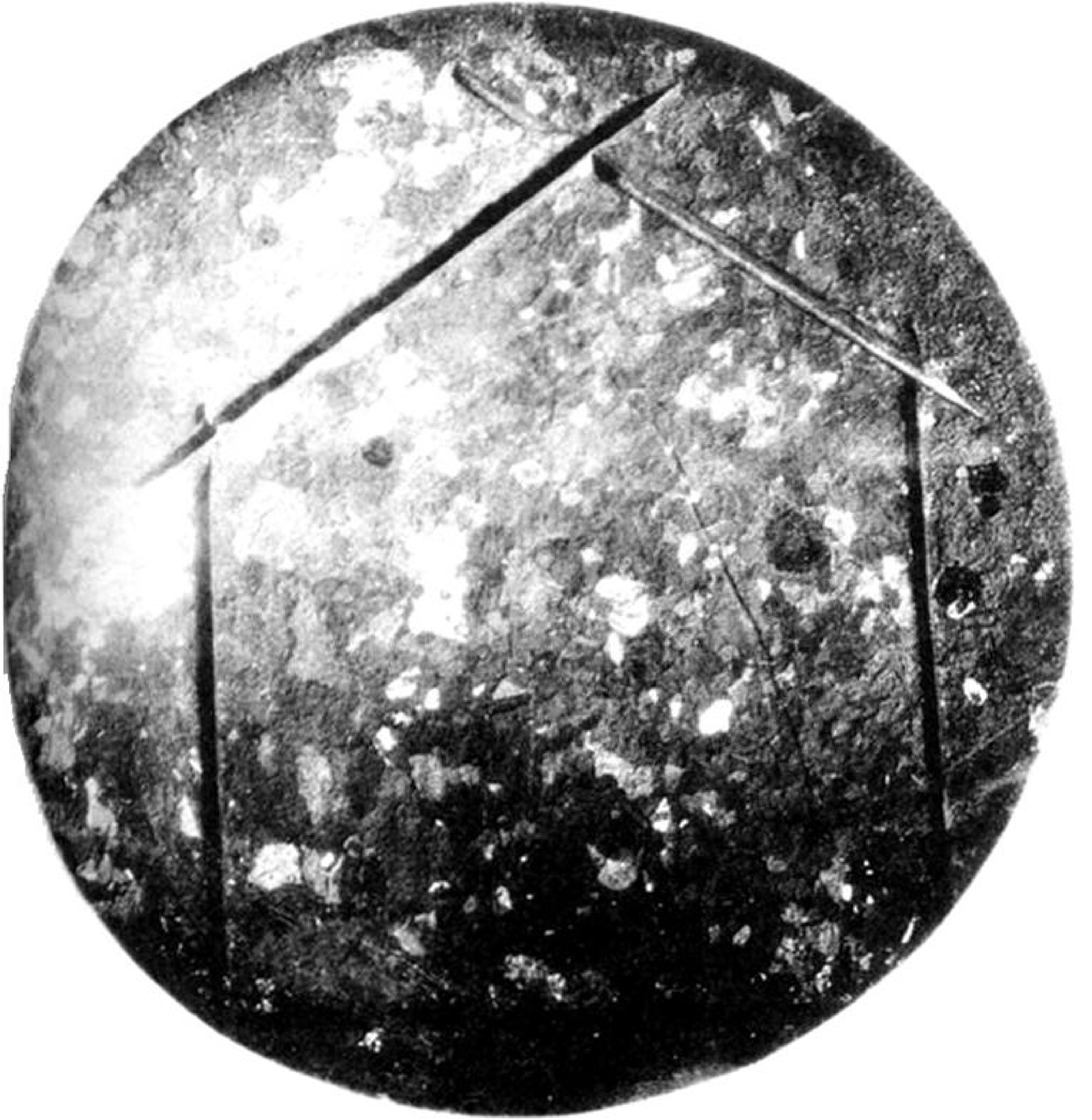

Fig. 24.—Same after 5 days 16 hours at 200° C. with incidence of light altered.

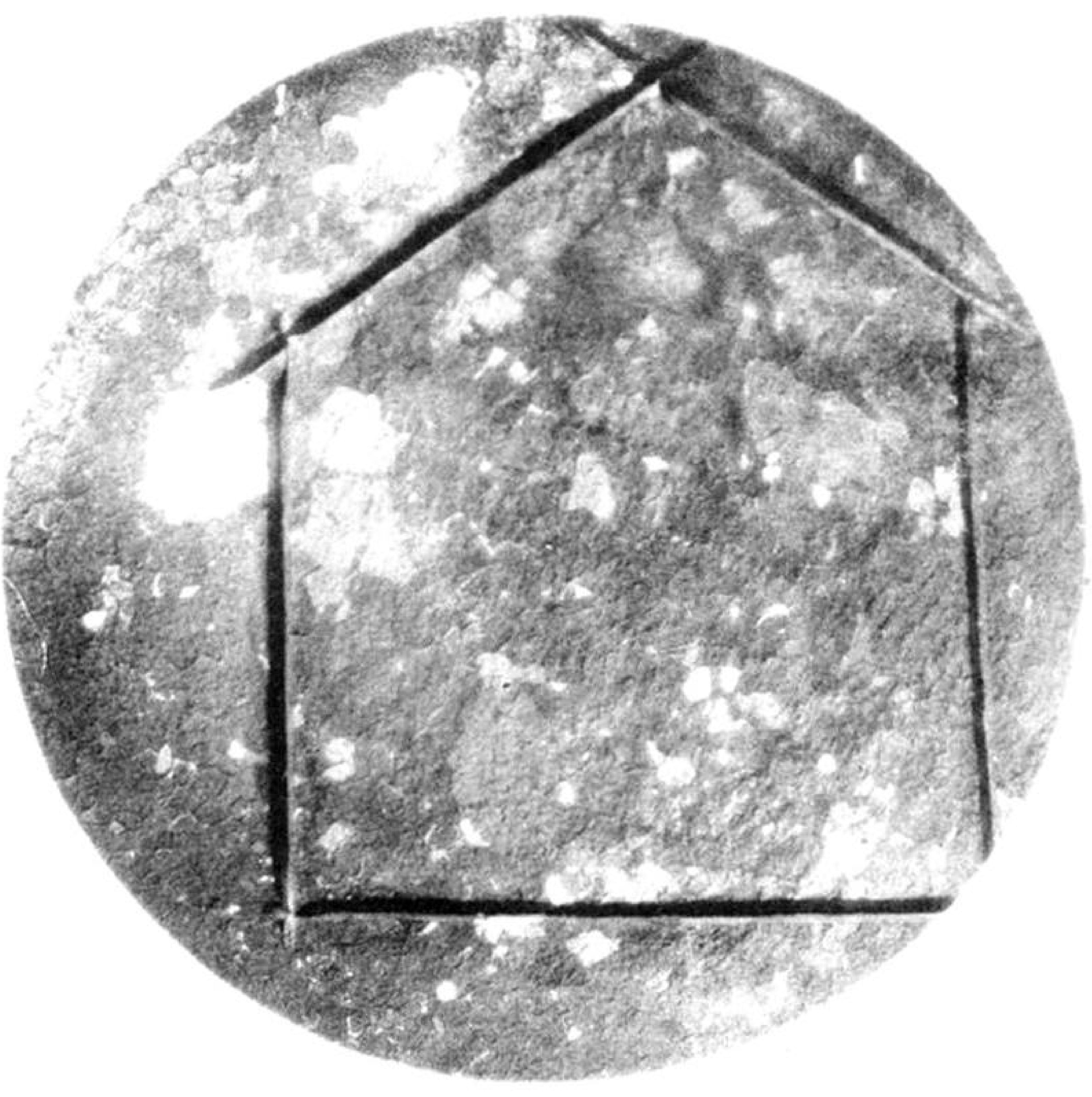

Fig. 25.—Same after 40 days at 200° C.

Fig. 26.—Same specimen as Fig. 25 (after 40 days at 200° C.) with incidence of light altered. × 8.

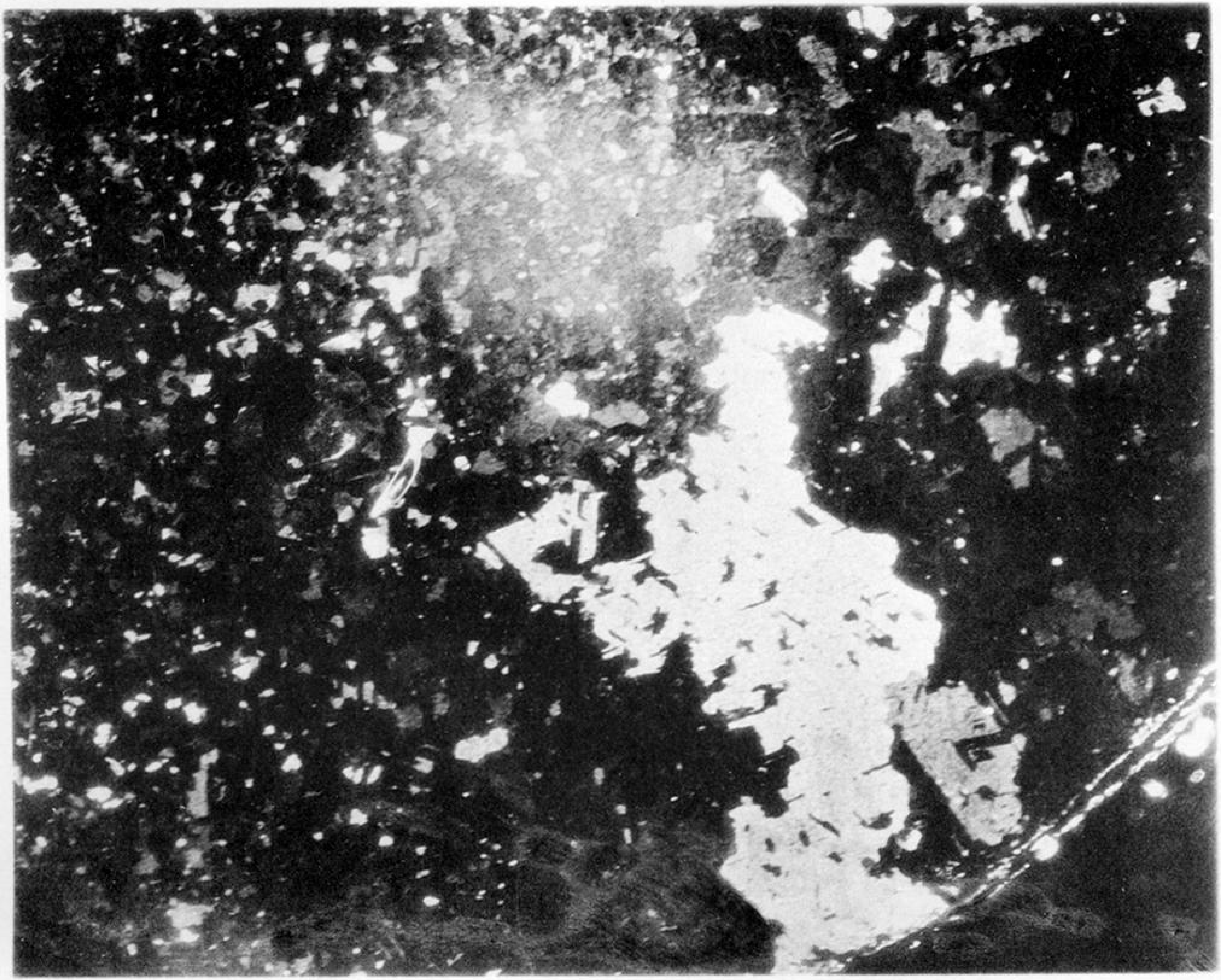

Fig. 27.—Crushed lead, after prolonged annealing. × 8.

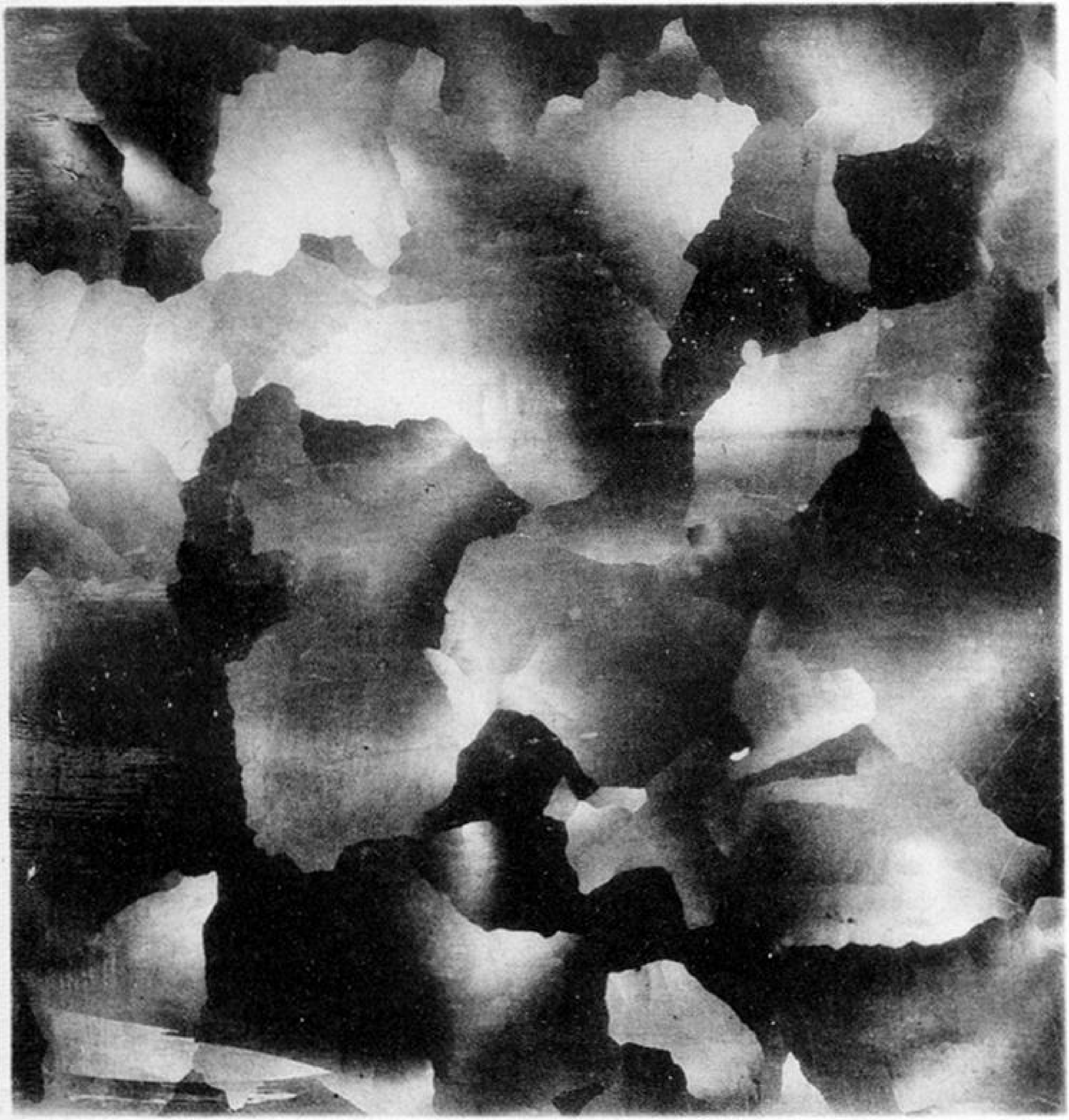

Fig. 28.—Tin-plate, etched. × ½.

Fig. 29.—Tin-plate, etched. × 100.

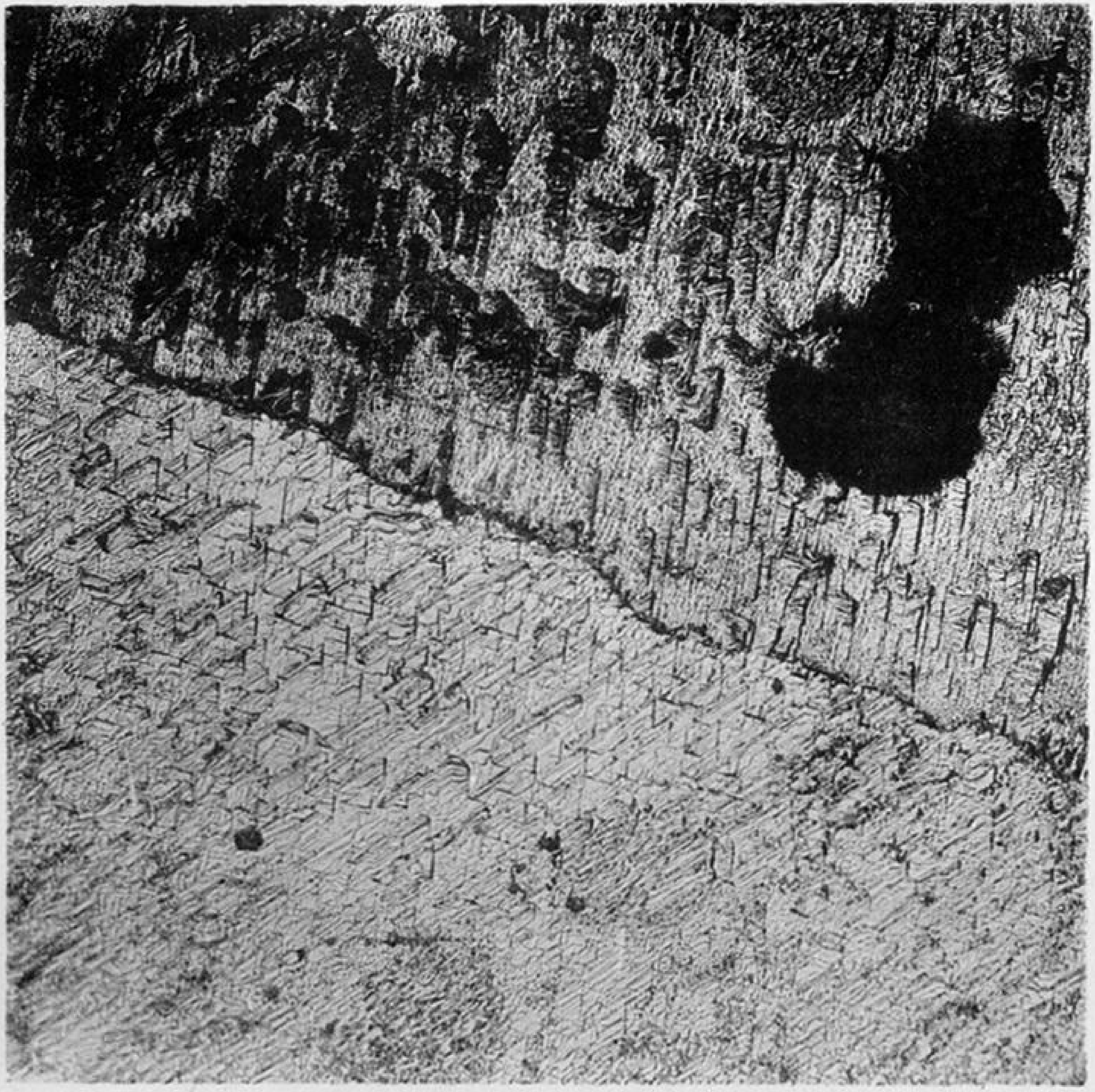

Fig. 30.—Tin-plate, etched. × 100.

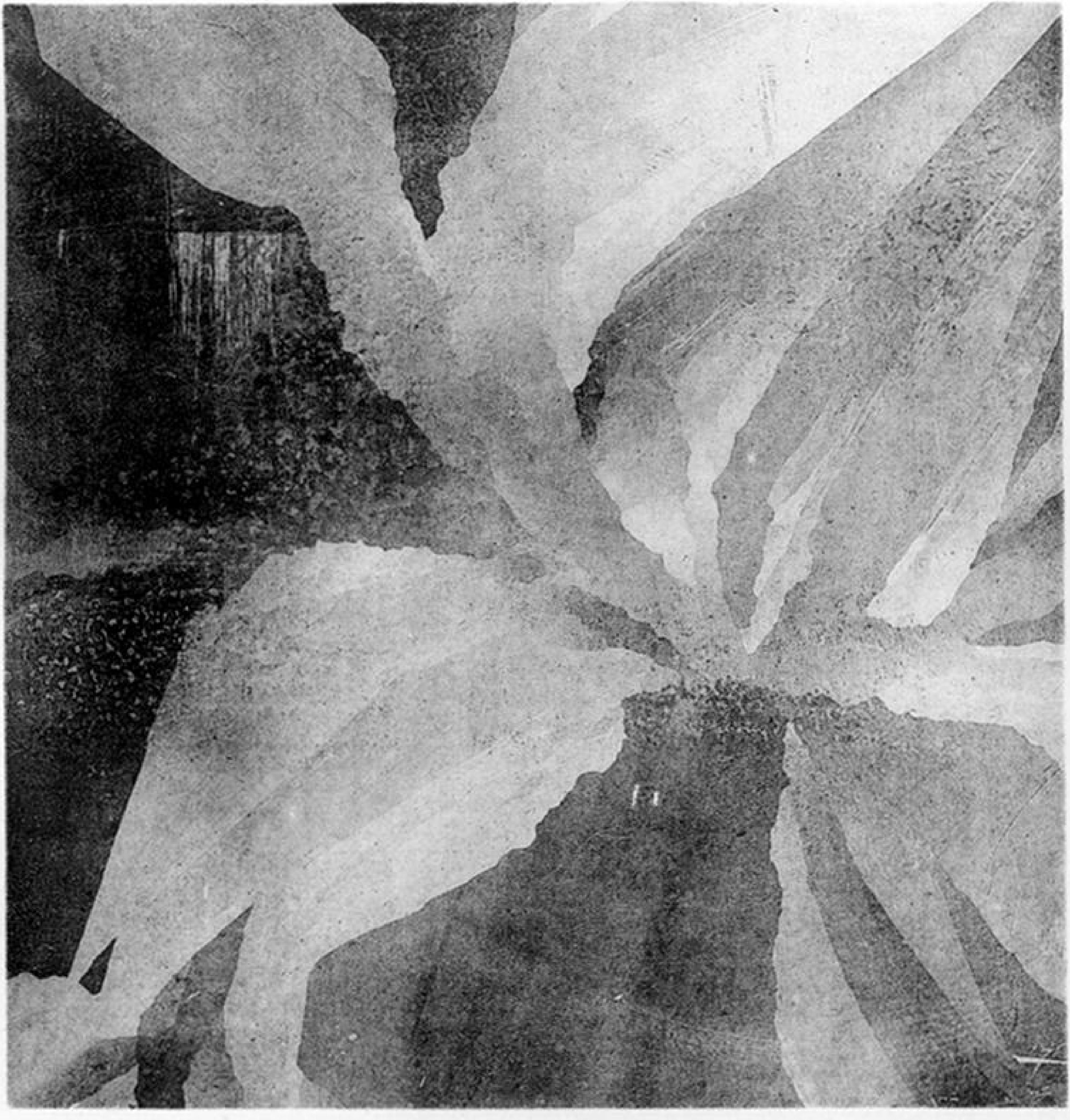

Fig 31.—Tin-plate, after re-melting the tin. × ½.

Fig. 32.—Tin-plate, after re-melting the tin and cooling quickly. × $\frac{1}{2}$.

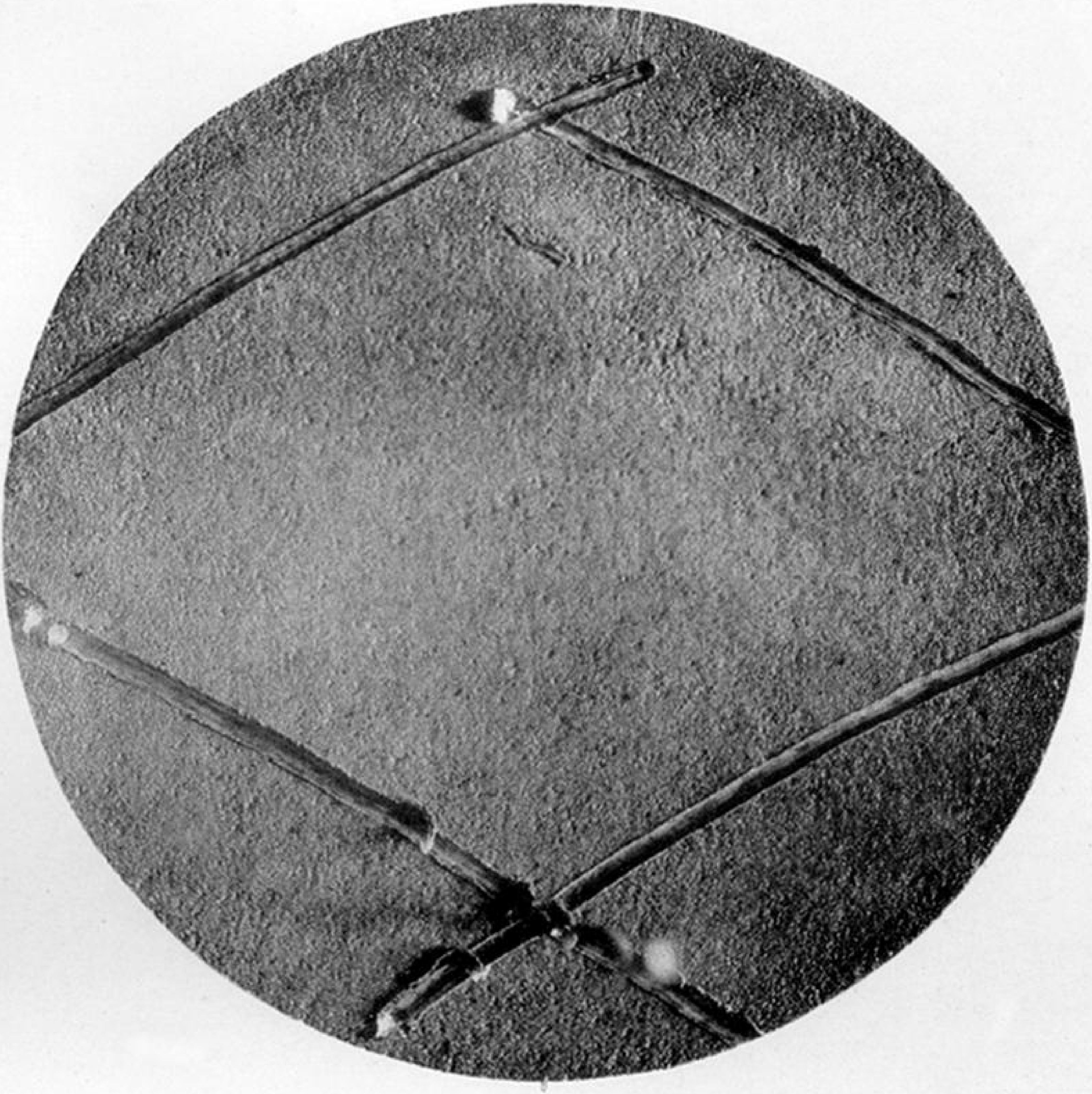

Fig. 33.—Cadmium, freshly strained. × 12.

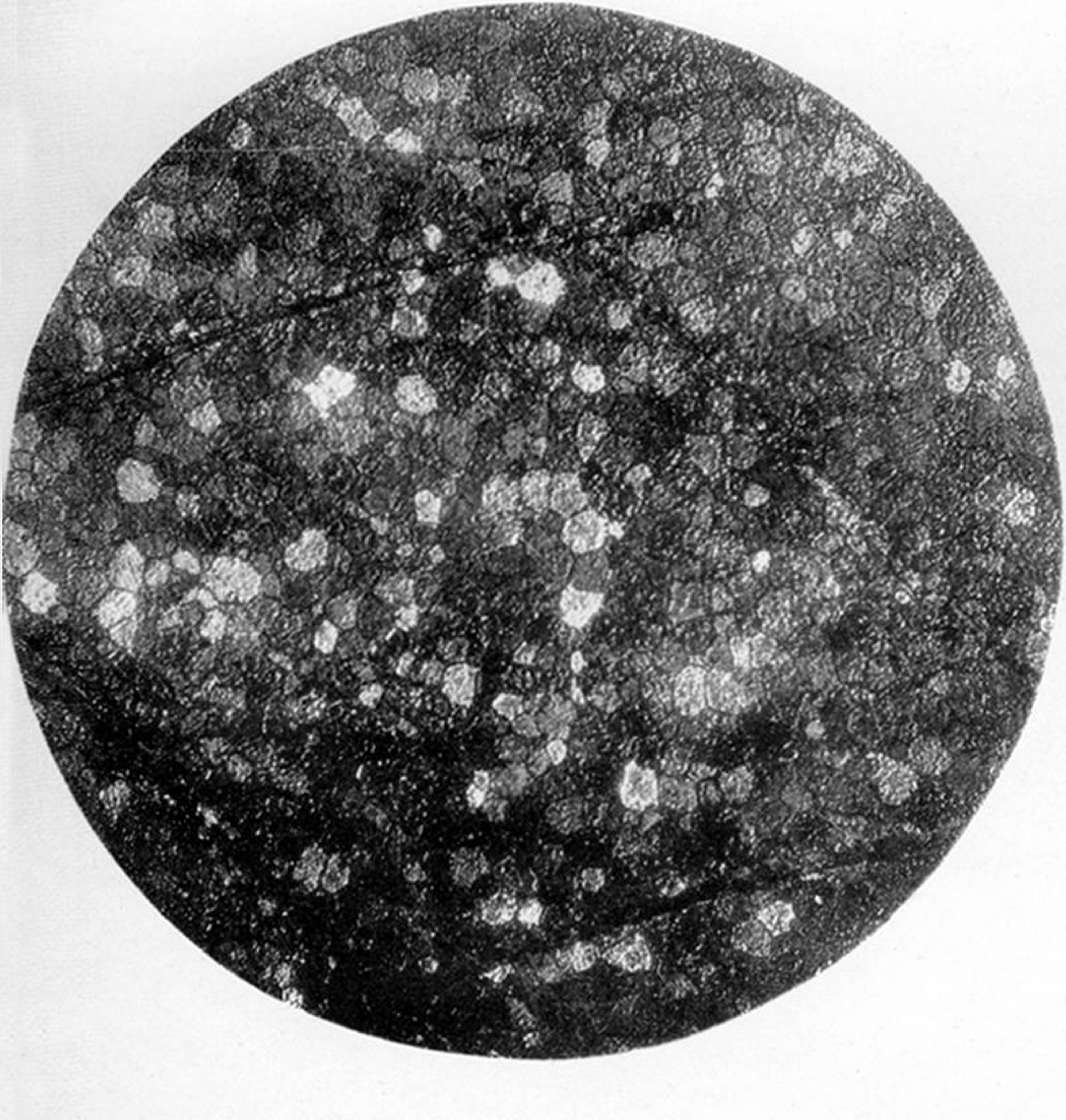

Fig. 34.—Same after 24 hours at 200° C.

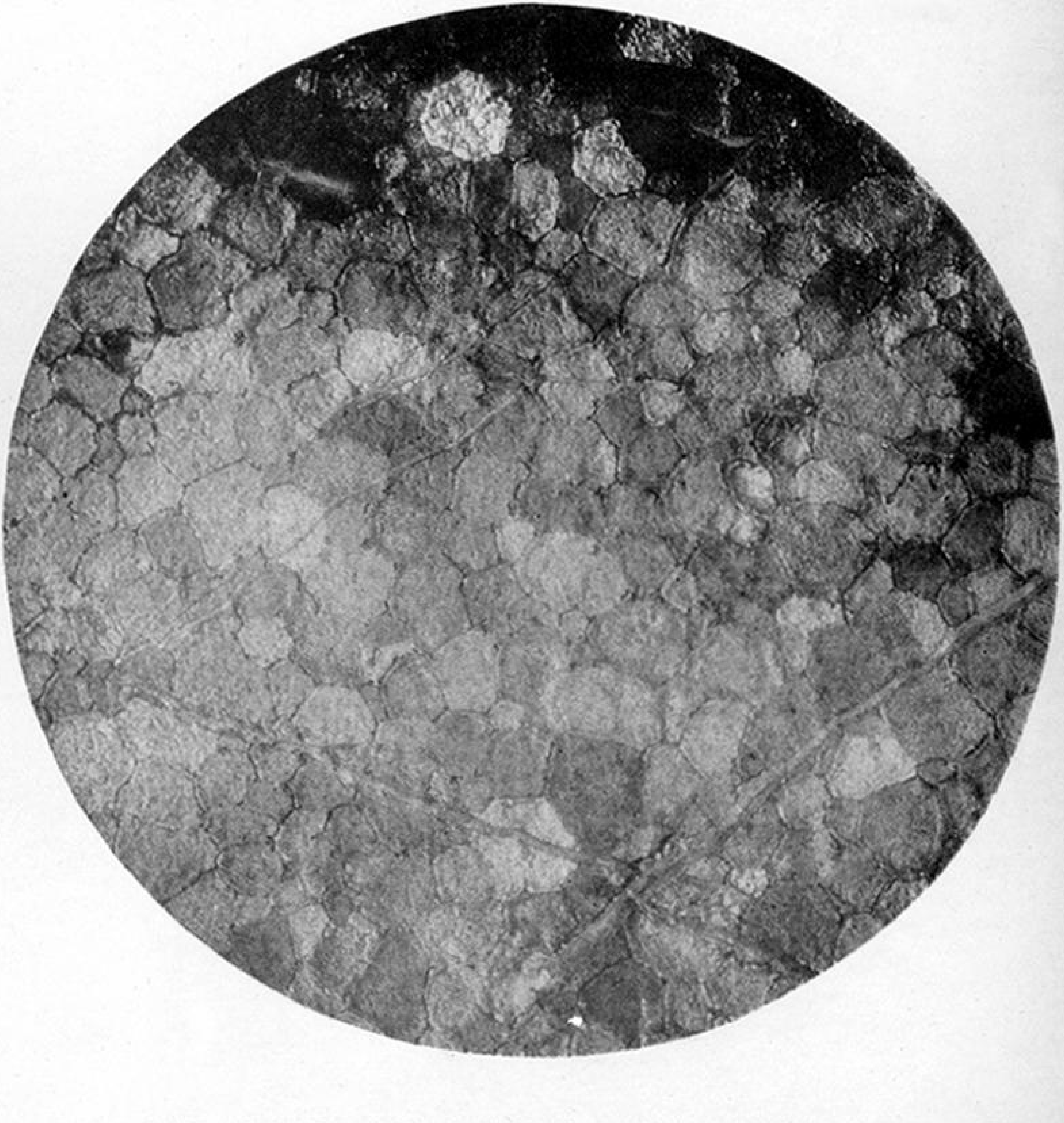

Fig. 35.—Same after seven days at 200° C.

Fig. 36.—Zinc, after heating at 200° C. × 8.

Fig. 37.—Weld in Lead. × 30.

Fig. 38.—Weld in Lead, with eutectic. × 30.