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THE EFFECTS OF RAPID COOLING UPON METALS AND ALLOYS.

PART II.



PART II. The Effect of the Rate of Cooling upon Certain Structural Features of Metals and Binary Alloys.

Introduction.

An investigation of the mechanical properties of alloys, if it is to be satisfactory, necessitates a knowledge not only of the proportions of the various constituents, but also of the degree of aggregation and the manner of distribution of these constituents after different conditions of treatment of the alloy. In this respect the investigation of Part I is deficient. The mechanical properties of a sensibly pure metal are modified by rate of cooling, mechanical distortion, and annealing ; those of an alloy are modified by the same three factors, and are changed also by a change in the proportions of the constituent metals. There are corresponding changes of structure, some of which are well known and some not so. This part of the subject is very wide, since the effects produced in different materials by the same treatment vary greatly. Accordingly the following paragraphs are devoted chiefly to a comparison of the structures of a few metals and alloys after being cooled with considerable rapidity, with the structures which are developed during a relatively slow rate of cooling, and to the changes which take place in both during short periods of annealing. It will be seen, in paragraph 16, that a chill cast eutectic may show what are effectively some primary crystals of one of its structural constituents, an unexpected feature which somewhat vitiates the calculations of Part I.

Most of the materials dealt with herein are not of importance from the engineer's point of view, but the method of experiment, a scientifically sound one, was to examine first a number of materials of relatively simple constitution and easy to manipulate, and to

proceed from these to more complex cases. The preponderance of the comparatively useless materials is merely due to the fact that the investigation as originally planned is at present far short of completion, a defect which it is intended to remedy as time becomes available.

11. The Effect of the Rate of Cooling, and of the Presence of Small Amounts of Foreign Material, upon the Size of the Grains of Nearly Pure Metals.

It has not yet been found possible to establish a definite relationship between the rate of cooling and the size of the crystal grains of a metal, partly because of the influence of other factors. Coarse crystallisation is favoured by slow cooling and absence of vibration ; agitation of the liquid metal at the freezing temperature assists greatly in the formation and distribution of nuclei, and therefore gives rise to a larger number of crystal aggregates with a consequent finer structure of the solid metal ; a rapid fall of temperature during the period of freezing often has a similar effect. The variations of structure caused by stirring, and by the introduction of nuclei into the freezing mass have not been investigated here, since they do not promise to be of industrial importance.

In a general way it may be said that as the rate of cooling is increased the grain size diminishes, but this may be due only indirectly to the change in the cooling rate. For if a mass of liquid, supposed without nuclei, is in a mould losing heat from its outer surface, crystallisation begins at the walls of the mould and spreads inwards ; each crystal aggregate assumes a pyramidal form, having its long axis approximately perpendicular to the surface of cooling. If all the heat is lost from the outer parts, and there are no nuclei within the interior mass of liquid, each tiny crystal is formed in the neighbourhood of a pre-existing one (supposing solidification already begun), to which it becomes attached. Thus, once a number of crystal grains sufficient to form a continuous crust has grown, this number is not increased during the solidification of the remaining metal ; the grains grow in size but not in number. In order that the number of grains shall be increased it is necessary

that there shall be germs within the liquid portion of the ingot. In an actual mass of metal it may easily happen that there are germs of a foreign material, or it may also happen that cooling is so irregular that the temperature falls sufficiently low at points within the mass for crystallisation to start at these positions before the inwardly growing crust has reached them. In the absence of either of these circumstances it may be possible for tiny crystals to be distributed by means of currents in the liquid mass. Of the existence of such currents there can be no question ; slight and unavoidable variations in the temperature at different parts set up convection currents, and if the liquid metal has been poured into the mould, as is usually the case, other currents, possibly very vigorous ones, are generated, and take a long time to die away altogether. The actual process of solidification appears to consist in the slight undercooling of the liquid in the immediate proximity of an existing crystal, followed by the abrupt formation of a crystal element of small but appreciable size ; the abrupt and discontinuous method of crystallisation is easily verified by simple observations. Some observers consider that the material about to crystallise becomes a drop separate from the rest of the liquid before it actually solidifies ; even if this be not so, the attachment of the new crystal to its immediate predecessor must be somewhat precarious at first. It seems not unreasonable that a relatively weak current ~~sh~~ould be sufficient to carry away the material about to crystallise, or even the newly formed crystal itself, and thus introduce a nucleus into a remote portion of the liquid mass. The more rapid the rate of cooling the stronger would be the convection currents, and the stronger also any currents set up by pouring, since a shorter time would elapse before crystallisation began ; hence more nuclei would be washed about in the mass and the number of grains would be correspondingly increased. A rather serious objection to this version

of what takes place is that, since all heat must be lost through the crust, crystallisation would still proceed in the immediate proximity of the crust and not around the new nuclei, unless these could be continually fed by a relatively cool current. It would be sufficient for the purpose, however, if certain of the new crystals, instead of being carried away from the crust, remained in its neighbourhood but were rotated through some angle by the liquid currents, and their orientation thus changed; each tiny rotated crystal would then become the starting point of a new grain.

The size of an elementary crystal <sup>(not crystal grain)</sup> formed at each step, subsequent to the first, of the discontinuous process of crystallisation depends upon the degree of undercooling of the liquid in this region; a relation which is probably approximately true <sup>at any small region of the mass</sup> after crystallisation has fully begun, is,

$$\begin{aligned} & \text{Mean number of degrees of undercooling} \times \text{mean mass of undercooled liquid} \times \text{Specific heat of liquid} \\ & = \text{Mass of new crystal} \times \text{latent heat of solidification} \end{aligned}$$

This assumes that all the undercooled material, by the solidification of a portion of it, is raised to the freezing temperature. Now rapid cooling in general increases the degree of undercooling, and therefore would seem to increase the size of the elementary crystals which build up the grains. The average size of the grains <sup>themselves</sup> depends upon the number of nuclei or original crystals formed, and the exact conditions which govern the formation of a nucleus are not known at present. A temperature below the freezing point of the metal is one condition, and when the degree of undercooling is considerable the variation of temperature throughout the mass is probably much greater than with slight undercooling, so that it is possible that the number of centres of crystallisation may diminish, and therefore the average size of grain may increase, after a certain rate of cooling is exceeded.

In attacking the subject in an experimental manner an important difficulty is due to the fact that a piece of metal has to be examined by means of sections. If the piece consisted of a number of equal polyhedra, say cubes or rhombic dodecahedra, all similarly directed, there would be a definite relation between the volume of a polyhedron, the shape and area of its cross section, and the position and direction of the plane of section ; the number of grains to a given volume could be determined from a prepared section of the piece. But in an actual piece of metal the polyhedra are unequal, they are irregular, and are oriented at random. The determination of the grain size, even as an average figure, is not then possible with accuracy. If each grain is approximately equiaxed, its volume is fairly definitely related to the area of a section taken through the centre of the grain. A section of a mass of metal cuts the grains at all kinds of distances from their respective centres, but since a central section is the largest, the size of grain is best determined from the largest polygons visible on the section. On the other hand this method ignores the possibility of a variation in the size of the grains ; it is probably <sup>better</sup> therefore to select a few of the largest polygons and average the areas of these. There is considerable probability that if the grains are of roughly equal size, are approximately equiaxed, and are directed at random, every section of a piece of metal will show about the same number of polygons to a given area, if this area is large in comparison with one of the polygons ; so that although the average area of a polygon is less than that of a central section of the average grain, it is an approximately constant fraction of the central section. The average area of a polygon would be then a measure of the grain size, and the volume of the average grain would be,

$$(\sqrt{a})^3 \times \text{constant}$$

where  $a$  is the area of the average polygon.

If the grains are not sensibly equiaxed any great degree of accuracy in the determination of the mean volume from a section is hopeless, and if they are not sensibly equal the measurement is of comparatively little use ; a preliminary examination of several sections of the same piece is therefore necessary for information on these two heads. When the grains are of considerable size , 1/10th inch or more in diameter, a number of parallel sections may be taken by repeatedly regrinding the surface of a specimen ; photographs of these parallel sections allow of reconstructing a grain or an assemblage of grains in its entirety. The writer has employed this method, but the particular examples chosen are not of interest here.

The problem of the determination of grain size is really a statistical one, and necessitates a large number of measurements before useful numerical data can be obtained. Only a few such measurements have been carried out at present, but these give promise of interesting results. A single example is sufficient here ; the subject is again dealt with briefly in paragraph 19. The section for which the data are given is that shown in Fig. 218, a narrow outer ring being excluded. The measurements were made from an enlargement of about 40 diameters. The best method of attacking the problem was, and still is, a matter of doubt. The most obvious beginning is to measure the area of each polygon ; this was done by means of a planimeter. There are 295 polygons with a total area of 161.65 square inches on the enlarged micrograph ; the mean area therefore is 0.548. The area of the largest polygon is 2.02, so that the ratio of maximum to mean is 3.69. In other examples this ratio was usually higher, lying between 4 and 5. If the number of polygons are plotted in relation to their relative area, a skew curve of error results, with a peak in the neighbourhood of 90 per cent. of the mean area ; in other cases the position of the peak varied from 40 to 80 per cent. of the mean area. This curve appears of no particular use.

Further consideration shows the necessity of drawing distinctions between the polygons. The most obvious way of distinguishing them is by the number of their sides. Thus in the present case the 295 polygons consist of 1 triangle, 26 quadrangles, 82 pentagons, 104 hexagons, 56 heptagons, 15 octagons, 8 nonagons, 1 decagon, and 2 undecagons. If these numerals are plotted against the number of sides to the polygon a fairly symmetrical curve results, with a peak at 6 sides. If the <sup>Sum of the</sup> ~~total~~ areas of each kind of polygon is plotted instead of their number the result is to give a slide to the previous curve in the direction of the larger number of sides, while leaving the position of the maximum unchanged; it is noticeable that the mean area for each group of polygons increases consistently with the number of sides. Examination of the first skew curve of error described above suggests that a better form of curve would be obtained if a linear dimension were used instead of an area; the one which suggests itself first is the maximum diameter of each polygon. The relation between the area and the square of the maximum diameter varies with the form of the polygon. For regular polygons this ratio increases with the number of sides from 0.433 for an equilateral triangle to 0.785 for a circle; the manner of variation is not continuous through odd and even sides alternately, but is slightly different according as the number of sides is odd or even. Similarly, for polygons of equal area, the length of the maximum diameter when plotted against the number of sides gives two nearly parallel straight lines, one referring to an odd, and the other to an even number of sides. When the polygons are not of regular shape the ratio between the area and the square of the maximum diameter varies considerably; for instance, in the regular four-sided polygon the ratio is 0.500, while in the 26 four-sided polygons in the example it varies from 0.33 to 0.52, with a mean value of 0.43. The problem thus involves a number of variable quantities about which no very

complete information has been yet secured.

As it appeared unlikely that a definite relation between the rate of cooling and the size of grain of a sensibly pure metal could be established at present, the study of the effect of the cooling rate was limited to the comparison of the structures found after very rapid cooling with those which originate during fairly slow cooling of a few metals. For rapid cooling, the metal, at a few degrees above its melting point, was poured into a split cylindrical cast iron mould, about  $3/8$  inch internal diameter and  $1\frac{1}{2}$  inches long, kept at atmospheric temperature. For slow cooling, the metal was first poured into a graphite mould of about the same size as the above; the mould containing the small ingot was then reheated in the gas furnace until the metal was remelted, and the whole was allowed to cool slowly. Fig. 47 is a cooling curve for the furnace. The metals employed were antimony, bismuth, cadmium, tin, and zinc. <sup>Transverse</sup> Sections were cut from the small ingots and photographed entire, with a uniform magnification of  $7\frac{1}{2}$  diameters, under oblique illumination, which more readily differentiates <sup>the</sup> grains than vertical illumination. A glance at Figs. 48 to 57 gives one an idea of the great differences in the manner of crystallisation of different metals subjected to similar treatment.

As regards the chill cast metals, antimony, bismuth, and zinc, Figs. 48, 50, and 56, show columnar crystals passing radially from the periphery to the centre of the piece. In the case of tin, Fig. 54, the columnar crystals do not quite reach the centre, a small middle region being occupied by a few grains which appear approximately equiaxed; an increase in the diameter of the mould would have exhibited this feature more clearly. The case of cadmium, Fig. 52, is remarkable, the radiating crystals at the periphery being extremely small and penetrating only a short way inwards; the greater part of the area of the section is occupied by small grains, approx-

imately equiaxed. The temperature of pouring the chill cast metals can be varied considerably without causing appreciable change of structure ; Figs. 58 and 59 show the appearance of bismuth and of tin poured at a temperature of  $750^{\circ}$  C.

Among the slowly cooled metals, bismuth, tin, and zinc, Figs. 51, 55, and 57, exhibit a very coarse crystallisation, the whole cross section showing only two grains in the case of bismuth, and possibly three for tin. The structure of the slowly cooled cadmium, Fig. 53, is similar to that of the quickly cooled sample, but is somewhat coarser. The slowly cooled antimony, Fig. 49, presents a relatively fine structure also, though the individual units are difficult to distinguish clearly in the photograph.

The metals employed above, though sold as pure, contain small amounts of various impurities. It is of interest to examine the effects of different impurities upon the structure of the chill cast and the slowly cooled metals. For this purpose the amount of impurity added was fixed at 2 per cent., and ingots were prepared of bismuth, cadmium, and tin, containing 2 per cent. each of four of the metals antimony, bismuth, cadmium, tin, and zinc, except that the tin-antimony <sup>mixture</sup> was omitted inadvertently.

Dealing first with bismuth, in the chill cast alloys the transverse dimension of the pyramidal grains is but little altered by the addition of 2 per cent. of zinc, Fig. 66, but is considerably reduced by antimony, cadmium, and tin, Figs. 60, 62, and 64. In the case of the ingot containing cadmium, Fig. 62, the pyramidal grains do not reach the centre, but in the other three cases they do so. As regards the slowly cooled ingots, the size of the grains is not reduced by antimony, tin, and zinc, Figs. 61, 65, and 67, but is somewhat reduced by cadmium, Fig. 63.

In the ingots of cadmium the scale of the structure of the chill cast metal is somewhat reduced by tin and zinc, Figs. 72 and 74, but

that of the slowly cooled metal is sensibly unaltered by these impurities, Figs 73 and 75. On the contrary, antimony and bismuth considerably increase the size of the grains of the chill cast cadmium; Figs. 68 and 70 show radiating crystals at the periphery, but in each case most of the section is occupied by nearly equiaxed polygons. The slowly cooled mixture containing bismuth, Fig. 71, is hardly coarser than the chill cast one ; but the slowly cooled cadmium-antimony alloy has much larger grains than when chilled, Fig. 69.

Figs. 76 to 81 show that for tin the size of neither the chill cast nor the slowly cooled grains is much changed by bismuth, cadmium, or zinc.

The effect of small quantities of one metal upon the grain size of another, with similar conditions of treatment, does not lend itself to classification so far as the few experiments above are concerned. The point seems worth further study, and the experiments are being continued with other metals.

12. The Size of the Primary Grains in a Binary Alloy, as affected by the Composition of the Alloy and by the Rate of Cooling.

The size of the primary crystal grains in an alloy is affected by the fact that the composition of the primary solid material is usually different from that of the liquid, and that there is a more or less extended interval of temperature during which crystallisation proceeds. The difference in composition between the solid and liquid portions of the mixture has the effect of temporarily depriving the liquid of crystallising material in the immediate neighbourhood of the newly formed crystals. Any currents in the liquid tend to equalise its composition, and the varying density caused by varying composition is in itself capable of generating feeble currents. If the currents do not bring sufficient new material forward to the existing crystals to supply the heat lost in radiation, &c., by means of the latent heat rendered available during the formation of new crystals, the temperature of the mass will fall until it is so low that a nucleus appears elsewhere, in a richer part of the liquid solution.

When the composition of the alloy is altered, in such a way that there is less of the primary structural constituent, the difficulty of supplying material for the growth of the primary crystals increases ; these crystals therefore become smaller, partly because there is less material to crystallise, and partly because the increased difficulty of diffusion leads to the formation of a greater number of nuclei. In an alloy of two structural constituents the primary crystals are not completely filled in, but retain to a greater or less extent their original skeleton form ; the determination of grain size in such a case can be interpreted only as the determination of the lengths of the axes of the grains. Sometimes a section suggests that small grains originating at separate nuclei

have become loosely strung together into a skeleton form, by their partial rotation in the liquid under the action of forces of crystallisation ; there is no direct evidence of such a rotation, but the primary crystals of an alloy poor in primary material are not infrequently of greater axial length than those of a richer alloy.

To illustrate the change in the size of the primary grains choice has been made of the bismuth-tin alloys containing more than 56 per cent. of bismuth, the composition of the eutectic of the series. The crystals of bismuth assume compact forms, of which the size is more easily apprehended by the eye than when the section shows interlacing dendrites. On account of the large size of the crystals <sup>of bismuth</sup> in slowly cooled alloys, the particular samples taken have been chill cast. Figs. 82 to 87 require no explanation to elucidate the continuous diminution in the size of the primary grains as the proportion of bismuth is diminished.

In a rapidly cooled alloy, crystal skeletons, when present, have branches which are thinner and less developed than when the alloy is cooled slowly, and this is the case whether the proportion of primary material is large or small. Numerous examples could be given, but a few will suffice. In Figs. 88 and 89, taken from an alloy containing 85 per cent. of copper and 15 per cent. of lead, there is a large proportion of the primary material, nearly pure copper ; the numerous small skeleton branches to be seen in the chill cast alloy are in striking contrast with the large ones of the slowly cooled mixture. Fig. 90, a slowly cooled bismuth-tin mixture containing 25 per cent. of tin, may be compared with Fig. 86, the same alloy when chill cast ; although the magnifications of the two micrographs are different, it is easily seen that the primary crystals in the slowly cooled mixture are enormously greater than in the quickly cooled one. In Figs. 91 and 92, taken from an alloy containing 25 per cent. of copper and 75 per cent. of bismuth, the primary material

is not very abundant ; the rate of cooling of the two pieces was not so greatly different as in the previous cases, and the difference in the development of the crystal skeletons of copper, though distinct, is not so striking.

### 13. Examples of the Varying Composition of the Primary Grains of a Solid Solution.

There is no need to dilate here upon the gradually varying composition of each crystal skeleton of a solid solution, from its centre to its periphery, when the rate of cooling is not excessively slow, since it has been dealt with quantitatively in Part I. A few examples of the corresponding type of structure, mentioned in paragraph 1, are given for the sake of illustration.

Fig. 93 shows a case in which the degree of solubility is very small, but the width of the light bismuth-rich network is evidence that bismuth is soluble in copper to an appreciable extent, probably about 0.5 per cent. Fig. 94, a lightly repolished and more highly magnified section of the same specimen, shows distinctly the fine network and the small globules of bismuth not held in solution. In Fig. 95 the degree of solubility is greater than in the last case ; the bright specks of undissolved silver are readily distinguished from the half-tone network of the silver-rich solution, which is itself rather sharply delineated from the dark copper-rich cores. Fig. 96 illustrates a case in which the degree of solubility is considerable ; the alloy would become a uniform solution if suitably annealed.

#### 14. Advantages of Rapid Cooling in Reducing Segregation.

One very useful effect of rapidly cooling certain alloys is the prevention of the gravitational separation of the constituents. During the period of partial solidification, if the density of the liquid differs from that of the primary crystals, these will tend either to float or to sink, more particularly when the rate of cooling is slow and when the primary crystals have simple forms with smooth surfaces. The alloys of antimony with lead and with tin furnish good examples. In Figs. 97 to 100 the flotation of the antimony-rich crystals in the slowly cooled alloys, and its prevention by rapid cooling are very evident. The method of casting white metal bearings is partly regulated by this fact. Fig. 139 similarly shows that the bismuth crystals sink to the bottom of a bismuth-tin alloy.

In alloys where the primary crystals take complex skeleton forms these become entangled with each other, and form a more or less complete network throughout the partially liquid mass, so that gravitational separation is largely prevented. The prevention is more complete with rapid cooling, as, for instance, in Fig. 101, a copper-lead alloy, where slow cooling would have permitted much of the liquid lead, now entangled among the skeleton branches of the copper and distributed with fair uniformity, to have collected at the bottom of the ingot. The smaller scale of the structure of rapidly cooled alloys when compared with slowly cooled ones necessitates, in cases where there are two structural constituents, a more uniform distribution of these constituents. Rapid cooling also permits of satisfactory castings of alloys in which, when slowly cooled, two separate liquid layers are formed; Fig. 101 is an example.

## 15. Traces of Fluid Currents retained by Solid Alloys.

When liquid metal is poured into a mould vigorous currents are set up ; if, as is usual, solidification is completed soon after pouring, the crystal skeletons may be deformed, their branches lying along the various streams, so that distinct indications of the fluid motion may be visible on the section of a casting. In Fig. 102 several small eddies can be detected, and one of these is shown more highly magnified in Fig. 103. With a somewhat slower rate of cooling the larger currents break up into smaller vortices, each consisting of a number of currents taking closed paths about a common centre, or arranged spirally ; they are reinforced or modified by convection currents due to local differences of temperature. These vortices virtually divide the liquid metal into a number of closed cells, the number of which may be increased by fission. The cellular structure developed in the liquid is often retained more or less perfectly by the solid. As the liquid approaches the point of solidification it becomes more viscous. The increased viscosity renders the eddies more stable - that is, it tends to prevent their division into smaller ones - but at the same time causes more rapid dissipation of energy, and tends to damp out the currents altogether. On the other hand, any viscosity of the liquid hinders the re-arrangement of molecules necessary to crystallisation. The resultant structure of the solid is thus determined partly by the forces of crystallisation, and partly by the system of circulation within the liquid. Generally speaking, the crystalline forces have the more powerful effect, but the opposite case is illustrated by Fig. 104, which represents the surface of a piece of zinc-iron alloy taken from a galvanising bath ; the details of the surface structure here suggest very strongly that the formation seen is due to eddies. The surface layer, about  $\frac{1}{2}$  inch thick, can be easily broken by the fingers along the boundaries of

the cells ; below the surface layer the structure is different, and the alloy is very friable. Unfortunately, this particular alloy experienced a recrystallisation after complete solidification, so that no traces of the closed currents within the cells could be found.

The evolution of gas within a solidifying mass of metal may give rise to local curvature of the crystal skeletons. Fig. 105 shows an apparent eddy in a silver-copper alloy ; there were several of these in the specimen, and regrinding the surface showed a number of small blowholes occupying positions beneath the apparent eddies. Fig. 106 shows a curious hollow primary crystal, and above it a much bent primary skeleton, in a copper-arsenic alloy which when liquid was freely evolving arsenic vapour.

16. The Effect of the Rate of Cooling upon the Structure of Binary Eutectics and of Eutectiferous Alloys.

The case of an eutectic alloy is similar to that of a pure metal in so far as solidification is completed at constant temperature. The liquid again crystallises from centres as a number of independent grains of irregular shape, but, instead of being formed of a single substance, each grain is a mixture of two different kinds of crystals in a relatively fine state of division. When these two substances are present in not very unequal proportions, a section of the eutectic appears divided into a number of irregular areas, and each of these shows bands, more or less curved, of the two constituents; the boundaries of the irregular areas are defined by the abrupt change in the direction of the bands on neighbouring grains, Fig. 107. If the volume of one constituent is much in excess of that of the other, the eutectic consists of a ground mass of the more abundant substance having in it bars and globules, or even small geometric crystals, of the other, Fig. 108.

An etched section of an eutectic mixture frequently shows no recognisable traces of regular crystalline orientation; when definite geometrical arrangements are found they indicate the predominance of the crystalline forces of one metal over those of the other metal. Desch and others have observed that a strongly crystalline metal, like bismuth or antimony, is apt to impress its own form upon an eutectic in which it is present. Each small particle of such a metal may take a form approximating to its usual crystal habit, or a group of such particles may arrange themselves as a crystal skeleton, and the second constituent of the eutectic merely fills the interstices. Thus, in Fig. 109, a section of the eutectic mixture of antimony and  $\text{SbCu}_2$ , the metal has assumed its ordinary crystalline form, while the compound acts as a filling material.

Casual inspection of this micrograph does not reveal whether the antimony or the compound has determined the form of crystallisation, since the small areas of both constituents have approximately the same triangular shape, and both are strongly crystalline substances. Examination of sections in which primary crystals of one or other of these bodies is present, however, shows that the ~~angular~~ extremities of antimony crystals are usually quite sharply angular, while those of  $\text{SbCu}_2$  are irregular and have no definite geometric form, so that the antimony is to be held responsible for the arrangement of the eutectic. Fig. 110 shows a common appearance in the bismuth-tin eutectic, the labyrinthine skeleton crystal being due to the predominating influence of the bismuth ; as in the previous case, the constituent which acts merely as a filling material, here the tin, may be compelled to assume pseudomorphic forms, Figs. 111 and 147.

In some cases the radiate appearance of eutectic grains is strikingly evident. In Fig. 112, a low-power photograph of the bottom part of an ingot of bismuth-tin eutectic, a few radiating grains may be seen, but examination under a higher power, Fig. 113, shows that the arrangement is ~~often~~ <sup>usually</sup> not a truly radiate one, but a skeleton crystallisation of bismuth. A truly radiate appearance has been noticed by Rosenhain and Tucker in the lead-tin eutectic, and the writer has found a somewhat similar arrangement on an ingot of pure tin, Fig. 114. A dendritic type of structure is to be found in many eutectics, but the outlines resemble more those of a feather than a fern, the branches being usually curved, Figs. 115, 116, and 117. In some cases the inclination of the branches to the central axis is indefinite, Figs. 118, 119, and 120, but in others it is approximately constant along the length of each dendrite, Figs. 121 and 122, suggesting that the form of growth is the result of the combined crystalline forces of the two materials which are solidifying together, or that the ~~axes of the skeleton~~ <sup>branches</sup> of the predominating

constituent are modified by the difficulty of securing crystallising material, and become curved, just as in the case of hoar-frost upon a window-pane. Whatever are the usual arrangements of the eutectic structure they do not seem to be much affected by the presence of primary crystals of either constituent.

Sections of some slowly cooled eutectics suggest that gravity may be an important cause of segregation even in completely liquid alloys. If the constituent metals are present in closely accurate eutectic proportions it is quite common to find primary crystals of the heavier constituent at the bottom of the ingot and primary crystals of the lighter constituent at the top, separated by an intermediate layer of pure eutectic. Thus, in Fig. 116, there are copper-rich primary crystals at the top, arsenic-rich ones at the bottom, and feathery dendrites of eutectic in the middle. In Fig. 112 some small crystals of bismuth can be seen, and the top of this ingot showed dendrites of tin. This effect, perhaps, is not to be ascribed entirely to a varying composition of the liquid mixture, since if cooling is slow many of the small solid particles unite to form larger ones, and these may float or sink in the liquid portion of the mixture; an example of such enlarged crystals is given in Fig. 123, where a dendrite of tin is in contact with a grain of bismuth. If, however, the action were entirely of this latter kind one would expect to find a few relatively large crystals of both constituents in the middle region of the ingot, but this is seldom the case.

The effect of rapid cooling upon the structure of an eutectic is usually twofold; there is first a development of the columnar type of formation, and secondly a more or less radical change in the distribution of the constituents. The radiating columnar crystals are seen to advantage in the chill cast eutectic of antimony and

$\text{SbCu}_2$ , Fig. 124. In this example the redistribution of the constituents is not much in evidence, but a few isolated skeletons of antimony may be detected in Fig. 124. Fig. 125 shows two such crystals to a larger scale ; they are embedded in a matrix of eutectic of much finer structure than that of the slowly cooled mixture, Fig. 120. The presence of these crystals of antimony might be merely an indication that the proportions of the mixture were not truly those of the eutectic. The same kind of result, however, is obtained with other eutectic alloys. For instance, the chill cast lead-antimony eutectic shows, in a ground mass of ill defined structure, a considerable proportion of lead skeletons, Fig. 126, more than would be accounted for by any probable inaccuracy in the proportions of the mixture. Similarly the chilled bismuth-tin eutectic shows skeletons of tin.

It is of some interest, therefore, to examine the effect upon the appearance of the chill cast alloy when the proportions of the constituents are varied somewhat to one side and to the other of the eutectic composition. A further point of interest is the effect of varying the temperature at which the molten mixture is poured into the mould. Some experiments on these lines were carried out with bismuth-tin alloys ; the mixtures were poured from three different temperatures,  $160^\circ$ ,  $300^\circ$ , and  $750^\circ$  C. ; the mould used was that described in paragraph 11.

The bismuth-tin eutectic contains about 56 per cent. of bismuth. Types of structure commonly to be seen upon sections of the slowly cooled mixture have been shown already in Figs. 107, 110, 121, and 122. Fig. 127 is from the middle of the slowly ingot which was afterwards remelted and used for the chilling experiments. Fig. 128 represents the centre of an ingot of this mixture when chilled from  $160^\circ$  ; the structure is on the whole coarser than that of the slowly cooled eutectic, well developed crystals of bismuth being found in

contact with skeletons of tin, while parts show a finer and laminated structure. At the edge of the ingot, Fig. 129, where the metal was in contact with the cold mould and the rapidity of cooling therefore greater, the general structure is finer than in the centre, but it is to be noticed that the dark skeletons of tin are relatively much more developed than the bismuth crystals, and are even larger as a rule than the tin skeletons at the centre. In this and succeeding sections the edge of the ingot is at the extreme right. When the pouring temperature is raised to  $300^{\circ}$  the tin skeletons show a more extended axial development, while the bismuth crystals disappear, Fig. 130 ; at the edge of the piece the dark skeletons grow chiefly in a direction approximately at right angles to the cooling surface, Fig. 131. When the pouring temperature is raised to  $750^{\circ}$  the structure approximates more nearly to that of the slowly cooled alloy. Fig. 132 shows one crystal of bismuth and a few skeletons of tin, but on the whole the constituents are well mixed ; the outer edge of the piece, Fig. 133, is not very different. These results seem to show that the more rapid the rate of cooling the greater is the development of the tin skeletons, and the more complete is the suppression of the larger crystals of bismuth. Heating the metal to a high temperature before pouring is equivalent to heating the mould and reducing the rate of cooling, but it does not follow that the lowest pouring temperature gives the most rapid rate of cooling ; on the contrary, it is probable that as the pouring temperature is raised above the freezing point of the metal the rate of cooling is at first more rapid, and that there is a more or less well defined pouring temperature which gives a maximum rate of cooling, this temperature varying with the nature of the mould and the condition of its surface. No attempt has been made to determine such a pouring temperature, but it is noticeable in the present series of alloys that those poured at  $300^{\circ}$  seem to have had their periphery more drastically chilled

than those poured at either  $160^{\circ}$  or at  $750^{\circ}$ .

Corroborative evidence of the preferential crystallisation of tin in these alloys is furnished by other mixtures ; some containing more than 56 per cent. of bismuth will be examined first. Fig. 134 Shows the fine eutectic structure of the centre of a slowly cooled ingot containing 60 per cent. of bismuth and 40 per cent. of tin ; the single crystal is a sufficient indication that bismuth is present in excess of the eutectic proportion. When chill cast from  $160^{\circ}$  the centre of the piece shows a few small crystals of bismuth and some imperfectly developed skeletons of tin, Fig. 135, but most of the area indicates that the segregation of the bismuth has been arrested at an intermediate stage ; at the edge of the section, Fig. 136, the tin shows a more complete development than the bismuth. When chill cast from  $300^{\circ}$  this mixture has an appearance very similar to that of the pure eutectic under similar circumstances, both at the centre and the edge, Figs. 137 and 138. As the proportion of bismuth is increased there is greater difficulty in preventing the formation of the larger crystals of this metal, but the rapidly cooled outside portions of chilled ingots show that a similar action is taking place. Fig. 139 is a vertical section through a slowly cooled ingot containing 70 per cent. of bismuth ; all the bismuth crystals but two have collected at the bottom. Fig. 140 shows shows the structure of the bottom part when more highly magnified, and Fig. 141 is taken at the edge of the layer of bismuth crystals. When chill cast from  $160^{\circ}$  the middle part of the ingot is like Fig. 142, the skeletons of bismuth being moderately well developed ; these skeletons become more attenuated towards the periphery of the ingot, and are hardly discernible as such at the extreme edge, while fairly large but irregular masses of tin appear, Fig. 143. When chilled from  $300^{\circ}$  the crystals of bismuth are more compact than in the preceding case, though of smaller diameter, both as regards the middle and the edge

of the section, Figs. 144 and 145 ; the dark inclusions of tin at the edge of the section are not so large as before.

Other mixtures were employed in which tin was the excess metal. The first contained 45 per cent. of tin, that is, only 1 per cent. more than in the eutectic. Fig. 146 shows a few dark primary skeletons of tin at the top of the slowly cooled ingot of this composition, while Fig. 147 exhibits the pseudomorphic arrangement of the excess tin at the bottom of the ingot. When chill cast from  $160^{\circ}$  the alloy, as was to be expected, showed small skeletons of tin at the centre, Fig. 148, but no crystals of bismuth of corresponding size ; the structure at the edge was similar but less coarse, Fig. 149. When chilled from  $300^{\circ}$  the development of the skeletons of tin was very striking, especially their radial arrangement at the periphery of the ingot. Fig. 150 shows the change in the arrangement from the periphery towards the centre. Fig. 151 shows to a larger scale the relatively well developed tin skeletons at the centre of the ingot, and Fig. 152 the long but attenuated ones at the edge and their columnar disposition. Pouring from  $750^{\circ}$  allowed a few bismuth crystals to develop at the centre, but the bulk of the mass, both at centre and edge, had the appearance of imperfectly separated eutectic, Figs 153 and 154. Increasing the proportion of tin in the alloy just has the effect of increasing the preponderance of the skeletons of this metal in the chill cast mixture. Only one example need be given. Fig. 155 shows the structure of the middle part of a slowly cooled ingot containing 50 per cent. of tin. When chill cast from  $160^{\circ}$  this alloy appeared like Fig. 156 at the middle and like Fig. 157 at the edge. Chilling from  $300^{\circ}$  caused considerable alteration in the tin skeletons at the middle, but little at the edge, Figs. 158 and 159.

The suppression of the growth, or rather of the aggregation, of bismuth crystals in the alloys seems to be due to the assumption

of compact forms by this metal in preference to skeleton forms. In the case of tin small particles of the metal solidify at considerable distances from the nucleus and yet arrange themselves as branches of the skeleton crystal. With bismuth the particles apparently experience a strong attraction towards the nucleus, and tend to move thence in radial directions. Evidence of such action is to be seen in many of the above sections, notably in Figs. 148 and 151 ; it becomes still more striking when these pieces are annealed, as will be seen in paragraph 21. Slowly cooled specimens often show a similar effect, as, for instance, in Fig. 141.

17. Example of the Presence of More Than Two Phases in a Binary Alloy which experiences a Transition when Partly Solid.

There is no need to give here more than one example of a type of structure that was discussed quantitatively at sufficient length in Part I. The case chosen is that of an antimony-tin alloy; the equilibrium diagram for the series is given in Fig. 45. The selected alloy contains 55 per cent. of antimony and 45 per cent. of tin. If cooled under conditions of equilibrium, the  $\alpha$ -crystals formed during the first period of crystallisation would react with the liquid and be converted entirely to  $\beta$  at  $430^{\circ}$  C., and the whole alloy would become solid, as uniform  $\beta$ , at about  $370^{\circ}$ . The chill cast alloy, Fig. 160, shows bright crystals of the antimony-rich  $\alpha$ -solution; these are enveloped in rounded masses of  $\beta$ , which etch somewhat darker than  $\alpha$ , and the interstices are filled with a dark tin-rich substance. The slowness with which equilibrium is reached in such mixtures can be judged from Fig. 161, a section of the same alloy cooled slowly in the furnace. Here, of course, the structure is on a larger scale, but the proportion of  $\alpha$ -crystals is not much diminished, though  $\beta$  has increased chiefly at the expense of the dark tin-rich inclusions, only a few of which remain. In Fig. 161  $\alpha$  appears darker than  $\beta$ , on account of the change in the etching reagent employed.

## 18. Changes in the Structure of Completely Solid Metals and Binary Alloys.

There are several varieties of instability of structure. In a pure metal, not subject to allotropic change, there may be instability of crystal size or of crystalline arrangement. For instance, the permanent distortion of a piece of metal renders the original arrangement unstable, and under favourable circumstances the piece becomes more or less completely recrystallised. In an alloy there may be the physical instability of crystal size or the chemical instability of the phases present at a certain temperature.

It is not unreasonable to expect that in a pure or nearly pure metal, cooled with extreme rapidity, the crystals may assume an arrangement which is less stable than that which develops under the more favourable conditions of slow cooling. Thus the structure of a rapidly cooled metal, in the course of time, may show a considerable change when compared with that of the slowly cooled one. A complication may be introduced by the occurrence of distortion of the metal on account of shrinkage or expansion, and this may be also expected of a more serious nature in the rapidly cooled than in the slowly cooled metal.

In eutectics and eutectiferous alloys, where the mode of crystallisation may be considerably changed by rapid cooling, a corresponding instability of structure might be expected to assert itself.

In alloys which suffer a chemical transformation after becoming completely solid, the manner in which the new phases grow and develop, and their arrangement at various stages when transition is only partially accomplished, are of great interest.

Although structural instability may become manifest at ordinary atmospheric temperatures the change is promoted by heating, so that

in the work to be described the specimens have been usually annealed at temperatures higher than atmospheric. Vibration may be expected also to favour a latent change, and some experiments were carried out to investigate this point. Small pieces were placed in a wooden tumbling barrel and rotated some millions of times. In some cases distinct changes of structure were noticed, but these must be ascribed, at least in part, to deformation of the outer skin, caused by the succession of small blows received by the specimens in the apparatus. The exact change due to vibration pure and simple is very doubtful, and the results of the experiments will not be considered here.

19. The Effect of Annealing upon the Structure of Chill Cast and of Slowly Cooled Metals, with and without Small Amounts of Added Impurity.

A number of specimens, some similar to and others the same as those described and illustrated in paragraph 11, were annealed for a period of 400 hours in an electrical heating apparatus, the surface of each specimen being polished, etched, and photographed at the end of 100, 200, and 400 hours. Generally speaking, the changes occur chiefly during the earlier periods of annealing, though one remarkable exception is noted. The most suitable annealing temperature is different for different metals, but as only the single apparatus was available the specimens were annealed in batches at a temperature of  $140^{\circ} \text{C.} \pm 5^{\circ}$ . This is considerably below the melting points of the pure metals employed, and of some of the eutectics present in the impure metals, and is slightly higher than those of the eutectics of bismuth-cadmium ( $138^{\circ}$ ) and bismuth-tin ( $133^{\circ}$ ). The method of treatment is certainly defective, but it is the best that could be managed under the circumstances.

Dealing first with the unadulterated metals, neither antimony nor zinc suffered a detectable change of structure, even after 400 hours ; a further period of 5 hours at a temperature of  $270^{\circ} \pm 8^{\circ}$  made no difference. Fig. 162 shows the chill cast bismuth in its original state, Fig. 163 after 100 hours, Fig. 164 after 200 hours, and Fig. 165 after 400 hours annealing ; these and succeeding sets of photographs are arranged as nearly as possible in similar position so that comparison may be easy. In Fig. 163 it is seen that rather more than one-half of the original pyramidal grains have broken up into smaller ones ; in Fig. 164 the change has progressed very slightly ; in Fig. 165 the size of the small grains has increased on the whole, and some have been apparently re-absorbed by the original pyramidal grains. It is to be noticed that several of the

original grains, notably those at the upper left-hand part of the section, show no sensible change, and that the disappearance of many of the small grains from Fig. 165 has left the boundaries of the ~~original~~ pyramidal grains sensibly identical with their original shape. It is considered that the appearances shown do not indicate any appreciable recrystallisation of the mass of the metal, but chiefly, or perhaps wholly, a recrystallisation of the surface film formed during the original grinding and polishing processes. It would have been possible to ~~prove~~ <sup>test</sup> this <sup>view</sup> by carefully polishing and etching the specimen alternately to remove the thin surface layer, but unfortunately the actual specimen was melted when the temperature of annealing was raised. Such a recrystallisation of the surface film on bismuth has been noted by the writer elsewhere ; in Fig. 166 ~~it~~ <sup>the film</sup> covers the whole surface, while in Fig. 167 most of it has been removed by light alternate polishing and etching. In this case the film recrystallised at atmospheric temperature. The alloy of bismuth with 2 per cent. of antimony, described below, affords another good example of such a film. The slowly cooled bismuth, Figs. 168 to 171, shows few traces of a surface film ; the reason is not known, but the initial preparation may have been carried out with more care. The growth of small grains around the edge of the sample during annealing is probably due to the unavoidable fractures, accompanied by distortion, which occur when this brittle metal is cut, and does not represent a mere surface change.

In the case of cadmium both the chill cast and the slowly cooled metal certainly recrystallise, the new crystals gradually growing in size as the period of annealing is prolonged, Figs. 172 to 177 ; the original structure is shown in Figs. 52 and 53. The chill cast tin recrystallised in a partial manner, that is to say, some new grains developed, some of the original grains increased in size, and some remained apparently unaltered during annealing,

Figs. 178 to 181. The slowly cooled tin showed almost complete recrystallisation after 100 hours annealing, Figs. 182 and 183, after which there was but little change, Figs. 184 and 185. When chill cast from  $750^{\circ}$  the recrystallisation, though less complete than in the case of slow cooling, was more so than in the metal chill cast from  $240^{\circ}$ ; the change subsequent to the first 100 hours annealing was again unimportant, Figs. 186 to 189. Careful trial in the case of cadmium and tin showed no appreciable surface film such as that on bismuth.

Comparing the results for the three metals, bismuth, cadmium, and tin, the first is sensibly unaltered during annealing, the second recrystallised throughout, so far as can be judged, and the third more or less completely according to circumstances. It is to be noted that the annealing temperature employed is least favourable to change in the cadmium, the metal of highest melting point, in which the change is apparently most complete.

The specimens of bismuth with an admixture of 2 per cent. of other metals, employed in the annealing experiments, were those already shown in their original condition in Figs. 60 to 67. The mixture containing 2 per cent. of antimony has been mentioned already as exhibiting a noticeable surface film. In Fig. 190, after 100 hours annealing, the recrystallisation of this surface film has largely obliterated the outlines of the underlying pyramidal grains; in Fig. 191, after 400 hours annealing, most of the film has been removed during repolishing, but there seems to have been also some recrystallisation of the mass of the metal when Fig. 191 is compared with Fig. 60. The existence of the surface film was conclusively proved in the case of the slowly cooled alloy containing antimony. Figs. 192 and 193 show the appearance after 100 and 400 hours annealing respectively; it is to be noted that only one of the large original grains is covered with the recrystallised film. Fig. 194

shows the specimen with the surface film partly removed by light re-grinding, polishing, and etching, and in Fig. 195 the removal is complete. A comparison of Fig. 195 with Fig. 61 shows that the long period of annealing has not altered the outlines of the original grains to any noticeable extent.

In the case of bismuth containing cadmium the annealing temperature was somewhat above the melting point of the bismuth-cadmium eutectic, so that the original polished surface became rough, and the structure after the first 100 hours annealing, Figs. 196 and 200, is not very clearly distinguishable as the surface was not re-ground. The cadmium is eventually dissolved by the bismuth, and the melting point of the solution is higher than  $140^{\circ}$ , so that there was no further trouble on this head. Fig. 197 shows the chill cast specimen after 200 hours, and Fig. 198 after 400 hours annealing. In this case there are only slight traces of a surface film, but the re-ground specimen, Fig. 199, showed the unexpected feature of smooth granular boundaries, when on the surface, Fig. 198, they exhibit innumerable small irregularities. The slowly cooled alloy shows considerable, but not by any means complete, recrystallisation after 400 hours annealing, Fig. 201.

The annealed bismuth-tin and bismuth-zinc mixtures, Figs. 202 to 205, show practically no change from the original conditions, Figs. 64 to 67, except that the solid solutions have become more nearly uniform. In Fig. 205 there appears to be a surface film, but this has not been examined carefully. Thus, on the whole, there is very little tendency to recrystallisation of bismuth when 2 per cent. of each of the various impurities is present.

The behaviour of the cadmium mixtures is more interesting, as might be expected from that of the sensibly pure metal. In the chill cast cadmium-antimony mixture there is relatively little change after 400 hours, Fig. 206, though the fact that the illumination here is

rather different from that of Fig. 68 makes comparison somewhat difficult ; there are slight traces of a surface film. In the slowly cooled mixture the surface film is well developed, and after annealing it gives rise to a remarkable appearance. Antimony is but slightly soluble in cadmium, and the original cadmium-rich grains, Fig. 69, are traversed by fine dark antimony-rich threads, which divide the polished section of each grain into a number of irregular closed cells, all of course ~~of course~~ of constant orientation in any one grain. After annealing, Figs. 207 and 208, the orientation of some of the cells appears changed, while that of others remains as before, so that each large grain appears to be resolved into a number of smaller ones ; a curious point is that the change of orientation usually occurs at one of the original antimony-rich boundaries, a feature which is somewhat analogous to the case of Fig. 193, where there is a film on one grain and not on the other. That the effect is a surface one can be seen from Fig. 209, annealed for 400 hours, where much of the film has been removed.

In the cadmium-bismuth alloy the melting of the eutectic causes roughening of the surface of the specimen, just as in the bismuth-rich mixture of the same two metals, but now the structure is very clearly defined in spite of the roughness, Fig. 210. Further annealing allows of the growth of some grains at the expense of others, Fig. 211 ; in Fig. 212 the granular boundaries after 400 hours annealing are superposed upon the remains of those developed by etching after 200 hours. Fig. 213 is the same as Fig. 212, but re-ground ; it is somewhat marred by a surface film, which is easily developed upon the annealed alloy, and recrystallises rapidly at the ordinary temperature. The slowly cooled cadmium-bismuth behaves in much the same manner as the above, but the grains are somewhat larger, both before and after annealing, Figs. 214 to 217. The cause of the curious markings on some of the grains of Fig. 215 was not discovered.

The rapid recrystallisation of the surface film at atmospheric temperature is exhibited by Fig. 217. The structure of these specimens before annealing is shown in Figs. 70 and 71.

The cadmium-tin alloy behaves much like cadmium-bismuth, but the relative growth of the crystalline grains is more considerable. The original structure of the chill cast and of the slowly cooled metal is rather fine, especially that of the former, Figs. 72 and 73. After 100 hours of annealing the chill cast metal has become somewhat coarser than the slowly cooled one, Figs. 218 and 221 ; the roughness of the surface of these specimens is again caused by the melting of the eutectic. Further annealing allows of the growth of some grains and the disappearance of others, and at the end of 400 hours the chill cast alloy cannot be distinguished from the slowly cooled one. It is remarkable that the rate of growth of the grains, which is evidently much less during the second 100 hours than during the first 100 hours, Figs. 219 and 222, is accelerated again during the third period of annealing, Figs. 220 and 223. A similar action, though much more pronounced, takes place in the chill cast cadmium-zinc alloy. Here at first there is a complete recrystallisation, so that at the end of 100 hours, Fig. 224, the structure is much finer than that of the original alloy, Fig. 74, just as in the case of pure cadmium. During the next 100 hours the growth is slow but distinct, Fig. 225, but at the end of 400 hours, Fig. 226, the structure is absolutely revolutionised, such that while the number of grains visible on the surface after 200 hours annealing might be numbered by thousands, after 400 hours there are only a dozen. The most curious feature of this case is that the slowly cooled alloy shows no such remarkable change, Figs. 227 to 229. A partial explanation, to which the appearance of Fig. 227 lends colour, is that a surface film was developed which covered the whole specimen until polished for the last time ; against this is to be placed the fact that even a careless

polishing of the annealed alloy - and annealed metals are generally most sensitive in this respect - failed to produce a film. The phenomenon evidently requires further investigation.

As regards the alloys of tin, of which the original structure is shown in Figs. 76 to 81, some behaved much like the metal itself, while others showed individual characteristics. The chill cast tin-bismuth alloy at the end of the first 100 hours annealing was almost completely broken up, Fig. 230, but the amount of change after further annealing was comparatively slight, Fig. 231. The slowly cooled mixture similarly recrystallised, Fig. 232, but the size of the grains increased continuously with the time of annealing, Figs. 233 and 234. The chill cast tin-cadmium alloy presented a remarkable appearance after annealing, each large pyramidal grain showing strings of tiny grains lying along the directions of the original skeleton axes, Fig. 235. This appearance at once suggests a surface film ; but there was no great change after a longer period of annealing, Figs. 236 and 237, and repeated polishing and etching after 400 hours annealing always gave the same apparent structure, which under the microscope is one of considerable beauty. In the slowly cooled alloy the eutectic has melted throughout a part of the specimen, and the structure of this part has been but poorly developed by the etching reagent. There is evidence here of an imperfectly developed surface film, for the skeleton forms seen in Fig. 79 are partly covered in Figs. 238 and 239, and reappear with considerable clearness and amplified dimensions in Fig. 240. What really happens to the grains of this alloy is doubtful. The chill cast tin-zinc alloy shows the development of a few small grains, which may or may not be merely on the surface, Figs. 241 to 243 ; in the slowly cooled mixture the break-up is more general, though portions of the original large grains may be still traced after 400 hours annealing, Figs. 244 to 246.

Looking back over all the sections, it is quite clear that annealing reveals no particular instability in the crystallisation of the chill cast as compared with the slowly cooled specimens. Occasionally, as in the case of cadmium containing 2 per cent. of tin, the growth of the grains in the chill cast metal is at first more rapid than in the slowly cooled metal ; at other times, as in the case of tin, the recrystallisation of the slowly cooled metal is far more complete than that of the chill cast ; in most cases there is comparatively little difference.

But the period of 100 hours annealing may be too long for evidence of an initial difference between the two states of the metal to remain noticeable ; such a difference might be detected best after a very short period of annealing. The most favourable condition for recrystallisation is the partial liquefaction of the mass. Accordingly some of the metals containing a 2 per cent. mixture of foreign material were heated until they showed signs of incipient melting, and they were then allowed to cool, the whole process lasting only a few minutes. In this way it was thought that any tendency to recrystallise would be exhibited by an abrupt change in orientation in portions of the metal - especially in regions where the eutectic had melted - which could be easily detected by lightly repolishing and re-etching the treated metal.

Fig. 247 shows the original appearance of bismuth containing 2 per cent. of cadmium. Fig. 248 is the same piece repolished and re-etched after the lower portion had been melted ; the original crystalline arrangement is seen to be unaltered up to the very edge of the melted portion. In the case of the slowly cooled mixture of the same composition, however, the treatment has resulted in a radical alteration of the orientation of various portions of the largest grain on the original section, Figs. 249 and 250 ; it is noticeable that the portions of changed orientation are nearly always

limited by the narrow cadmium-rich boundaries of the bismuth skeleton arms. This change took place in a time which did not exceed five minutes. For the bismuth-tin alloy no change was observed in either the chill cast or the slowly cooled metal. The other bismuth-rich mixtures were not tried.

The cadmium-bismuth and cadmium-tin mixtures became more or less completely recrystallised. The change was most noticeable in the former, but there was no characteristic difference between chill cast and slowly cooled metal, Figs. 251 to 254. In the case of cadmium-tin the change is less noticeable on account of the fineness of structure, but it is none the less unmistakable, Figs. 255 to 258 ; the slowly cooled mixture after reheating is still of coarser structure than the chill cast after similar treatment, but this may be accidental, since the times of reheating could not be made exactly the same in both cases.

The chill cast tin-bismuth alloy recrystallised completely when heated to incipient melting, Figs. 259 and 260. The slowly cooled mixture changed in a less radical way, Figs. 261 and 262 ; difficulty was experienced in getting a satisfactory micrograph of the original section with oblique illumination, and Fig. 261 was taken with vertical illumination. The chill cast tin-cadmium alloy was unfortunately melted completely through inadvertence ; the slowly cooled mixture showed partial recrystallisation, though this is not very distinct in Figs. 263 and 264.

Thus the experiments involving incipient melting agree with the annealing experiments in showing no general instability of the crystals of the rapidly cooled metals as compared with the slowly cooled ones. In the cases where there is much recrystallisation it seems to occur indifferently in chill cast and slowly cooled metal, as with the cadmium-bismuth, cadmium-tin, and tin-bismuth mixtures ; in the bismuth-cadmium alloy there is a change in the slowly cooled

and none in the chill cast metal. Although the results of these experiments in the direction sought are largely negative, the information obtained indirectly is of value, particularly as regards the persistence of surface films and their perfect simulation of a possible internal structure of the metal concerned, and also as regards the remarkable changes of crystallisation in alloys containing cadmium.

When 2 per cent. of antimony is present in cadmium the alloy oxidises in a remarkable manner, emitting red fumes and becoming rapidly converted to a frothy mass of brick-red colour. There is no particular difficulty in preparing the alloy in a gas furnace, but the reaction begins as soon as the melted mixture is removed from the furnace, and takes place to some extent during slow cooling in the furnace if the infiltration of air is not prevented. The alloy when annealed in the air at a temperature of about 250° C. experiences the same change.

In studying the problem of grain size, as set forth in paragraph 11, some sections of the annealed alloys which exhibited a well defined polygonal structure were examined, namely Figs. 214, 215, 216, 218, 220, 221, and 223. After excluding an outer ring from each specimen, the area of each polygon was measured, and the skew curve of frequency, already described, was drawn for each specimen. The results are not claimed to be of great value at present, but they afford interesting comparisons, and are given in Table XXXV; the growth in the size of the grains during annealing is well shown, and also the accelerated growth in the cadmium-bismuth alloy during the last stage, but it would be unwise to insist on other features while the data are so scanty.

TABLE XXXV. Details of polygonal structure of annealed alloys.

Illustration	Composition of alloy	Treatment of alloy	Relative size of mean grain area	Ratio of largest grain to mean grain area	Approximate position of peak of skew curve of frequency, in terms of mean grain area
Fig 214	Cd 98, Bi 2	Slowly cooled, annealed 100 hours	80.7	4.32	'46
" 215	"	" " 200 "	94.6	4.81	'40
" 216	"	" " 400 "	181.0	4.85	'41
" 218	Cd 98, Sn 2	Chill cast, annealed 100 hours	54.8	3.69	'90
" 220	"	" " 400 "	151.7	4.34	'49
" 221	Cd 98, Sn 2	Slowly cooled, annealed 100 hours	40.5	3.75	'75
" 223	"	" " 400 "	113.0	4.53	'55

20. The Effect of Annealing upon Distorted Chill Cast and Slowly Cooled Metals.

It was not intended originally to observe the changes in the structure of metals and alloys when these are annealed after having suffered permanent distortion ; but the presence of Neumann's lamellae on many of the sections, for instance, Figs. 50, 56, and 59, may be regarded as evidence of some degree of deformation, possibly arising while the metal was cooling ; and there are signs also, for instance on Figs. 50, 51, 54, and 55, that some distortion was caused during the cutting of the sections and the preparation of the polished surfaces. In some cases, for instance, Figs. 178 and 179, these latter markings remained sensibly unaltered after a long period of annealing, but in cases where much recrystallisation occurred, for instance, Figs. 182 and 183, they were obliterated. It was advisable, therefore, for <sup>the</sup> purpose of comparison, to anneal the various metals and alloys already examined after they had been distorted to some extent. Fresh specimens were accordingly cut from the small ingots, and these were squeezed in a single direction in the vice so as to become approximately elliptical in shape ; the relative distortion was made about the same for all the specimens, though it is not perfectly identical throughout. The amount of distortion of the whole section and of individual grains can be judged by comparing Fig. 265 with Fig. 266, and Fig. 268 with Fig. 269. The distortion is greatest in two triangular zones, each having for its base one of the new straight boundaries of the squeezed piece, and having its apex at the centre of the section ; the regions outside this double triangle experience less distortion. There is an obvious advantage in having a varying degree of distortion throughout the specimen, as the changes in the more distorted parts can be compared with those in the less distorted ones. Previous experiments having shown that in many cases

the changes of structure are most rapid in the early stages of annealing, the present series of specimens were examined at the end of 1, 2, 5, 20, and 100 hours after the commencement of annealing.

After the specimen shown in Fig. 265 had been squeezed, the surface, which was now rough and lumpy, was filed flat and repolished. Beyond the change in the shape of the pyramidal grains, the only evidence of distortion consists in a few Neumann's lamellae at the left of Fig. 266. Annealing made but little change, only a few small new grains being noticeable in the neighbourhood of the flat sides after 100 hours at  $140^{\circ}$  C. The slowly cooled bismuth, after distortion, showed an interesting development of Neumann's lamellae, Fig. 269, which by comparison with the original section, Fig. 268, are seen to be <sup>approximately</sup> parallel to the cleavages. In metals like bismuth, where cleavage lines can be readily developed by etching, it is sometimes necessary to use special illumination to distinguish cleavages from lamellae, but in Figs. 268 and 269 the distinction is clear. Fig. 270 shows a considerable growth of new grains in the middle region of the piece after one hours' annealing, but the appearance remained practically unchanged after 100 hours.

In the case of cadmium both specimens show a relatively fine recrystallisation in the middle zone, and apparently little change in the outer regions, Figs. 271 to 274. The fine scale of all the structures makes detailed comparison difficult.

Tin is a metal which is very susceptible to the effects of distortion. The structure of the newly squeezed metal was difficult to reveal in a satisfactory manner by etching, Figs. 275 and 278. The middle regions of the chill cast specimen recrystallised rapidly, Fig. 276 showing the appearance after 2 hours annealing. The growth of the grains progressed continually; Fig. 277 shows the appearance after 100 hours. It is noticeable that some of the original large grains remain practically unchanged at the end of this period, though

they exhibit numerous lamellae. Much the same sort of action is to be observed in the slowly cooled specimen, Figs. 278 to 280. This sample, especially in Fig. 279, appears to contain a considerable degree of impurity, though the metal employed was bought as pure grain tin. There is but little likelihood of appreciable metallic contamination, and the most probable substance to suspect is tin oxide; the matter has not been investigated yet. The structure of the metal chill cast from  $750^{\circ}$  varies in a manner similar to the above, Figs. 281 to 284.

Dealing next with the metals adulterated with 2 per cent. of foreign material, Fig. 285 shows the chill cast bismuth-cadmium mixture. This experiences marked recrystallisation, beginning in the middle region, Fig. 286, and spreading gradually outwards, Figs. 287, 288, and 289, until the whole mass is involved, Fig. 290. The change in the slowly cooled mixture is of a similar nature, Figs. 291 to 295, but is not perhaps quite so complete at the end of the experiment. The bismuth-tin alloy, both chill cast and slowly cooled, remains practically unchanged by the treatment, Figs. 296 to 299.

The cadmium alloys show very pronounced recrystallisation. The chill cast cadmium-bismuth mixture, Fig. 300, at the end of one hour's annealing has recrystallised to the extent shown in Fig. 301, and the process continues uninterruptedly to the end of the experiment, Figs. 302 and 303. The slowly cooled alloy behaves similarly, Figs. 304 to 307, but <sup>changes</sup> to an even more marked extent. In the cadmium-tin alloy the recrystallisation is relatively slow during the earlier stages of annealing, but shows little falling off in rate at the end of 100 hours, so that the final structure is as coarse as in the previous case, Figs 308 to 315.

The tin-bismuth alloy behaves much the same as the unadulterated tin, though the new crystals grow at a slower rate, Figs. 316 to 321. The change observed in the chill cast tin-cadmium mixture is of

exactly the same nature as in the undistorted specimen ; strings of small grains develop along the skeleton axes of each original grain, Figs. 322 and 323. In the present case, however, the new grains appear to develop more fully, Fig. 324, and at the end of 100 hours the original granular boundaries are partly obliterated, Fig. 325. The slowly cooled alloy shows rapid recrystallisation at first, Figs. 326 and 327, with but little change afterwards, Fig. 328.

The experiments reveal curious variations in the degree of sensitiveness of the metals to the effect of distortion followed by annealing. Thus, chill cast bismuth is practically inert, while the slowly cooled metal shows considerable recrystallisation ; bismuth containing 2 per cent. of cadmium recrystallises entirely, while bismuth containing 2 per cent. of tin shows no change. Comparing Figs. 162 to 264 with Figs. 265 to 328, and the more and less greatly distorted parts of the latter with each other, leads to the following conclusions. Bismuth when undistorted shows no tendency to recrystallise, and even when distorted the chill cast metal does not recrystallise readily. Cadmium recrystallises whether distorted or not, but more readily in the former case. Slowly cooled tin recrystallises in both cases ; if chill cast it may not change unless distorted, but this is doubtful. In bismuth containing 2 per cent. of cadmium distortion increases the rate of growth of crystals in the annealed metal, but bismuth containing 2 per cent. of tin remains inert whether distorted or not. Cadmium containing 2 per cent. of bismuth or of tin recrystallises rapidly whether distorted or not. Tin containing 2 per cent. of bismuth recrystallises more readily after distortion if chill cast, but shows little difference between the two states if slowly cooled ; tin containing 2 per cent. of cadmium shows much more marked recrystallisation when distorted than when not.

As regards the specimens in which distortion was not deliberately

caused, Figs. 162 to 264, it is considered that the changes of crystallisation observed are due either to inherent instability of the original crystalline arrangement, or to the effect of distortion arising during cooling, except in cases where there is a surface film, and in a few instances, like Fig. 171, where recrystallisation around part of the edge of the section may arise from distortion caused during the cutting of the section. It is intended to repeat a few of the observations for the purpose of confirmation.

21. The Effect of Annealing upon the Chill Cast Eutectic and Rich Eutectiferous Alloys of Bismuth and Tin.

The effect of annealing upon the chill cast bismuth-tin alloys of paragraph 16 has been studied also. In these experiments the temperature was  $100^{\circ}$  C., and the period of annealing was 300 hours for some specimens and 200 hours for others. The slowly cooled eutectic, when annealed at  $100^{\circ}$  for 300 hours, showed no sensible change in appearance, but there was reason for expecting a change in the chill cast eutectic. The bismuth-tin alloys of paragraph 16 were prepared in March 1909, but owing to pressure of other matters most of them had to be laid aside without examination. A few were somewhat roughly prepared and photographed. Figs. 329 and 330 are from the eutectic alloy chill cast from  $160^{\circ}$ , and Figs. 331 and 332 are from the mixture containing 45 per cent. of tin chill cast from  $300^{\circ}$ . These micrographs, particularly the first two, are marred by scratches, but if they are compared with Figs. 128, 129, 151, and 152, taken from the same specimens, lightly repolished and etched after a period of nearly five years, a remarkable difference will be observed in the appearance of the ground mass in each case. In the earlier micrographs, Figs. 329 to 332, the structure of the ground mass is fine and nebulous, with occasional patches which show better definition; in the later ones the two constituents of the ground mass are always distinct from each other. If Fig. 329 be compared with Fig. 128 it is readily noticed that the sharp angularity of the crystals of bismuth in the former is altogether lost in the latter; comparing Fig. 331 with Fig. 151 the dendrites of tin in the latter no longer arrest the attention as in the former. The comparatively careless preparation of the earlier micrographs might be urged as the reason of the bad definition of the ground mass, but the clearness with which the other details of the structure are shown militates strongly

against this view. The change in the appearance of these sections after a five years' interval is regarded by the writer as evidence of a slow but continuous rearrangement of the constituents of the samples at atmospheric temperature during that period.

The annealed specimens were actually annealed over boiling water nearly five years ago also, but were not examined until recently. They show two noticeable features. The first is the segregation of the constituents into larger masses, a common result of annealing ; the second is the arrangement of many of the particles of bismuth in skeleton form, a feature which helps to confirm the observation that the crystallisation of the slowly cooled eutectic is determined chiefly by the bismuth. The first is evident on all the micrographs, from Fig. 333 to Fig. 352. The second is most striking on Figs. 333, 341, and 342 ; it may be noticed also on Figs. 135, 148, and 151, those specimens having been virtually annealed, but to a less extent than the ones of the present paragraph. Information relating to Figs. 333 to 352 is given with the illustrations, and no further description is necessary here.

## 22. Modifications of Structure produced by the Growth of a New Phase in a Completely Solid Alloy.

In alloys subject to transformation after becoming completely solid, there is considerable hindrance to the formation of the new phase. For the reaction necessitates diffusion through the solid mass, always a slow process, and possibly the migration of small crystals ; it may also involve a change of volume of the mass. In cases where the original alloy consists of grains of a solid solution this solution is seldom perfectly uniform ; as a rule the outer or more recently formed portions of each grain have a composition which approximates, more nearly than that of the central portions of each grain, to the composition of the new phase about to develop. That this is the case is readily seen from equilibrium diagrams for such alloys. Accordingly the growth of the new phase usually begins at the granular boundaries of the original phase, so that these no longer appear as fine lines, but become an irregular network of appreciable width. Thus in Fig. 353, a chill cast alloy of 57 per cent. of copper with 43 per cent. of antimony, the development of the purple compound  $SbCu_2$  has been checked in its earliest stages, and only a narrow irregular purple band *(purple in the actual specimen)* surrounds the grains of the solid solution. As the new phase grows the borders of the grains become thicker, and often throw out branches into the interior of the grains; new and apparently independent growths also begin at various positions within each grain. The location of the starting points of the latter is probably determined by spots of richer composition enmeshed within the skeleton branches of the grain during its formation, just as the spots of bismuth are enmeshed within the grains of copper in Fig. 94. The new phase may grow out in skeleton manner much as if the surrounding medium were liquid instead of solid. In Fig. 354, from the same alloy as Fig. 353 but slowly cooled, the growth from the

boundaries has proceeded in skeleton manner. In Fig. 355, a copper-zinc alloy containing 54 per cent. of zinc, the small skeletons of the new phase are more distinct. (The smaller granulation within the large grains in this micrograph is due to the fact that the alloy has been reheated).

In other cases the development of the new phase in the interior of each grain takes place partially or wholly along the cleavage directions of the grain, or along selected cleavages. Thus in Fig. 356, a copper-zinc alloy containing 68 per cent. of zinc, there are three cleavages in each grain sharply outlined by the new phase. In Fig. 357, a copper-aluminium alloy containing 12 per cent. of aluminium, there is a similar structure, though less neatly defined. In both of these examples there is very little development of the new phase at the granular boundaries. In Fig. 358, an alloy of 65 per cent. of copper with 35 per cent. of tin, the granular boundaries are moderately well marked, but the new phase has developed chiefly in straight parallel bands, of which there is only one system in each grain. As the new phase develops the bands along the cleavages become thicker, and sometimes retain their arrangement unchanged. At other times, as in Fig. 359, a copper-tin alloy containing 23 per cent. of tin, the bands apparently break up into irregular elongated globules; or they may throw out plant-like skeleton growths, as in Fig. 360. The exact manner in which the growth proceeds varies with the individual phases concerned, the relative proportions of the phases, and the rate of cooling.

The reason for the growth of the new phase along the cleavage directions is obscure. It may be that the argument applied above to each grain of a solid solution often holds good for each elementary geometric crystal which goes to build up that grain, so that in cases where the cleavages are parallel to the crystal faces, *as in the octahedron,* or to some of them, *as in the hexagonal pyramid,* the same explanation suffices. Or, if the growth of the new

phase is accompanied by increase of volume, it would take place preferably where the mechanical resistance to this increase is least, namely at the granular boundaries and at the cleavages, or at selected cleavages of least resistance. The partiality of the new phase to develop at the granular boundaries and cleavages explains why a transition has the effect of weakening and embrittling many alloys, more especially when the new phase is itself brittle.

## Summary of Part II.

There is no definite relation between grain size and rate of cooling when a melted metal is poured into a small mould.

The grain size of different metals cooled under similar conditions varies greatly with the metal.

The grain size of a metal cooled under certain conditions may suffer considerable alteration if a small amount of foreign metal is added to the mass.

The size of the primary grains of an alloy is diminished by increasing the rate of cooling, and by diminishing the proportion of primary material present.

Quickly cooled alloys may retain traces of currents which existed in the fluid mixture.

Quickly cooled eutectics may show primary skeletons of one of the constituents.

Quickly cooled metals do not show, on the whole, any particular instability of crystalline arrangement as compared with that of the slowly cooled metals.

A surface film is readily formed upon certain metals and alloys, and this recrystallises when annealed, in such a manner as to simulate a possible real structure of the mass.

Certain metals and alloys, when annealed after being considerably distorted, show little or no tendency to recrystallise ; others recrystallise more or less completely, and usually with more considerable rapidity in the earlier stages.

The above statements are deduced from the behaviour of antimony, bismuth, cadmium, tin, zinc, and certain alloys of these metals, and also of a few other alloys.

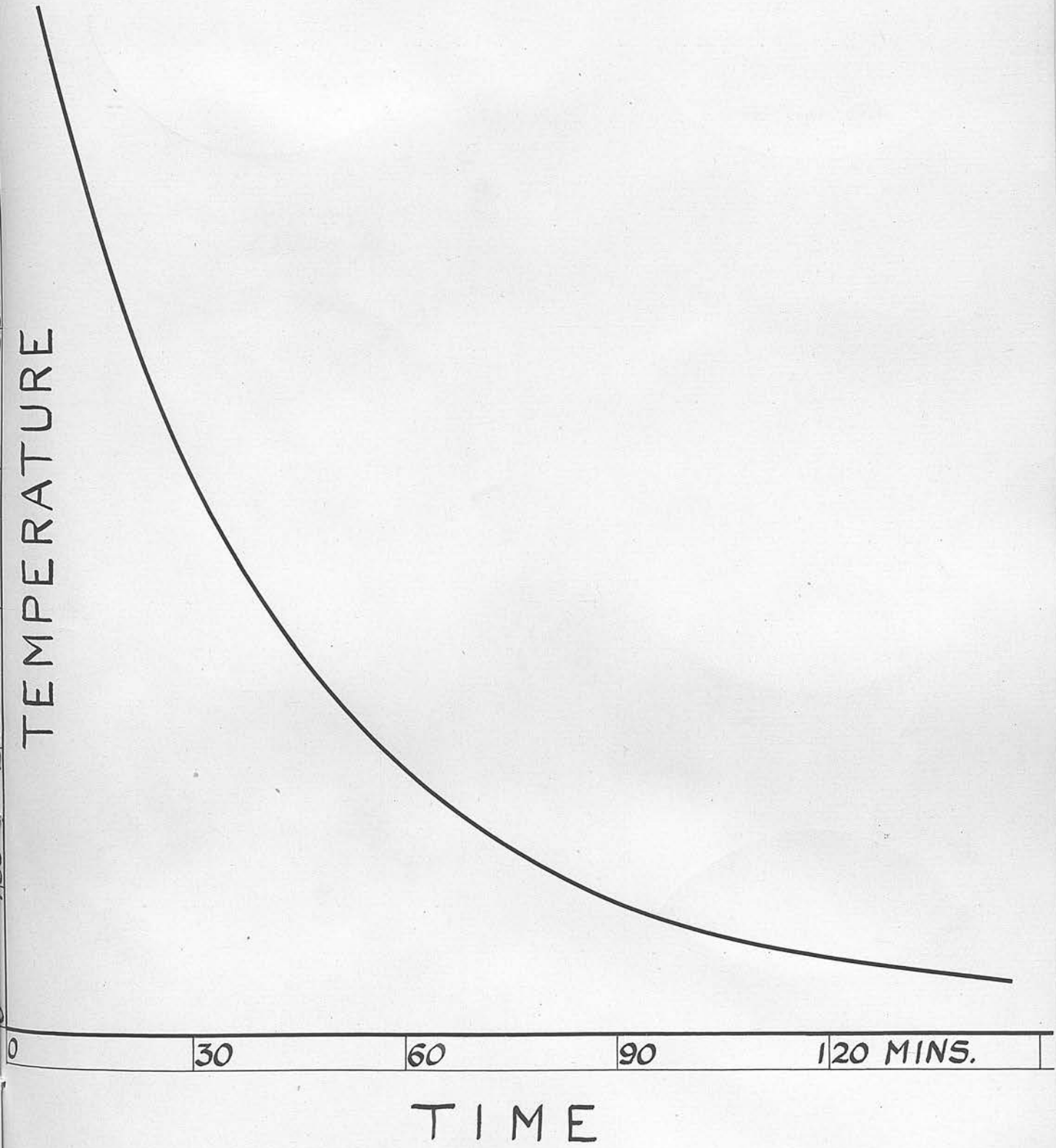


FIG. 47. Cooling curve of gas furnace.

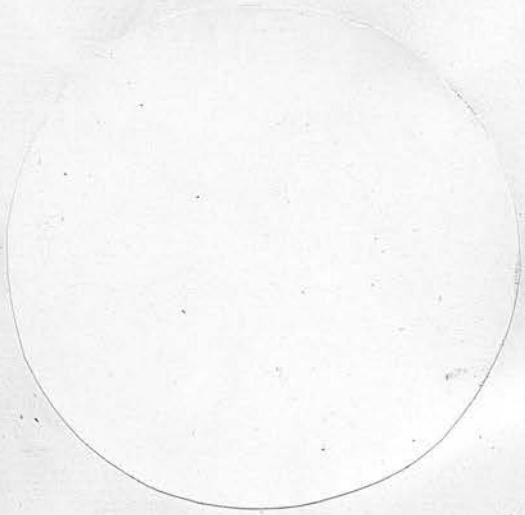


FIG. 48. Antimony, chill cast from  $650^{\circ}$ ; etched with ferric chloride.

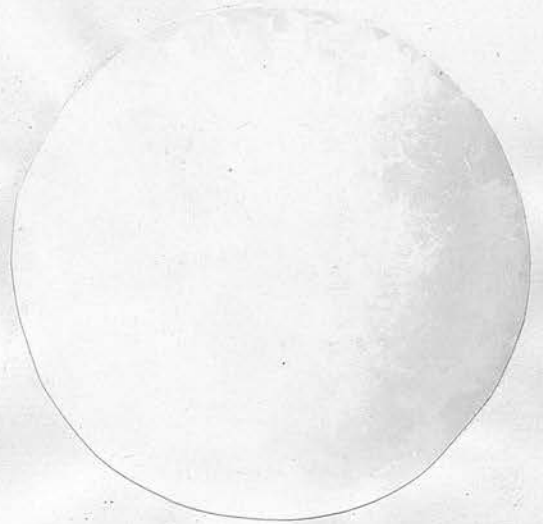


FIG. 49. Antimony, slowly cooled; etched with ferric chloride.

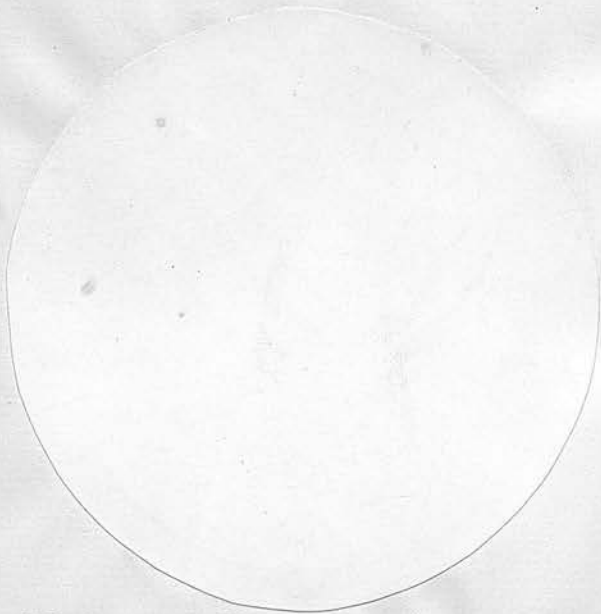


FIG. 50. Bismuth, chill cast from  $280^{\circ}$ ; etched with ferric chloride.

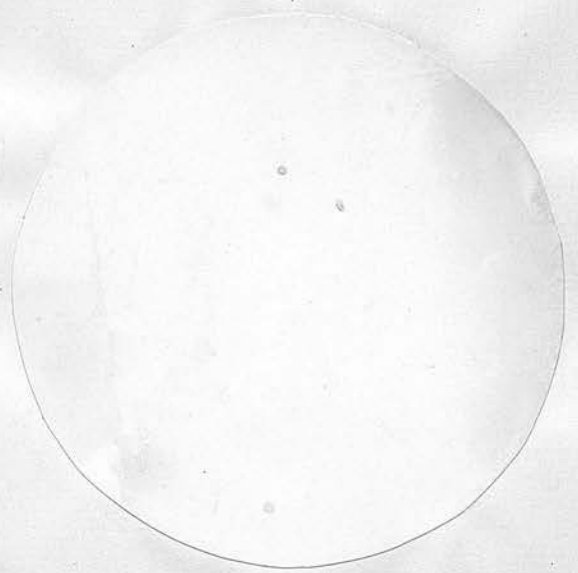


FIG. 51. Bismuth, slowly cooled; etched with ferric chloride.

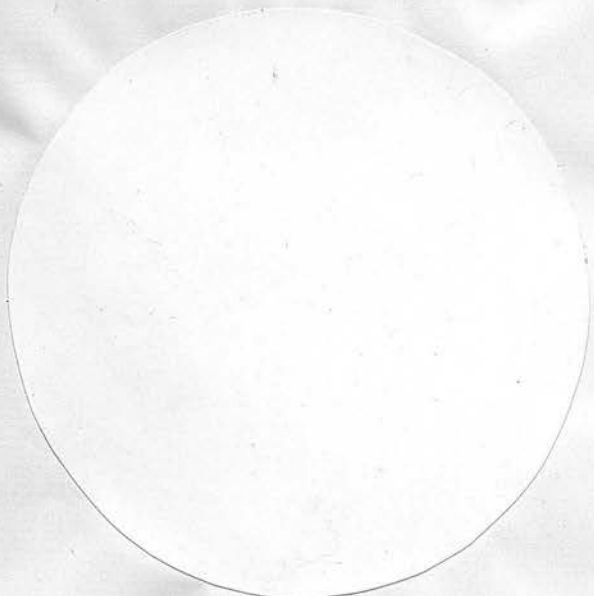


FIG. 52. Cadmium, chill cast from  $330^{\circ}$ ; etched with iodine.

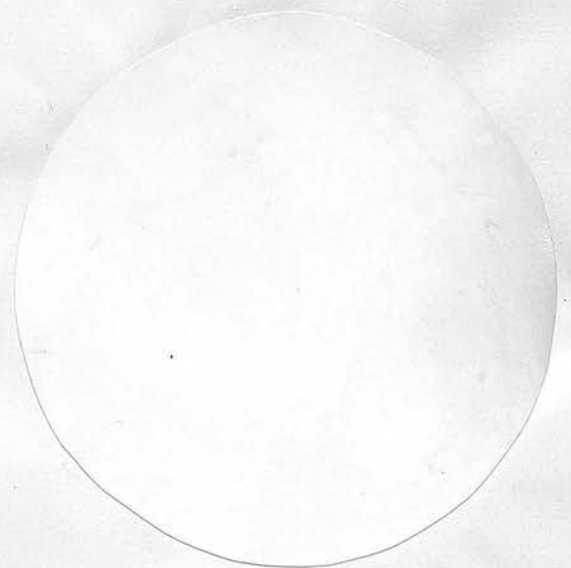


FIG. 53. Cadmium, slowly cooled; etched with iodine.

All magnified  $7\frac{1}{2}$  diameters

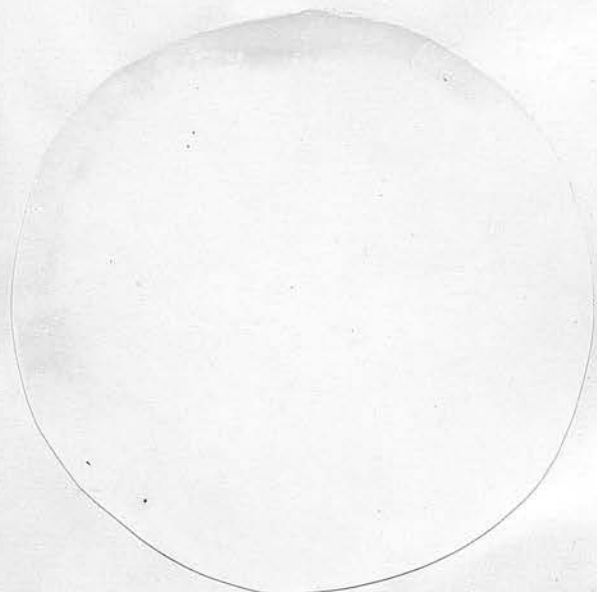


FIG. 54. Zinc, chill cast from 240°; etched with ferric chloride.

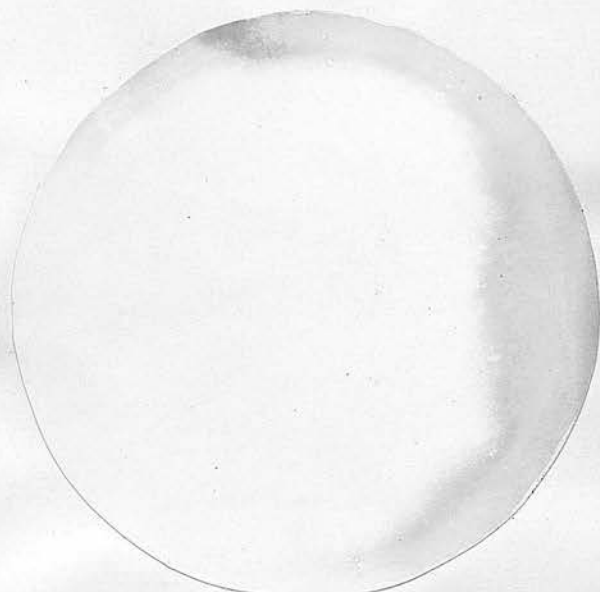


FIG. 55. Zinc, slowly cooled; etched with ferric chloride.

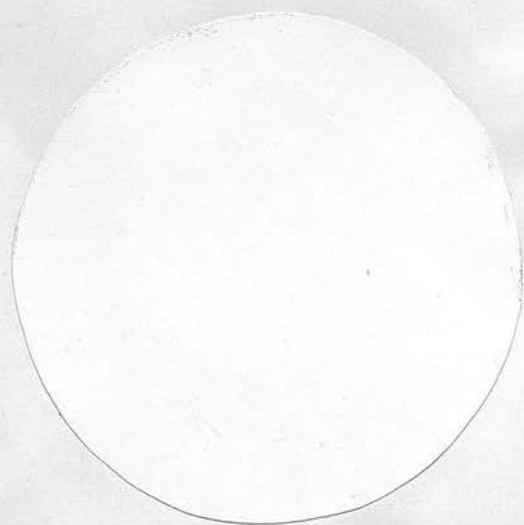


FIG. 56. Zinc, chill cast from 430°; etched with iodine.

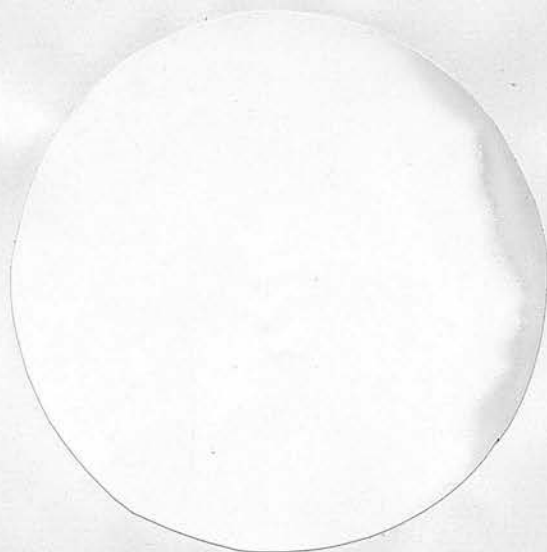


FIG. 57. Zinc, slowly cooled; etched with iodine.

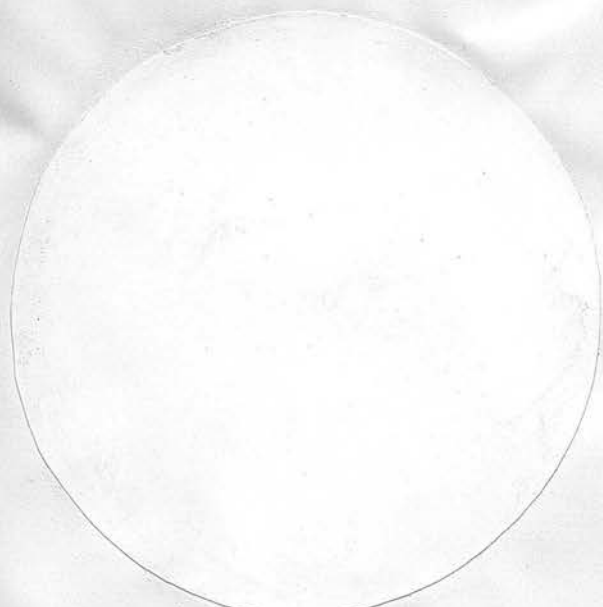


FIG. 58. Bismuth, chill cast from 750°; etched with ferric chloride.

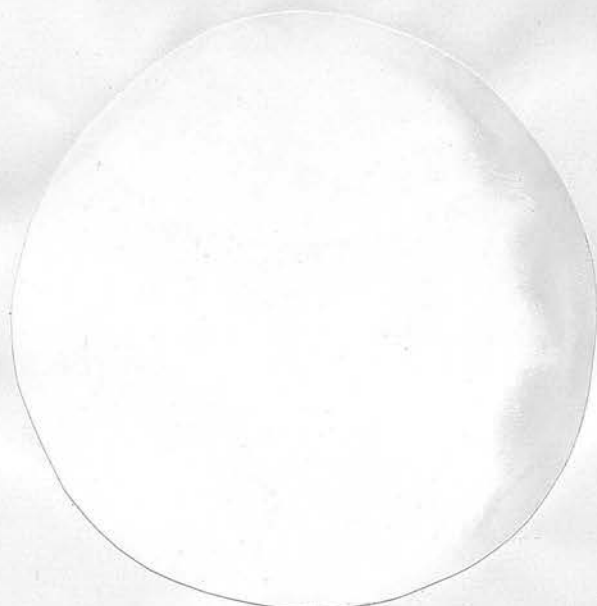


FIG. 59. Zinc, chill cast from 750°; etched with ferric chloride.

All magnified  $7\frac{1}{2}$  diameters

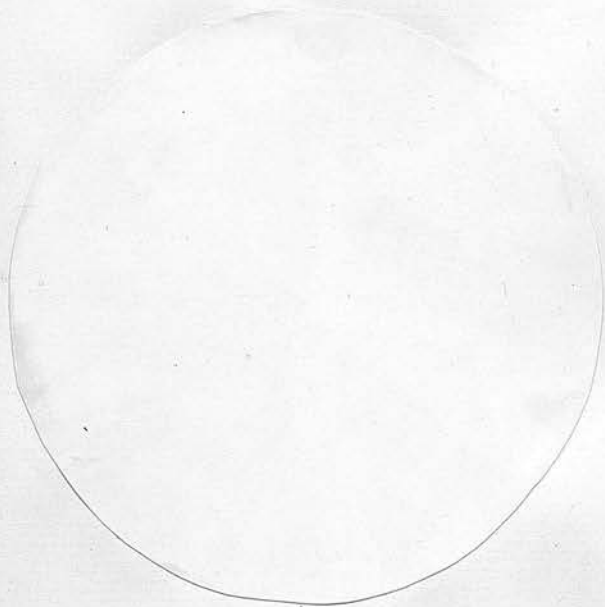


FIG. 60. Bismuth 98, antimony 2 per cent.; chill cast from  $280^{\circ}$ .

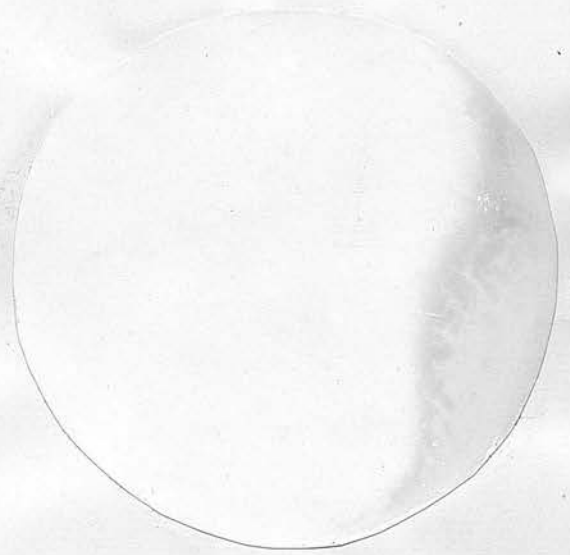


FIG. 61. Bismuth 98, antimony 2 per cent.; slowly cooled.

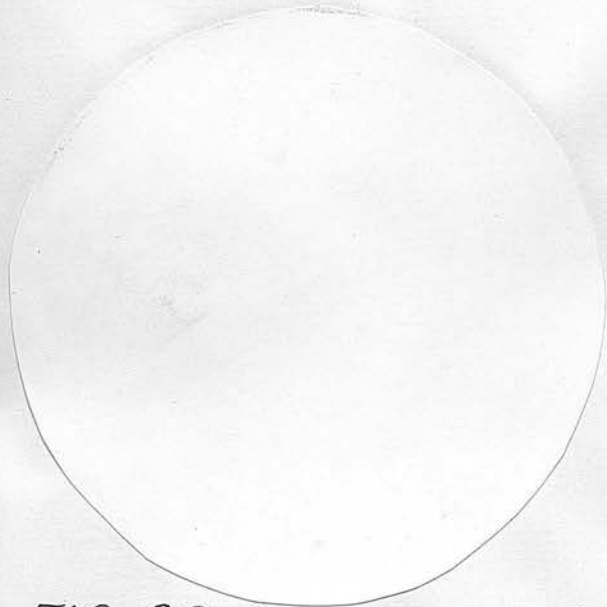


FIG. 62. Bismuth 98, cadmium 2 per cent.; chill cast from  $280^{\circ}$ .

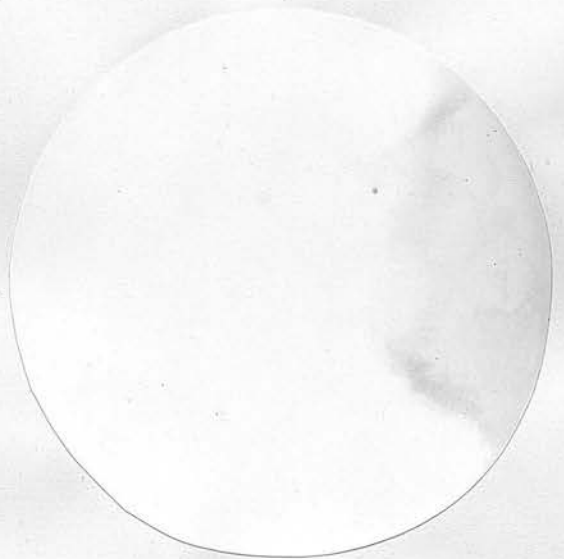


FIG. 63. Bismuth 98, cadmium 2 per cent.; slowly cooled.

All etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

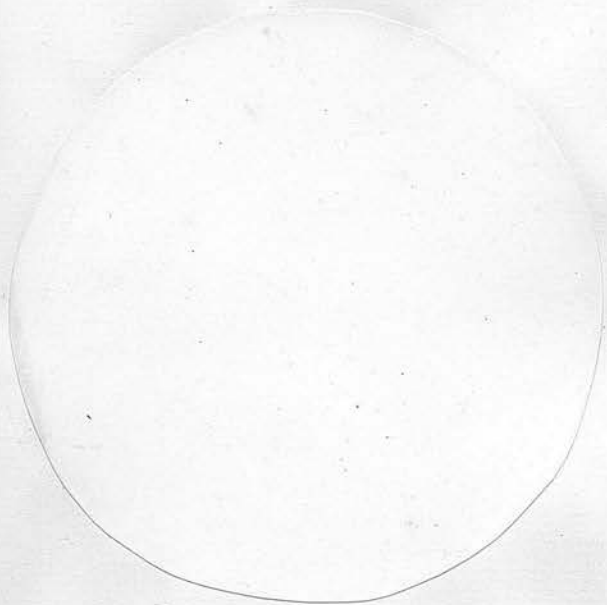


FIG. 64. Bismuth 98, tin 2 per cent.; chill cast from 280°.

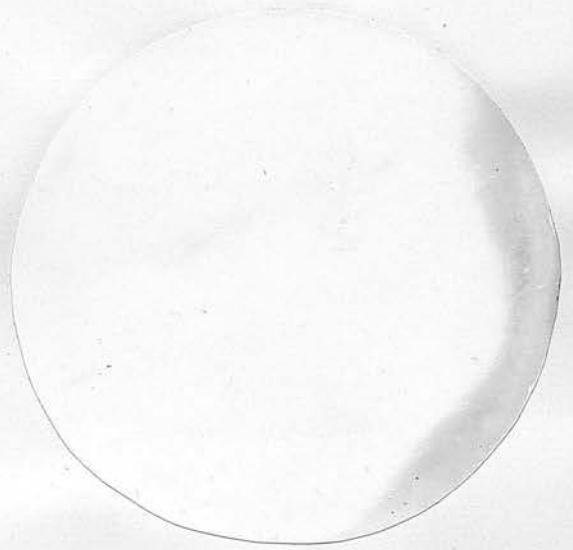


FIG. 65. Bismuth 98, tin 2 per cent.; slowly cooled.

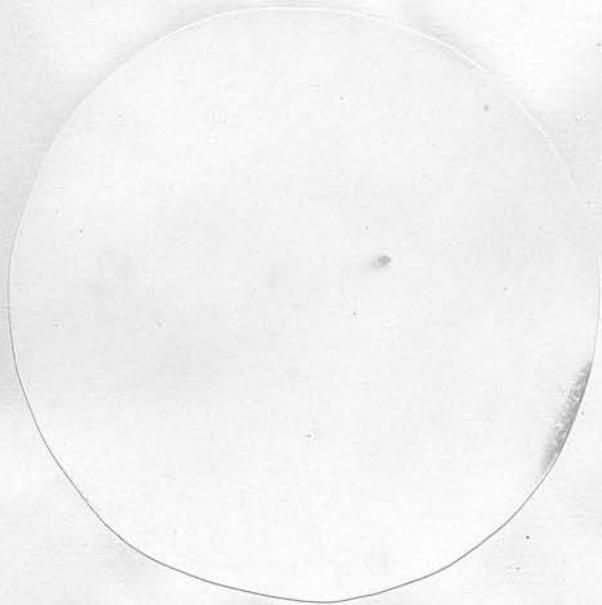


FIG. 66. Bismuth 98, zinc 2 per cent.; chill cast from 280°.

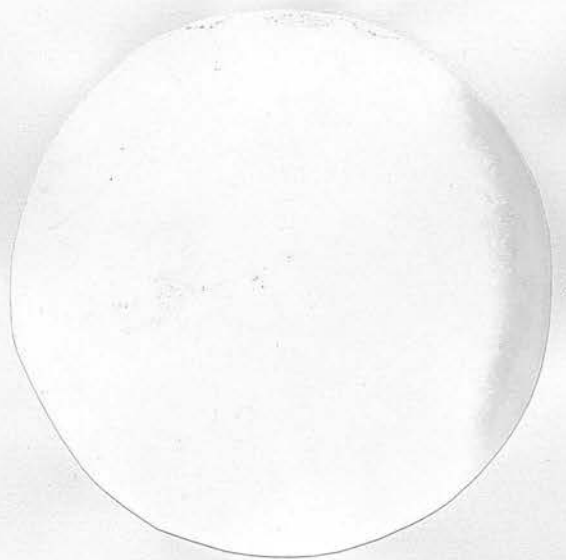


FIG. 67. Bismuth 98, zinc 2 per cent.; slowly cooled.

All etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

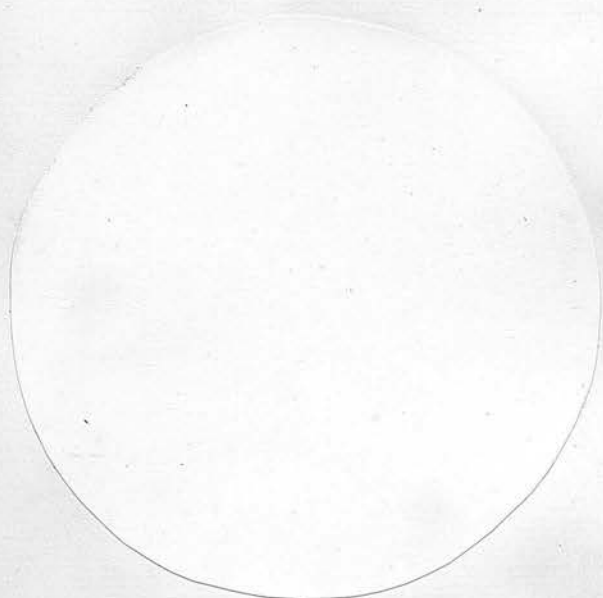


FIG. 68. Cadmium 98, antimony 2 per cent.; chill cast from  $330^{\circ}$ .

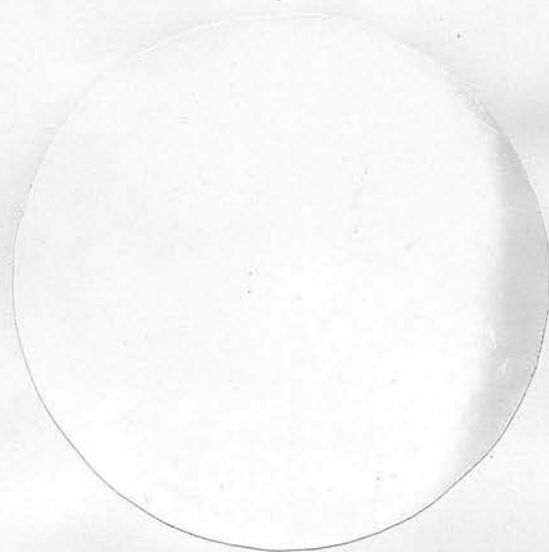


FIG. 69. Cadmium 98, antimony 2 per cent.; slowly cooled

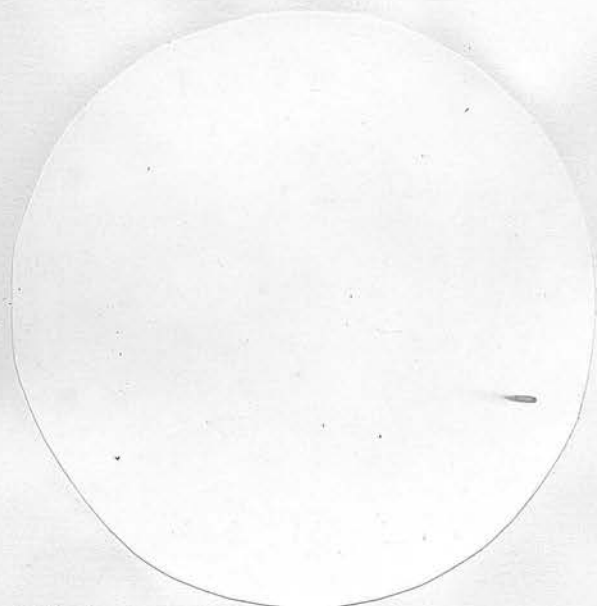


FIG. 70. Cadmium 98, bismuth 2 per cent.; chill cast from  $330^{\circ}$ .

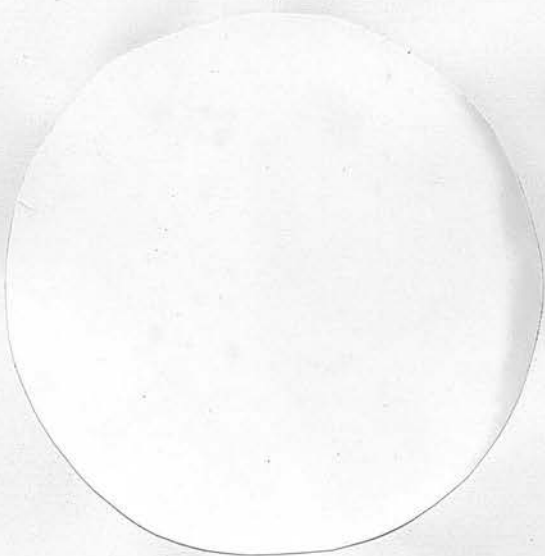


FIG. 71. Cadmium 98, bismuth 2 per cent.; slowly cooled.

All etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

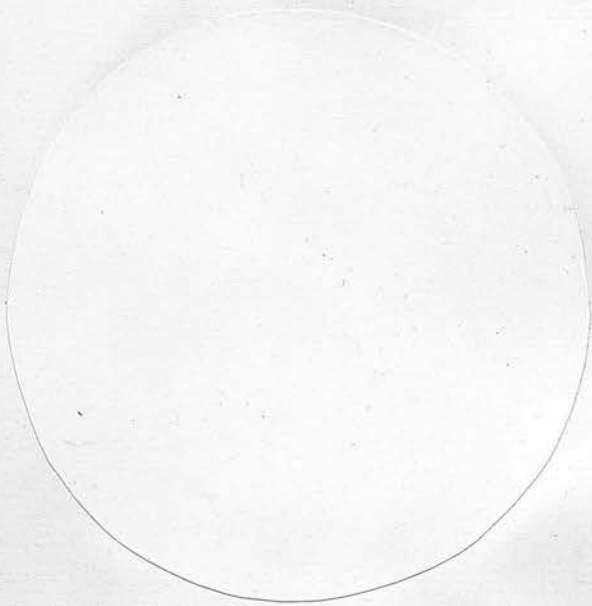


FIG. 72. Cadmium 98, tin 2 per cent.; chill cast from  $330^{\circ}$ .

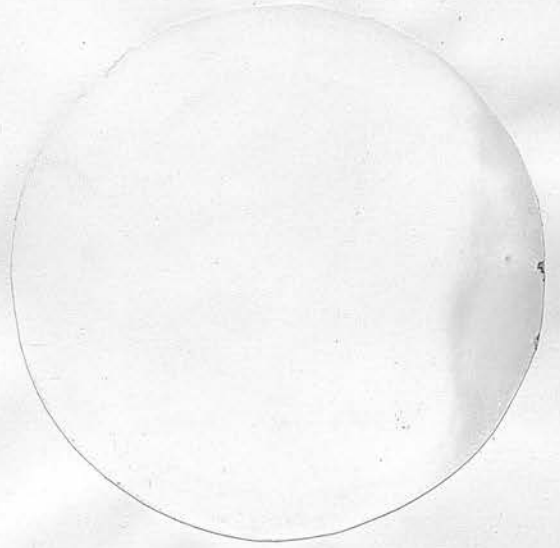


FIG. 73. Cadmium 98, tin 2 per cent.; slowly cooled.

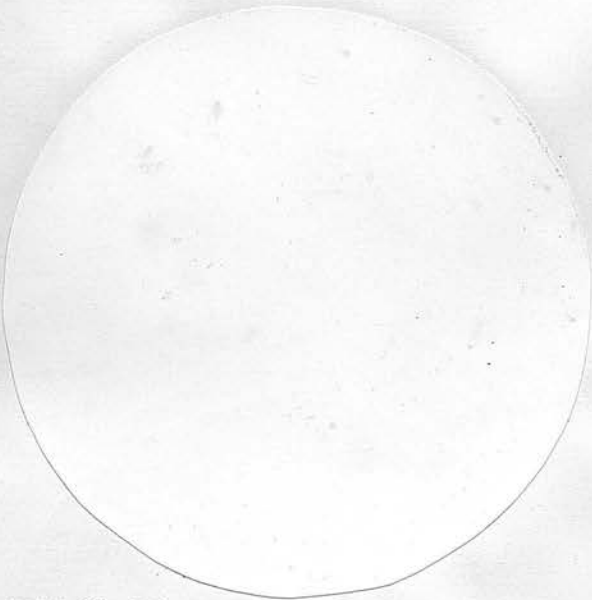


FIG. 74. Cadmium 98, zinc 2 per cent.; chill cast from  $330^{\circ}$ .

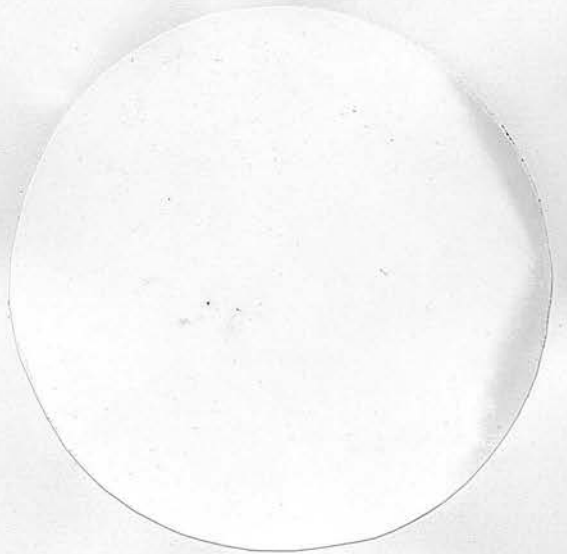


FIG. 75. Cadmium 98, zinc 2 per cent.; slowly cooled.

All etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

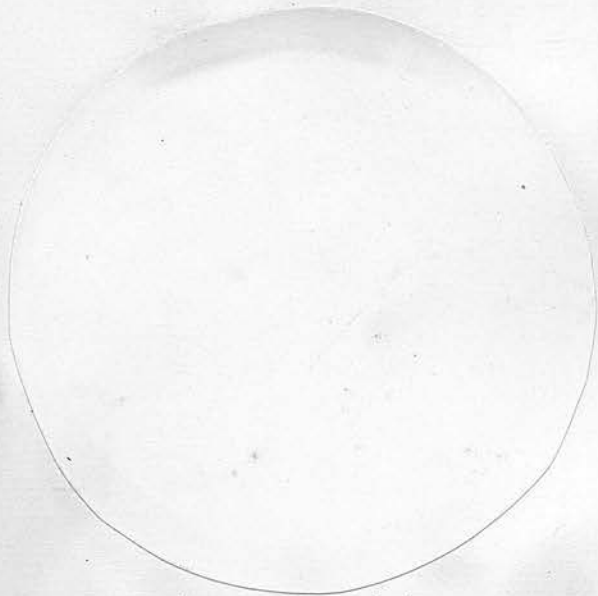


FIG. 76. *Zn* 98, bismuth 2 percent.;  
chill cast from 240°.

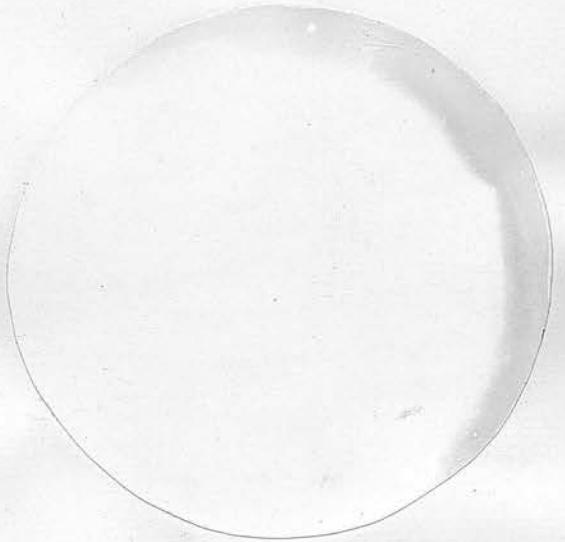


FIG. 77. *Zn* 98, bismuth 2 percent.;  
slowly cooled.

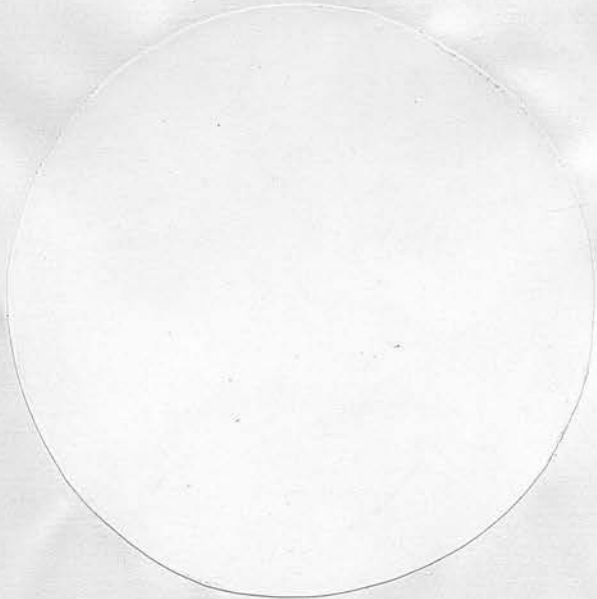


FIG. 78. *Zn* 98, cadmium 2 percent.;  
chill cast from 240°.

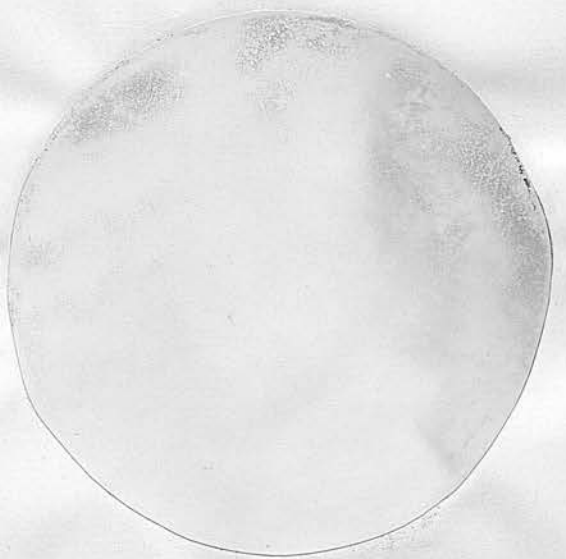


FIG. 79. *Zn* 98, cadmium 2  
percent.; slowly cooled.



FIG. 80. *Zn* 98, zinc 2 percent.;  
chill cast from 240°.

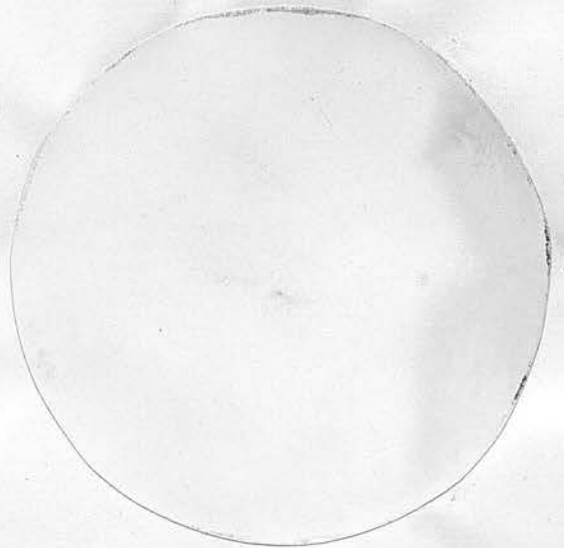


FIG. 81. *Zn* 98, zinc 2 percent.;  
slowly cooled.

all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

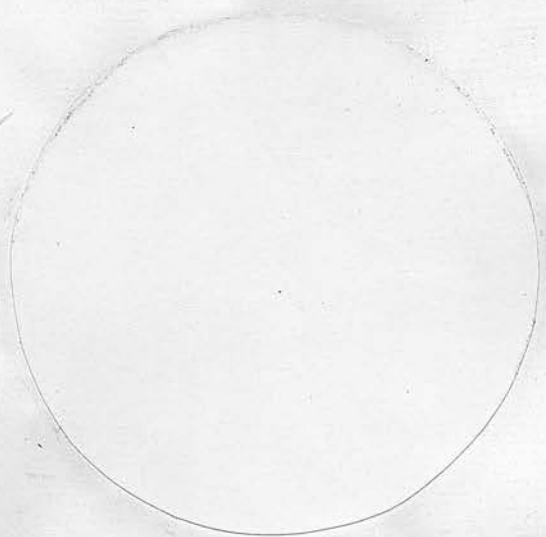


FIG. 82. Bismuth 99, tin 1 per cent.

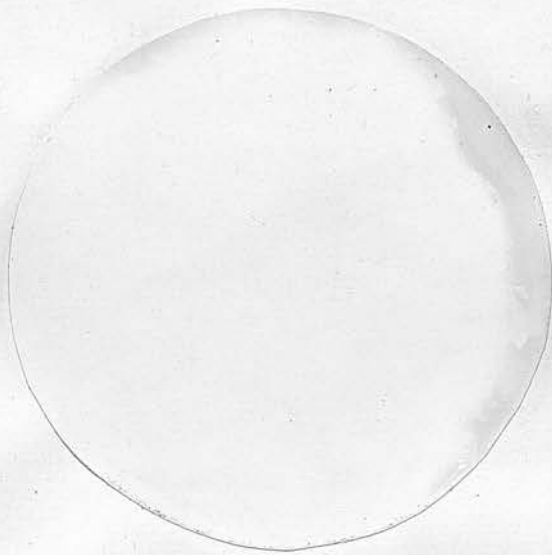


FIG. 83. Bismuth 95, tin 5 per cent.

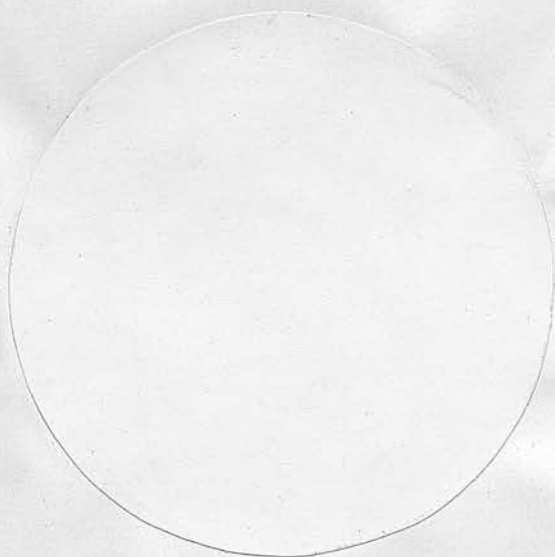


FIG. 84. Bismuth 90, tin 10 per cent.

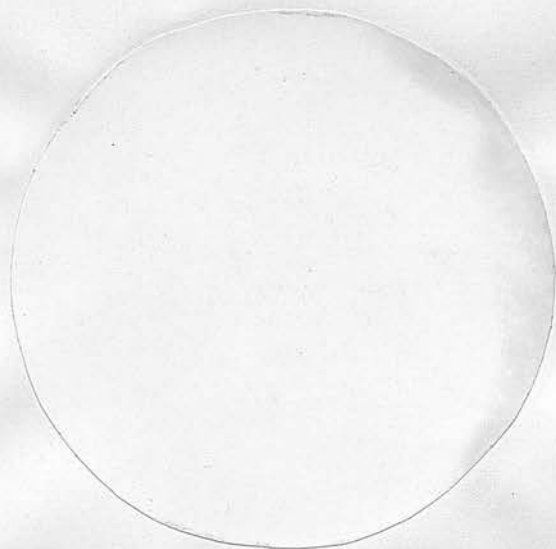


FIG. 85. Bismuth 85, tin 15 per cent.

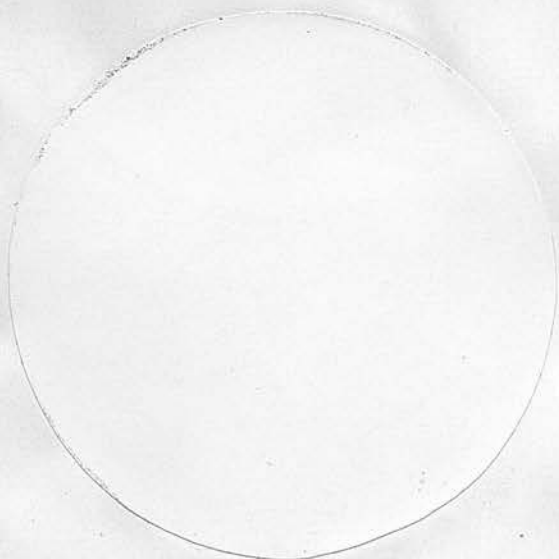


FIG. 86. Bismuth 75, tin 25 per cent.

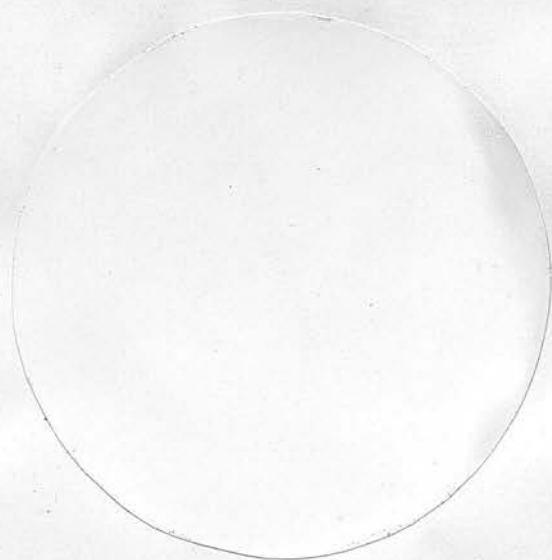


FIG. 87. Bismuth 65, tin 35 per cent.

All chill cast, etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

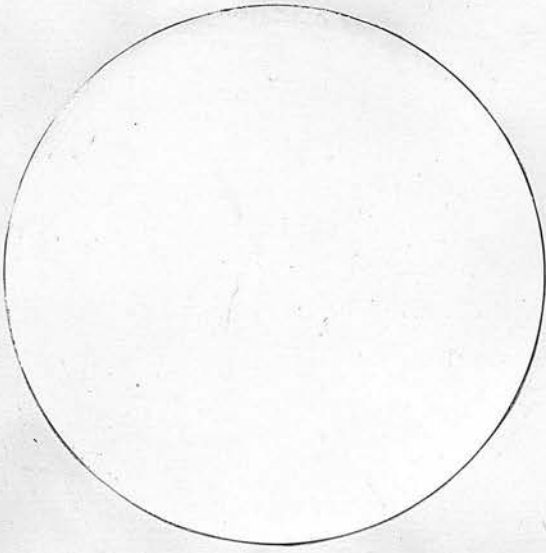


FIG. 88. Copper 85, lead 15 per cent.; chill cast; etched with ammonia; magnified 100 diameters

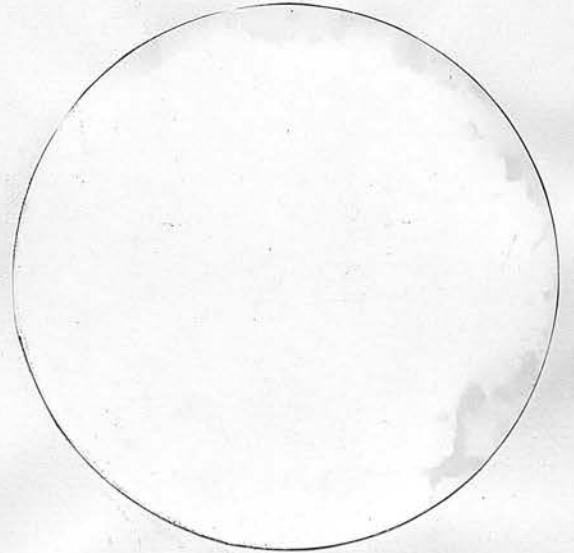


FIG. 89. Copper 85, lead 15 per cent.; slowly cooled; etched with ammonia; magnified 100 diameters.

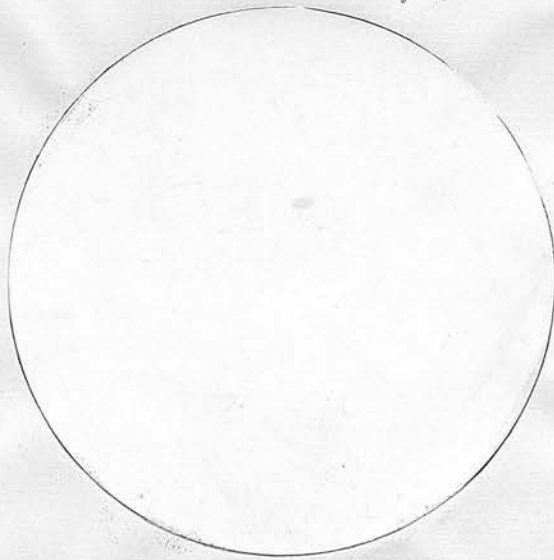


FIG. 90. Bismuth 75, tin 25 per cent.; slowly cooled; etched with nitric acid; magnified 25 diameters

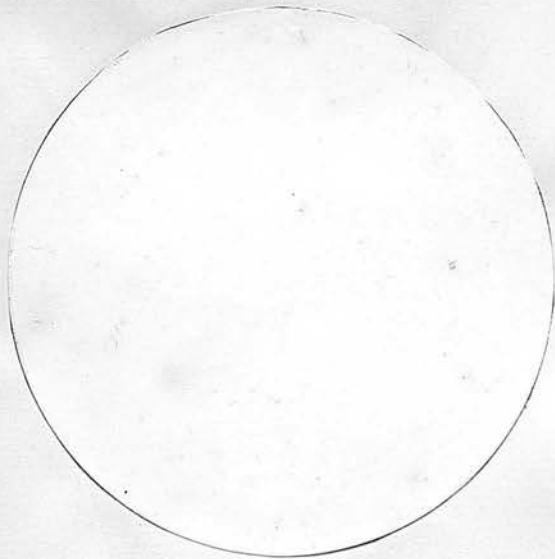


FIG. 91. Copper 25, bismuth 75 per cent.; quickly cooled; etched with nitric acid; magnified 25 diameters.

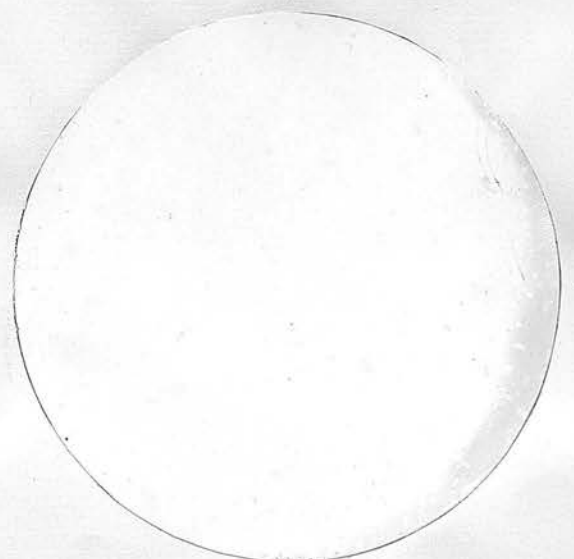


FIG. 92. Copper 25, bismuth 75 per cent.; slowly cooled; etched with nitric acid; magnified 25 diameters.

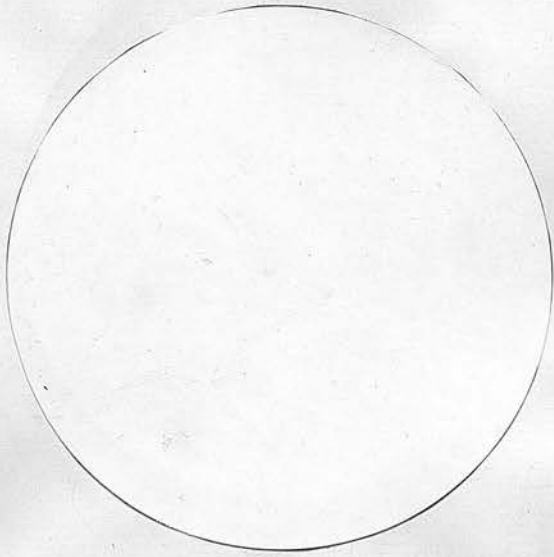


FIG. 93. Copper 99, bismuth 1 per cent; slowly cooled; etched with ammonia; magnified 50 diameters.

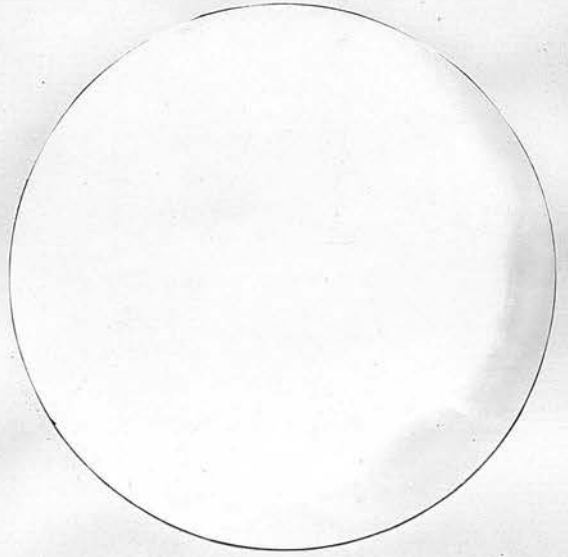


FIG. 94. Copper 99, bismuth 1 per cent; slowly cooled; etched with ammonia and repolished; magnified 100 diameters.

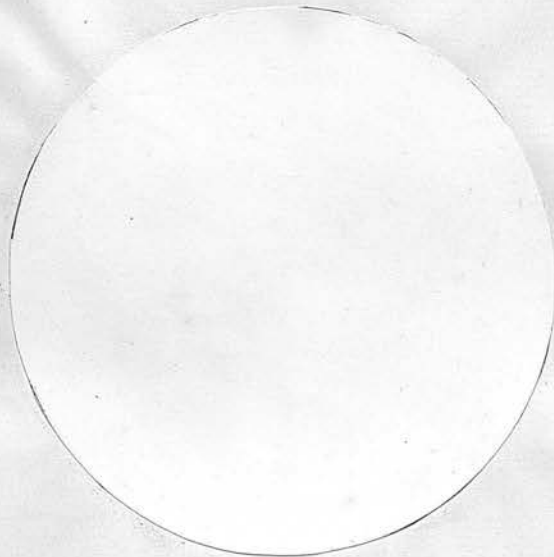


FIG. 95. Copper 96, silver 4 per cent.; slowly cooled; etched with copper-ammonium chloride; magnified 100 diameters.

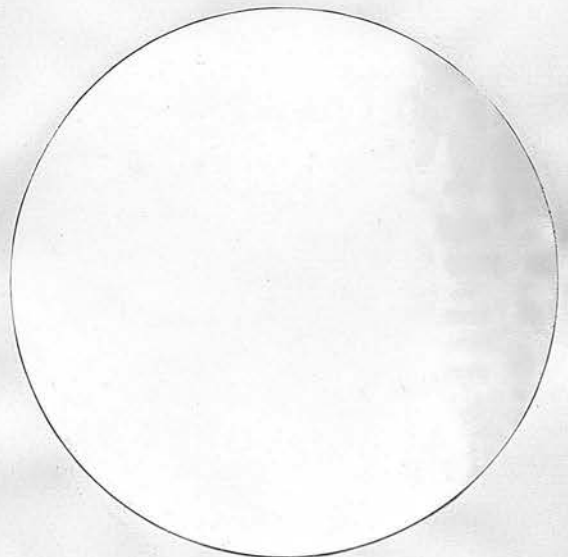


FIG. 96. Copper 90, tin 10 per cent.; slowly cooled; etched with ammonia; magnified 100 diameters.

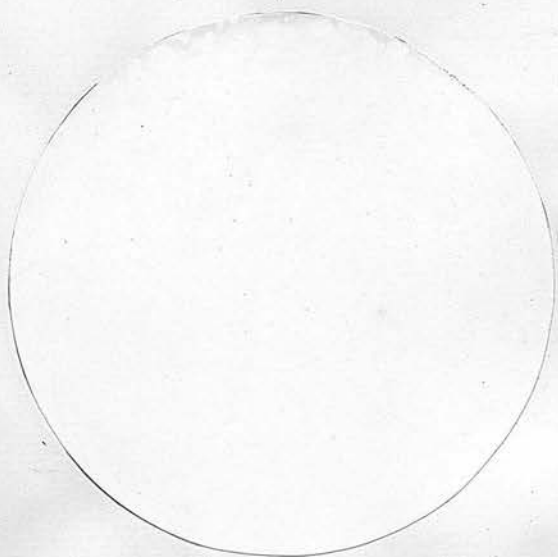


FIG. 97. Lead 83.5, antimony 16.5 per cent.; slowly cooled; etched with picric acid; magnified 50 diameters.

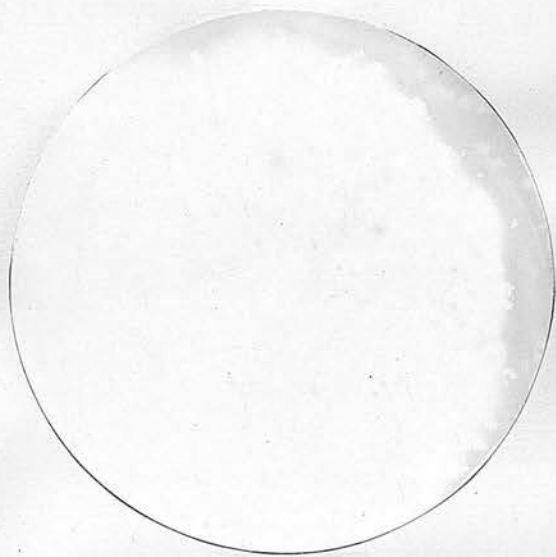


FIG. 98. Lead 83.5, antimony 16.5 per cent.; chill cast; etched with picric acid; magnified 50 diameters.

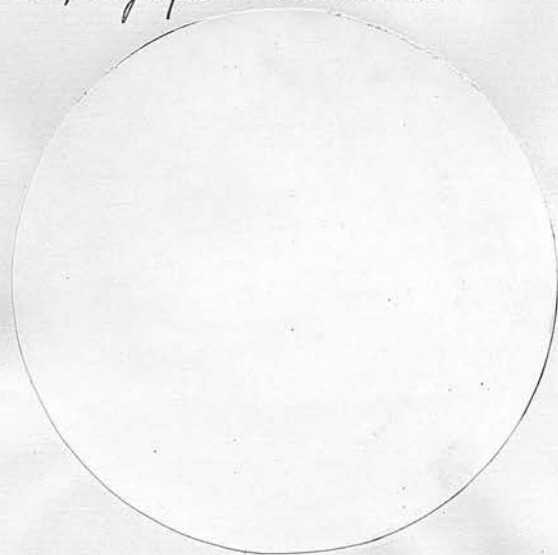


FIG. 99. In 80, antimony 20 per cent.; slowly cooled; etched with nitric acid; magnified 25 diameters.

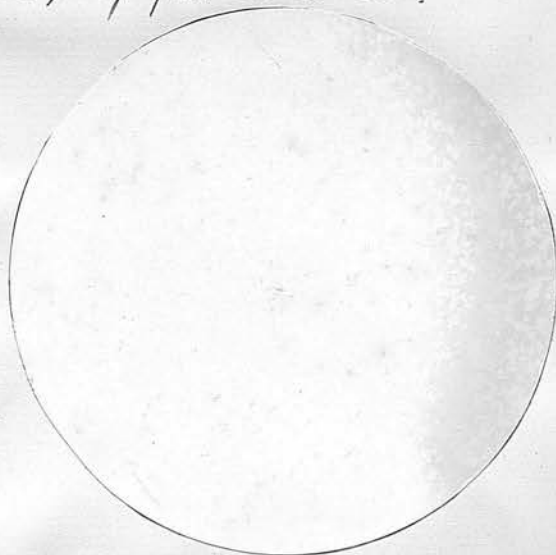


FIG. 100. In 80, antimony 20 per cent.; chill cast; etched with nitric acid; magnified 25 diameters.

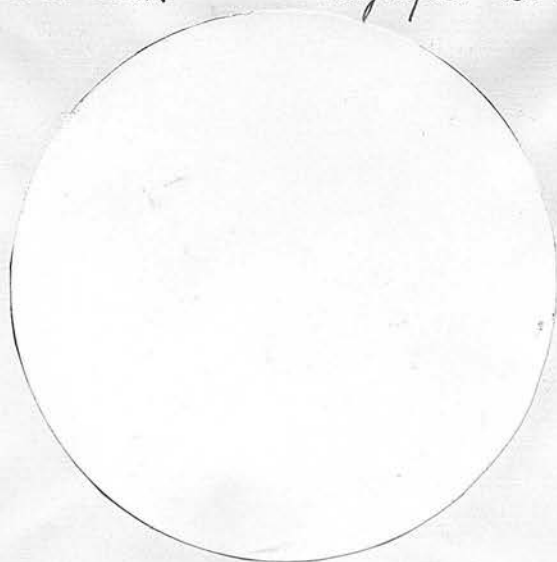


FIG. 101. Copper 70, lead 30 per cent.; chill cast; etched with ammonia and repolished; magnified 100 diameters.

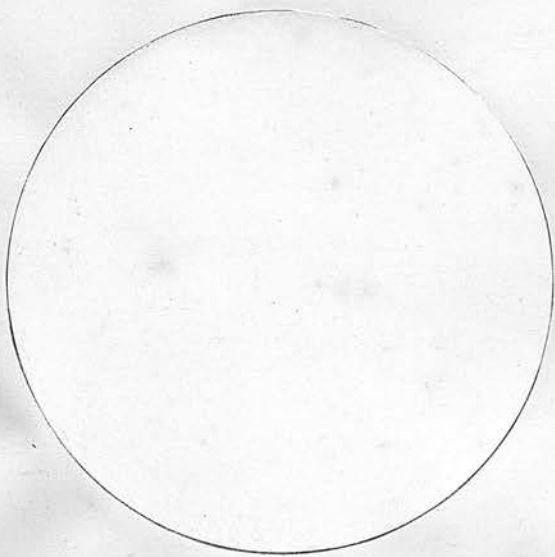


FIG. 102. Copper 88, tin 10, lead 2 percent.; chill cast; etched with ammonia; magnified 25 diameters.

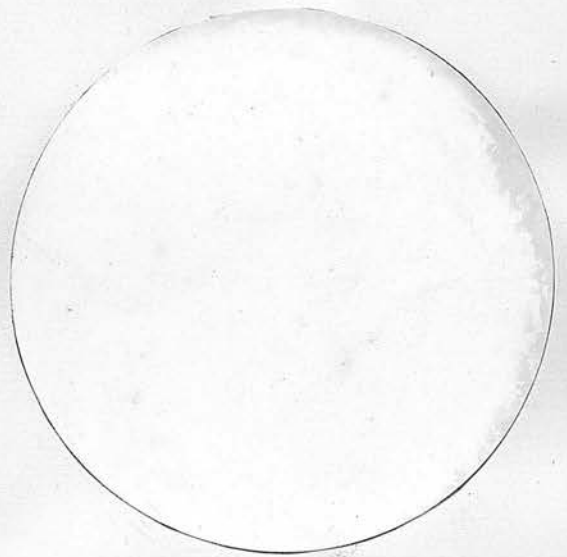


FIG. 103. Copper 88, tin 10, lead 2 percent.; chill cast; etched with ammonia; magnified 100 diameters.

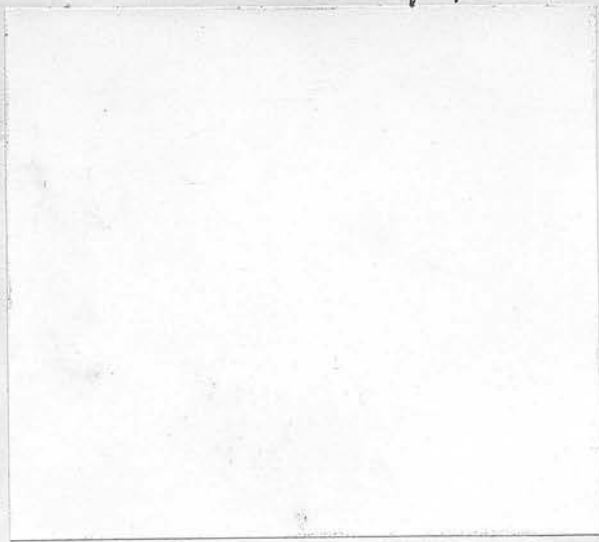


FIG. 104. Surface of impure zinc from galvanizing bath; magnified  $1/2$  diameters.

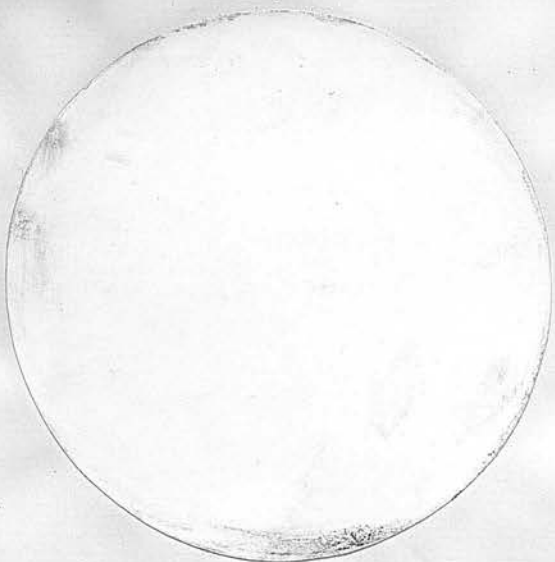


FIG. 105. Copper 59, silver 41 per cent.; slowly cooled; etched with copper-ammonium chloride; magnified 100 diameters.

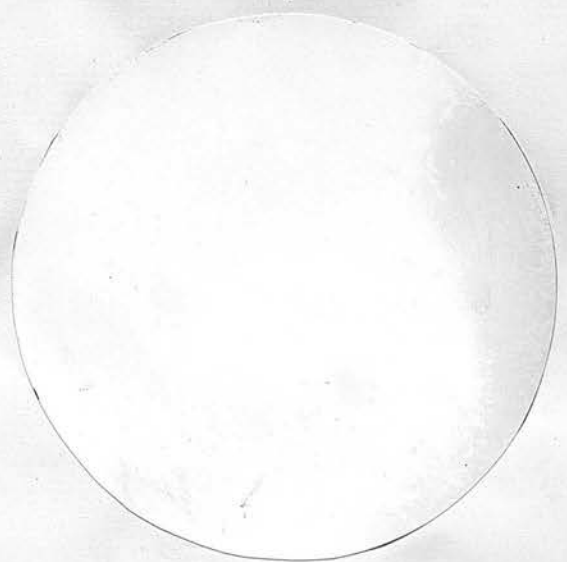


FIG. 106. Copper 58, arsenic 42 percent.; slowly cooled; etched with nitric acid; magnified 100 diameters.

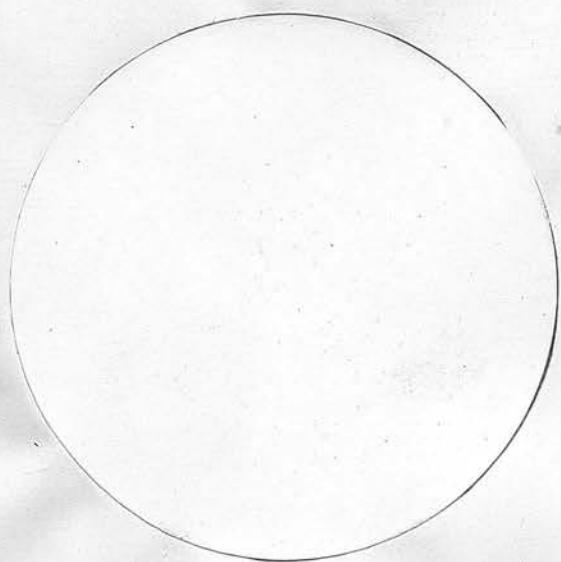


FIG. 107. Bismuth-tin Eutectic; slowly cooled; junction of two grains; etched with ferric chloride; magnified 100 diameters

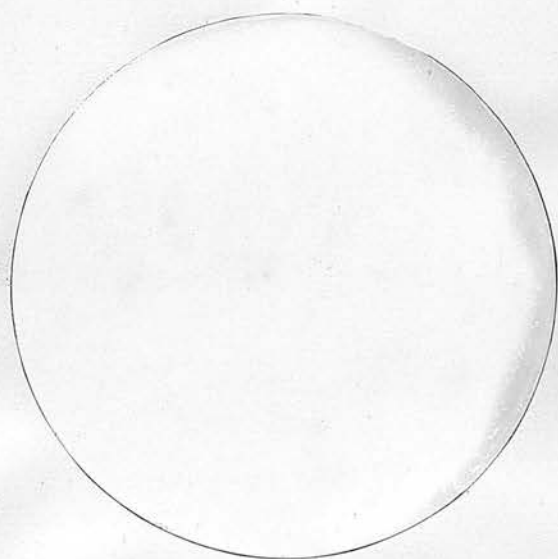


FIG. 108. Lead-antimony Eutectic; slowly cooled; etched with picric acid; magnified 100 diameters.

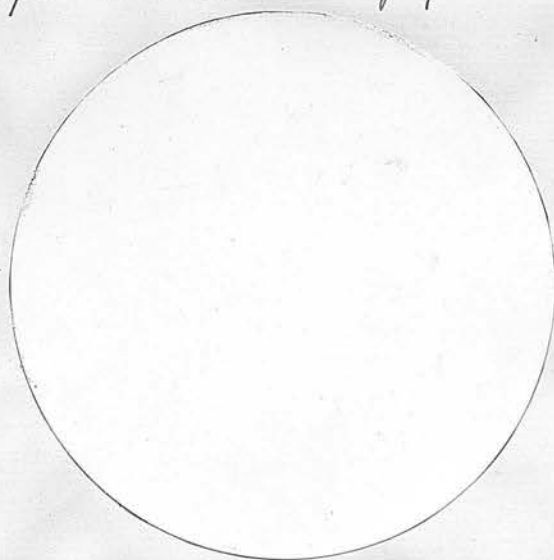


FIG. 109. Copper-antimony Eutectic; slowly cooled; etched with nitric acid; magnified 100 diameters.

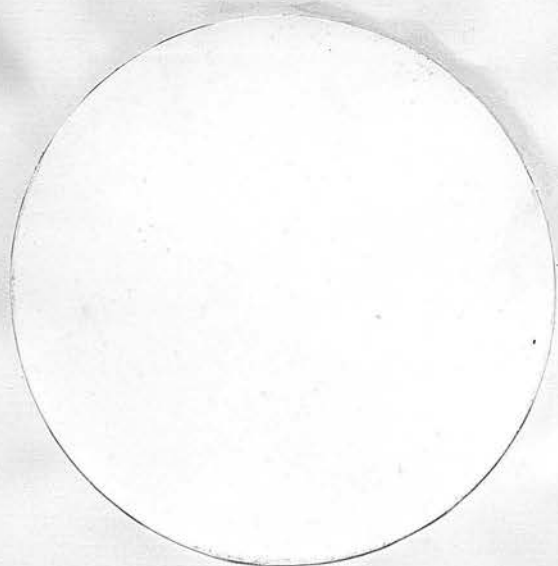


FIG. 110. Bismuth-tin Eutectic; slowly cooled; etched with nitric acid; magnified 75 diameters.

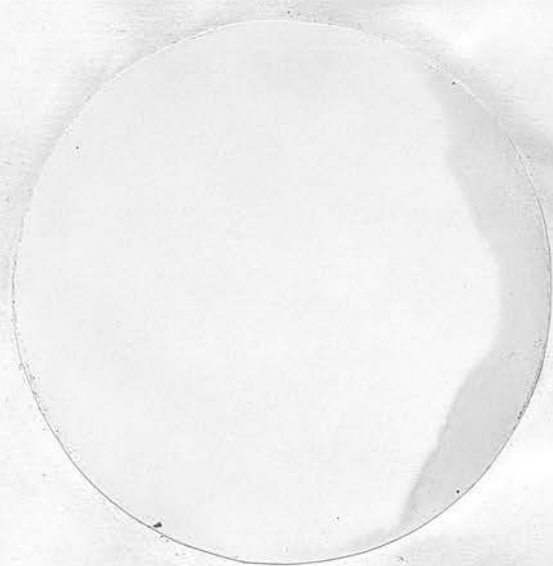


FIG. 111. Bismuth-tin Eutectic; slowly cooled; pseudomorphs of tin; etched with ferric chloride; magnified 100 diameters.



FIG. 112. Bismuth-tin Eutectic; slowly cooled; bottom of ingot; etched with ferric chloride; magnified 5 diameters.

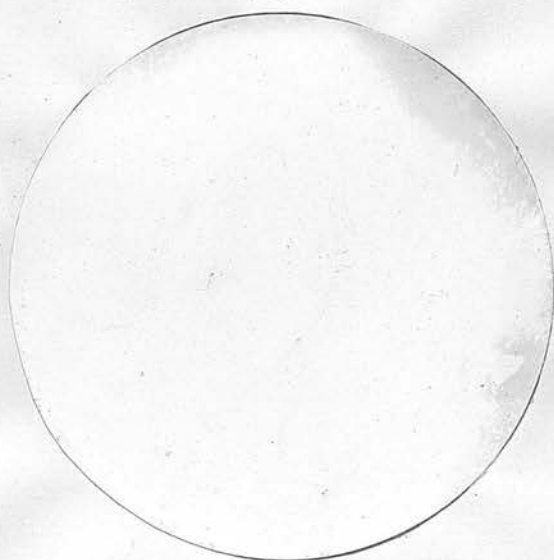


FIG. 113. Bismuth-tin Eutectic; slowly cooled; etched with ferric chloride; magnified 100 diameters.

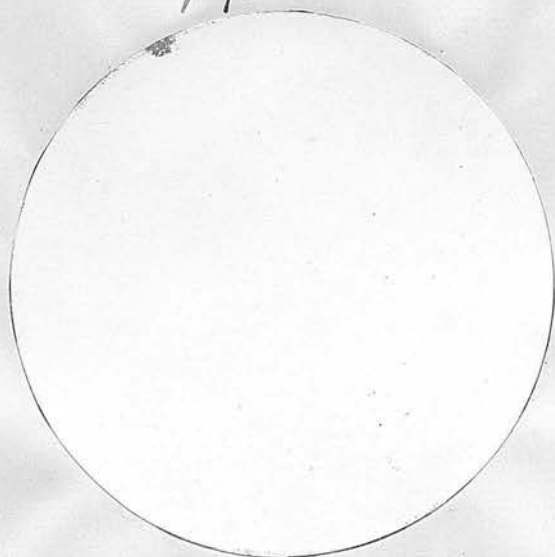


FIG. 114. Tin, slowly cooled; surface of ingot; magnified 10 diameters.



FIG. 115. Copper-silver Eutectic; slowly cooled; etched with copper-ammonium chloride; magnified  $7\frac{1}{2}$  diameters.



FIG. 116. Copper-arsenic Eutectic; slowly cooled; etched with copper-ammonium chloride; magnified  $7\frac{1}{2}$  diameters.

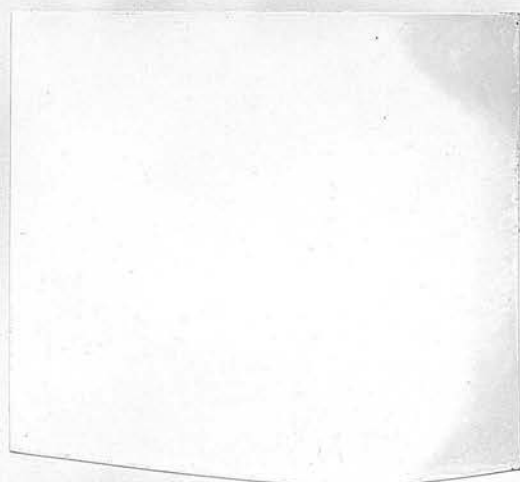


FIG. 117. Copper-antimony Eutectic; slowly cooled; etched with ferric chloride; magnified  $7\frac{1}{2}$  diameters.

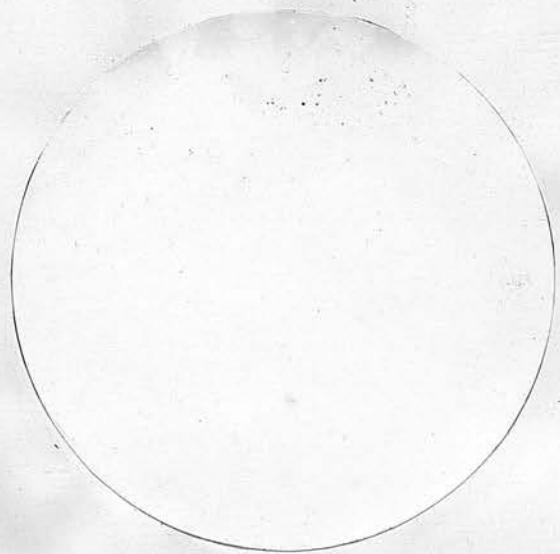


FIG. 118. Copper-arsenic Eutectic; slowly cooled; radiate formation; etched with copper-ammonium chloride; magnified 100 diameters.

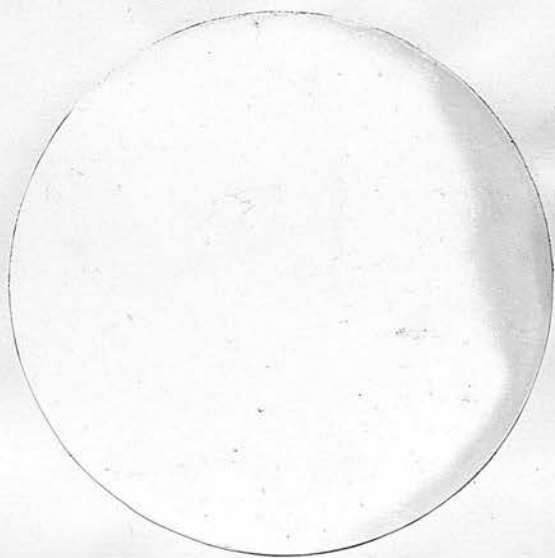


FIG. 119. Copper-antimony Eutectic; slowly cooled; feathery formation; etched with ferric chloride; magnified 20 diameters.

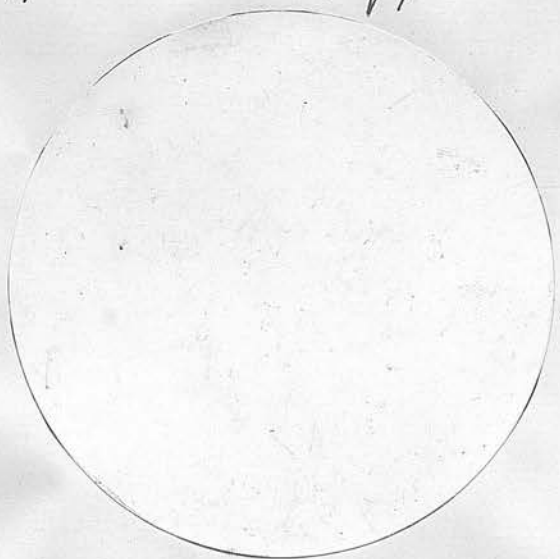


FIG. 120. Copper-antimony Eutectic; slowly cooled; etched with ferric chloride; magnified 100 diameters.

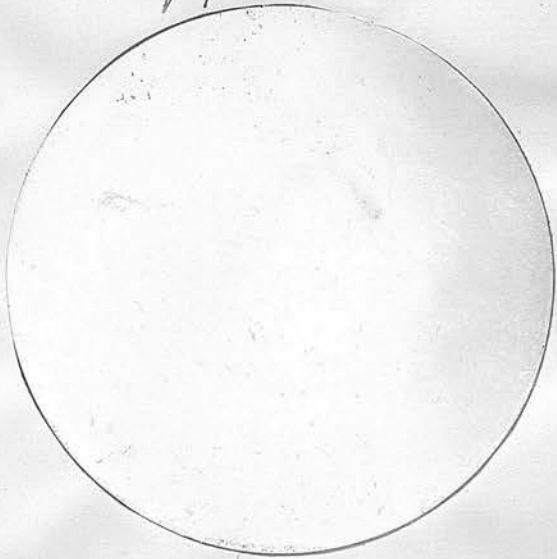


FIG. 121. Bismuth-tin Eutectic; slowly cooled; feathery formation; etched with ferric chloride; magnified 100 diameters.

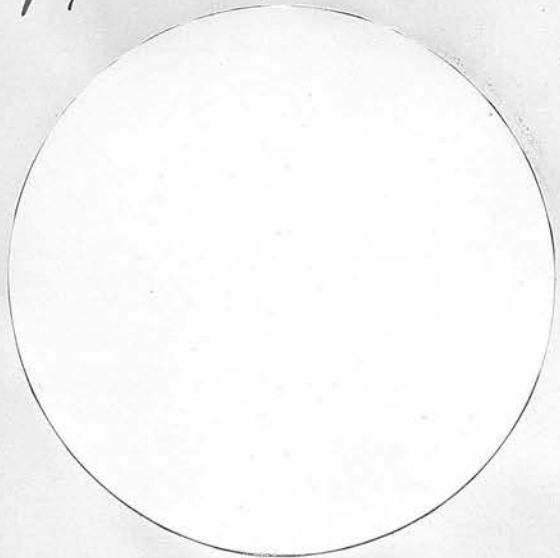


FIG. 122. Bismuth-tin Eutectic; slowly cooled; etched with nitric acid; magnified 100 diameters.

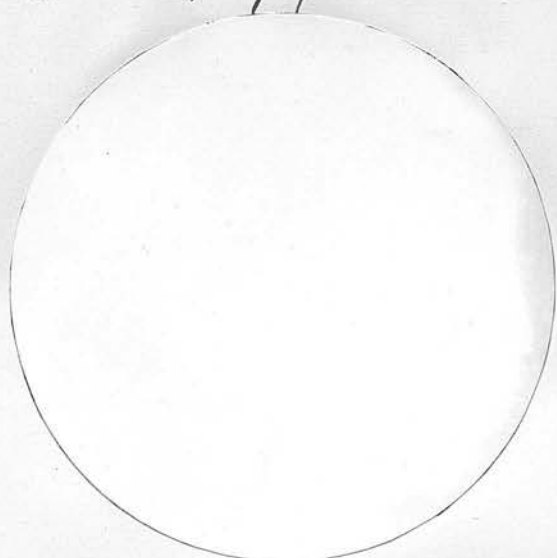


FIG. 123. Bismuth-tin Eutectic; slowly cooled; tin and bismuth crystals in contact; etched with nitric acid; magnified 150 diameters.

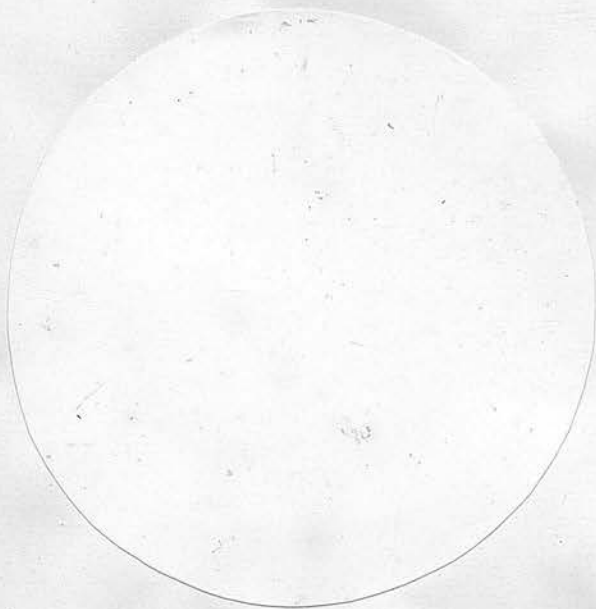


FIG. 124. Copper-antimony eutectic; chill cast from  $550^{\circ}$ ; etched with ferric chloride; magnified  $7\frac{1}{2}$  diameters.

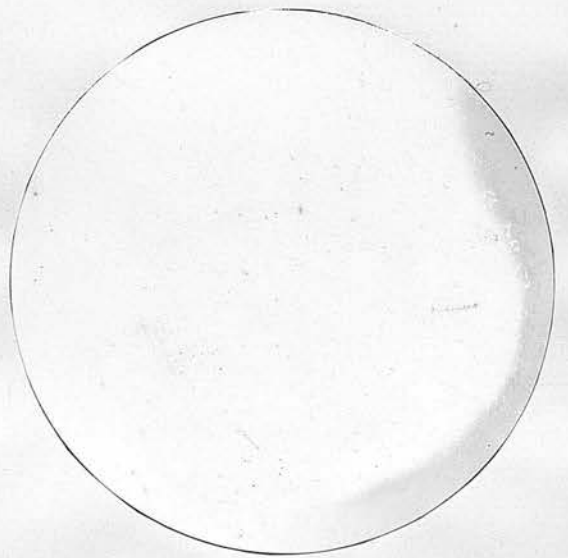


FIG. 125. Copper-antimony eutectic; chill cast from  $550^{\circ}$ ; etched with ferric chloride; magnified 100 diameters.

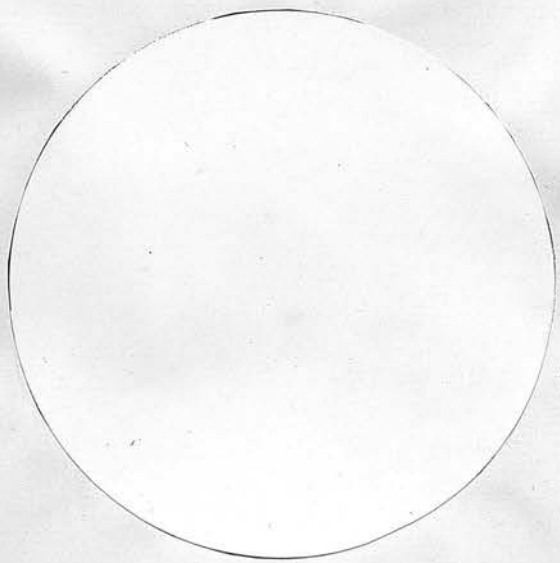


FIG. 126. Lead-antimony eutectic; chill cast from  $260^{\circ}$ ; etched with nitric acid and lightly repolished; magnified 100 diameters.

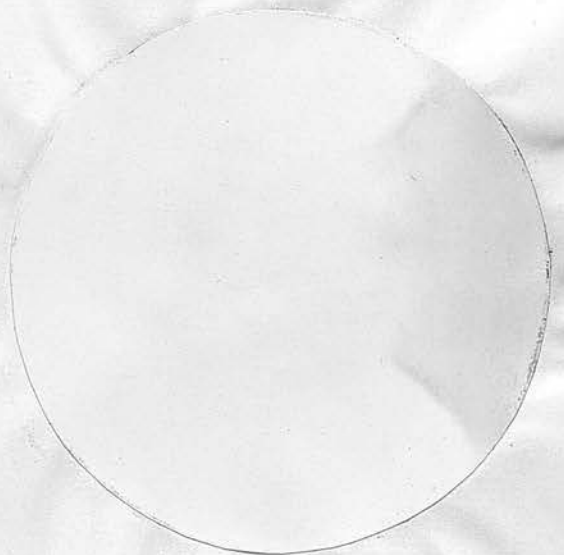


FIG. 127. Bismuth-tin eutectic; slowly cooled; middle of ingot; etched with ferric chloride; magnified 100 diameters.

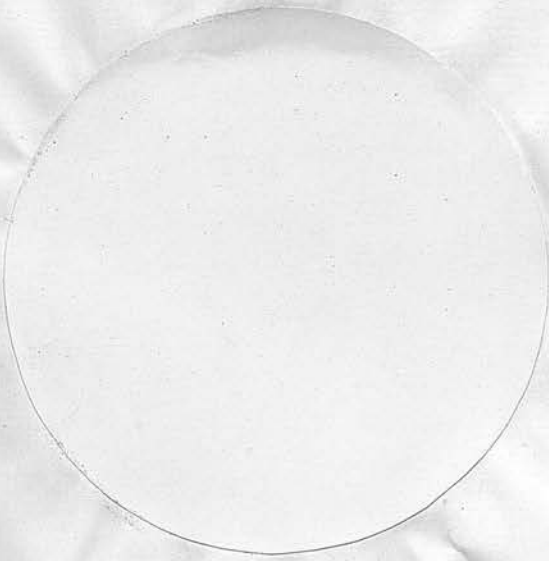


FIG. 128. Middle of ingot.

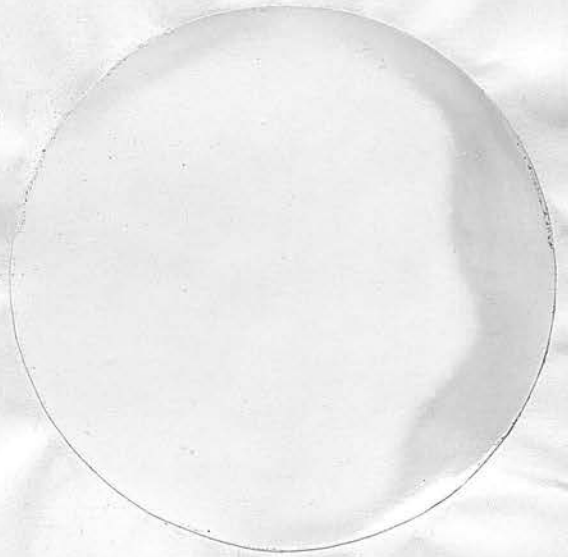


FIG. 129. Edge of ingot.

*Chill cast from 160°*

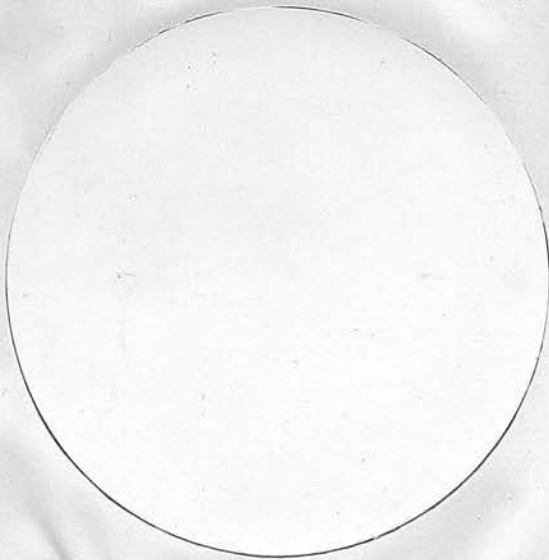


FIG. 130. Middle of ingot

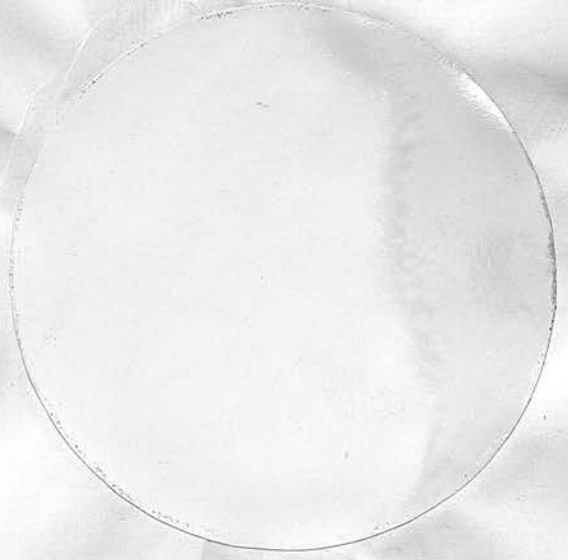


FIG. 131. Edge of ingot

*Chill cast from 300°*

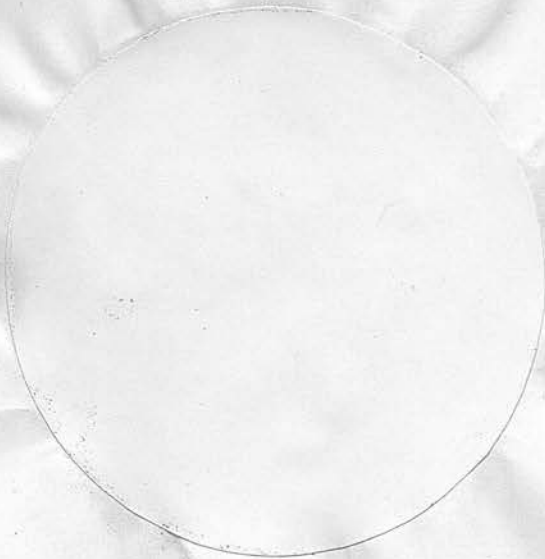


FIG. 132. Middle of ingot.

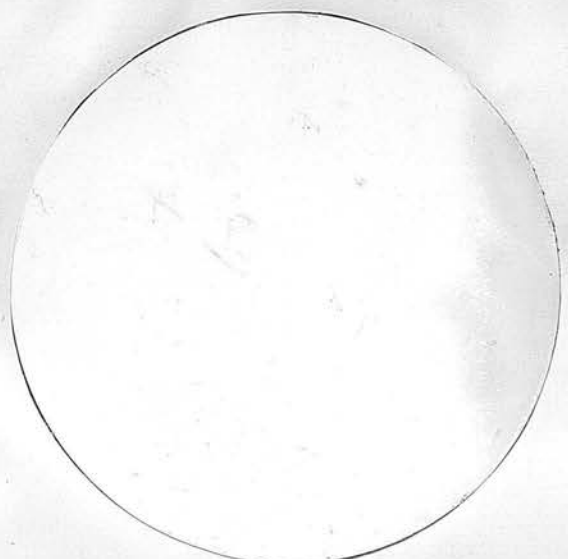


FIG. 133. Edge of ingot.

*Chill cast from 750°*

*Bismuth-tin Eutectic ; all etched with ferric chloride, and magnified 100 diameters*

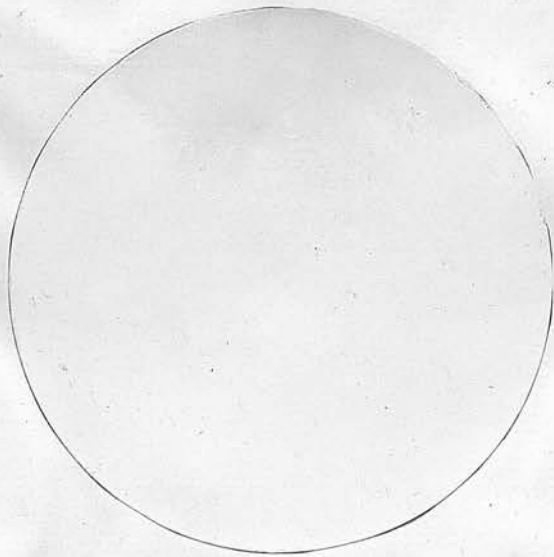


FIG. 134. Slowly cooled; middle of ingot.

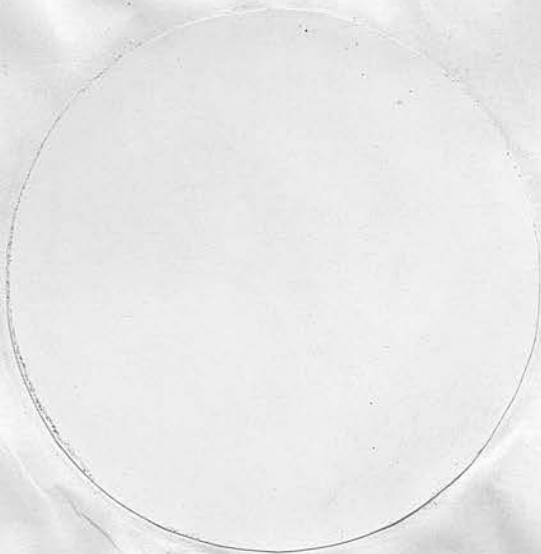


FIG. 135. Middle of ingot.

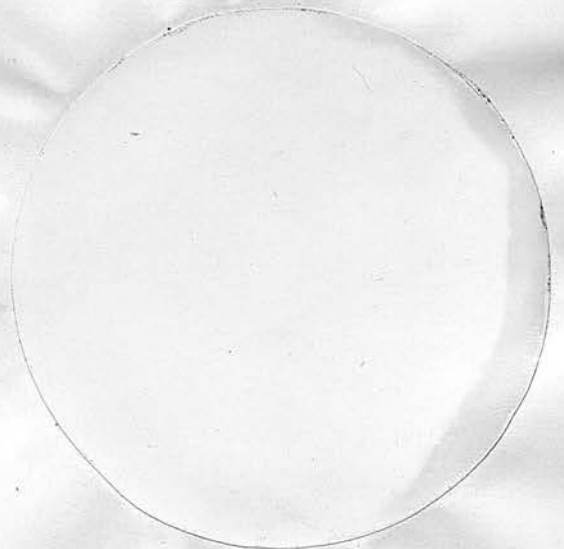


FIG. 136. Edge of ingot.

Chill cast from 160°.

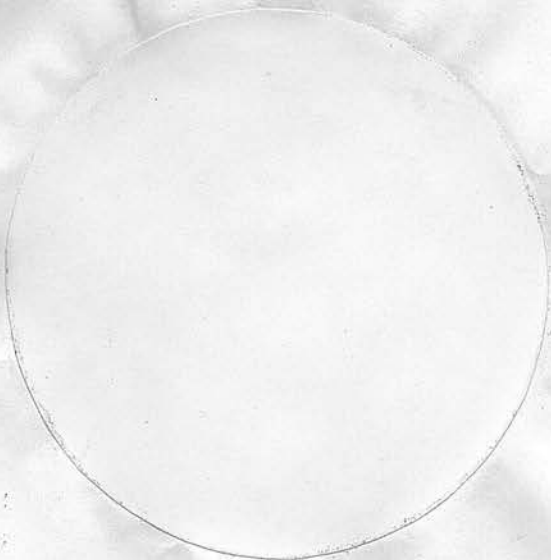


FIG. 137. Middle of ingot.

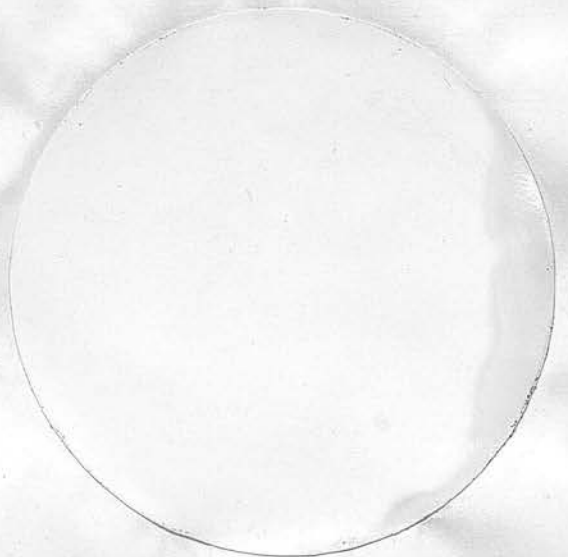


FIG. 138. Edge of ingot.

Chill cast from 300°.

Bismuth 60, tin 40 percent.; all etched with ferric chloride, and magnified 100 diameters



FIG. 139. Slowly cooled.  
magnified  $7\frac{1}{2}$  diameters

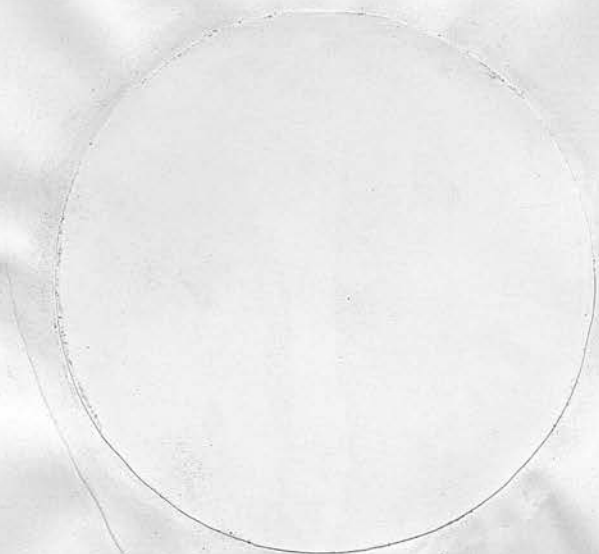


FIG. 140. Shear bottom of ingot.

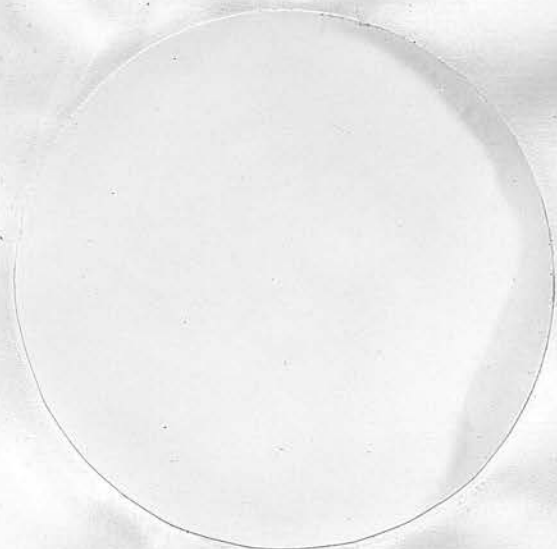


FIG. 141. Edge of layer of bismuth crystals.

Slowly cooled.

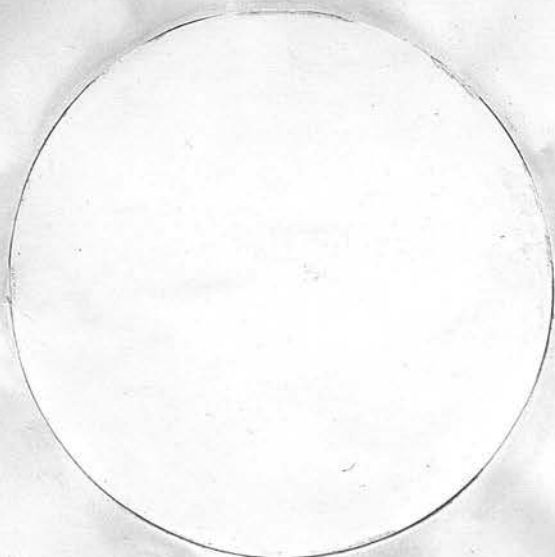


FIG. 142. Middle of ingot.

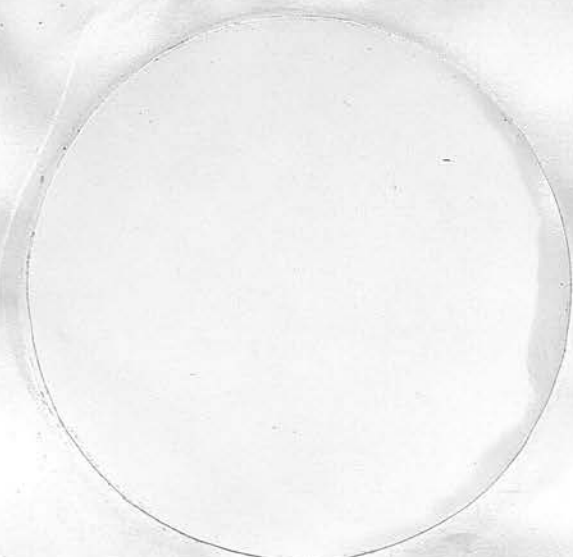


FIG. 143. Edge of ingot.

Chill cast from  $160^{\circ}$

Bismuth 70, tin 30 percent.; all etched with ferric chloride, and magnified 100 diameters

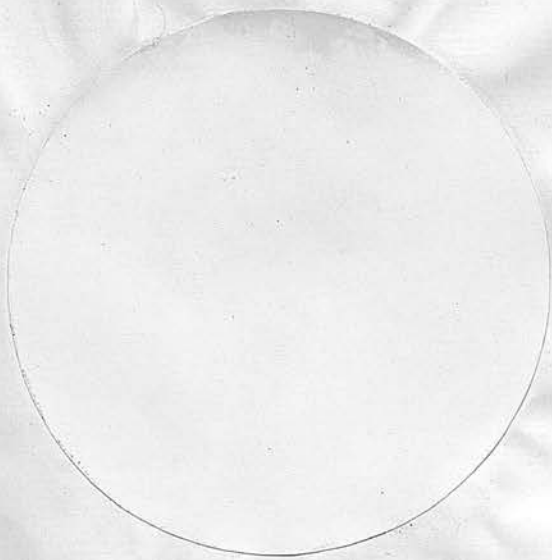


FIG. 144. Middle of ingot.  
Bismuth 70, tin 30 per cent.; chill cast from  $300^{\circ}$ ; etched with ferric chloride; magnified  
100 diameters.

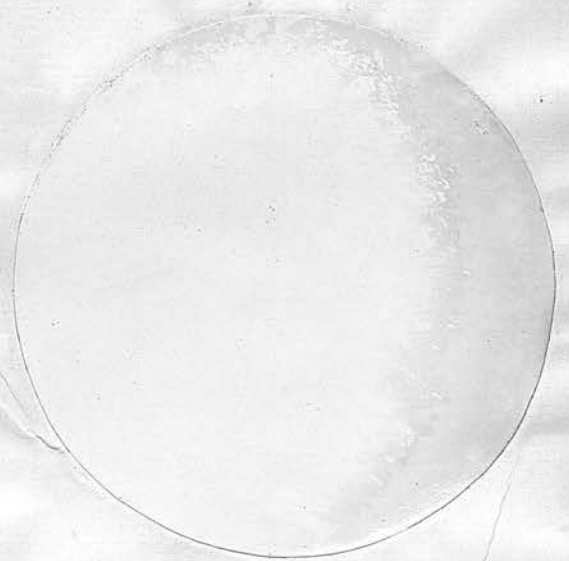


FIG. 145. Edge of ingot.

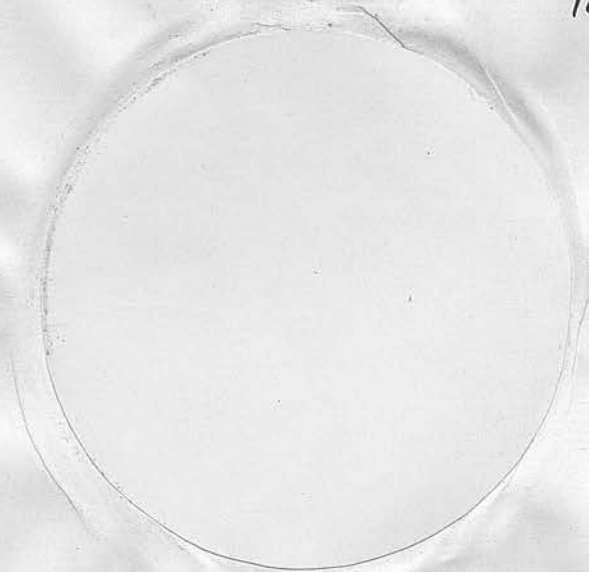


FIG. 146. Top of ingot.  
Slowly cooled



FIG. 147. Bottom of ingot

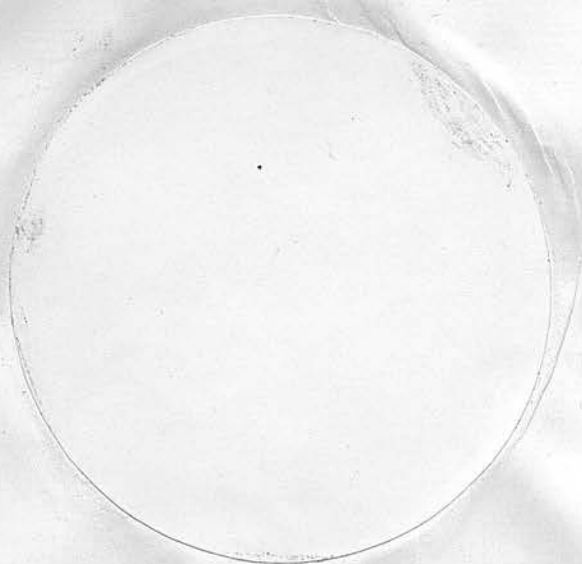


FIG. 148. Middle of ingot.  
Chill cast from  $160^{\circ}$

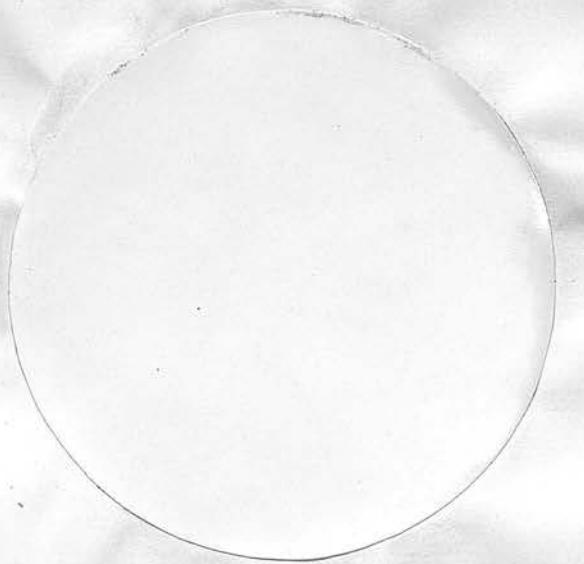


FIG. 149. Edge of ingot.

Bismuth 55, tin 45 per cent.; all etched with ferric chloride, and magnified 100 diameters.

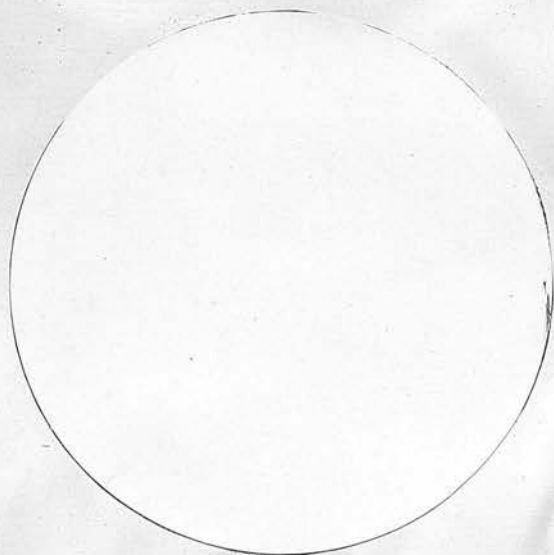


FIG. 150. Bismuth 55, tin 45 per cent.; chill cast from  $300^{\circ}$ ; etched with nitric acid; magnified 25 diameters.

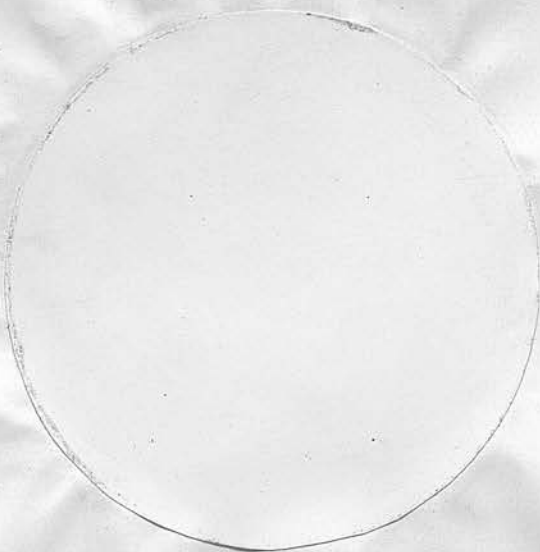


FIG. 151. Middle of ingot.

Chill cast from  $300^{\circ}$

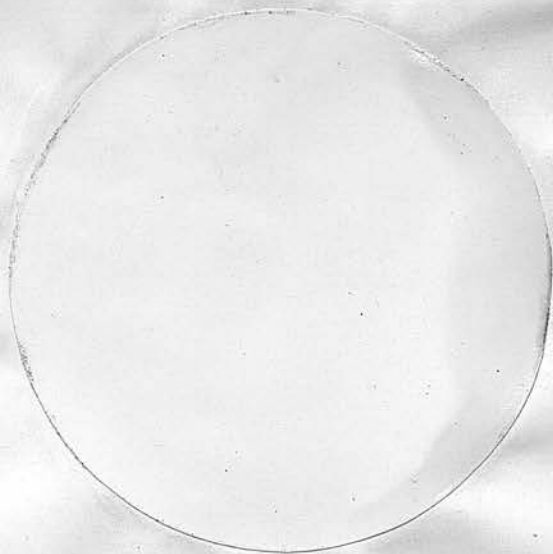


FIG. 152. Edge of ingot.

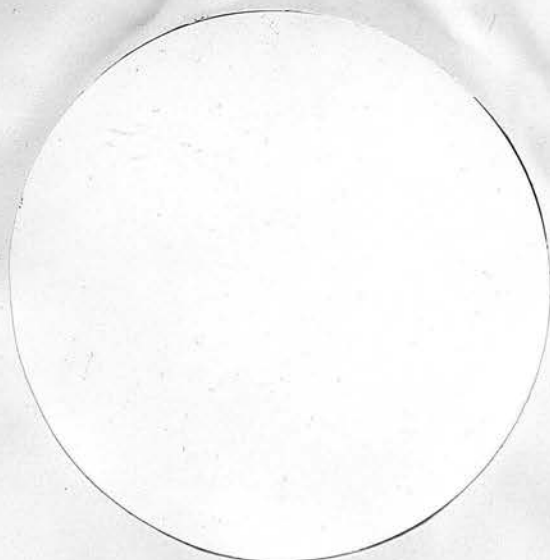


FIG. 153. Middle of ingot.

Chill cast from  $750^{\circ}$

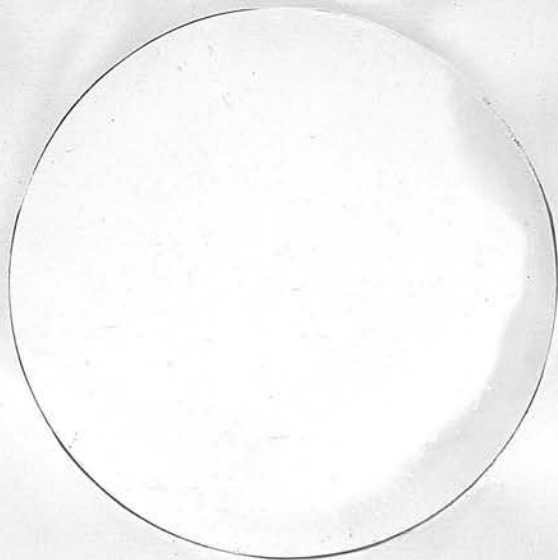


FIG. 154. Edge of ingot.

Bismuth 55, tin 45 per cent.; all etched with ferric chloride, and magnified 100 diameters.

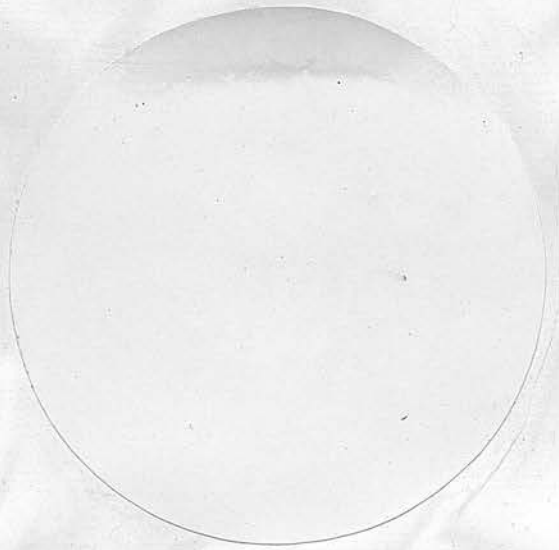


FIG. 155. Slowly cooled; middle of ingot.

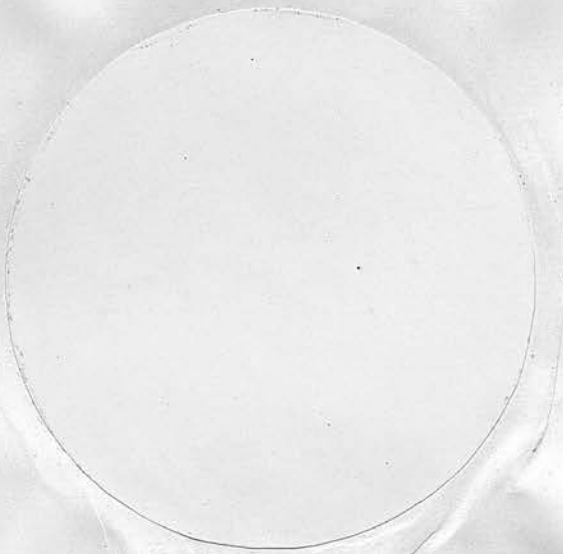


FIG. 156. Middle of ingot.

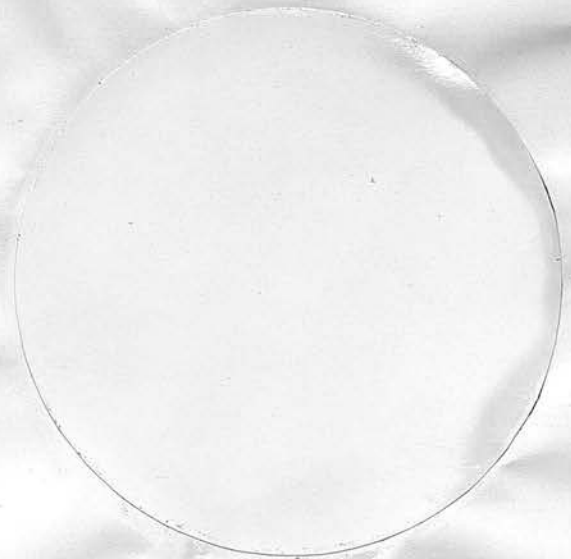


FIG. 157. Edge of ingot.

Chill cast from  $160^{\circ}$

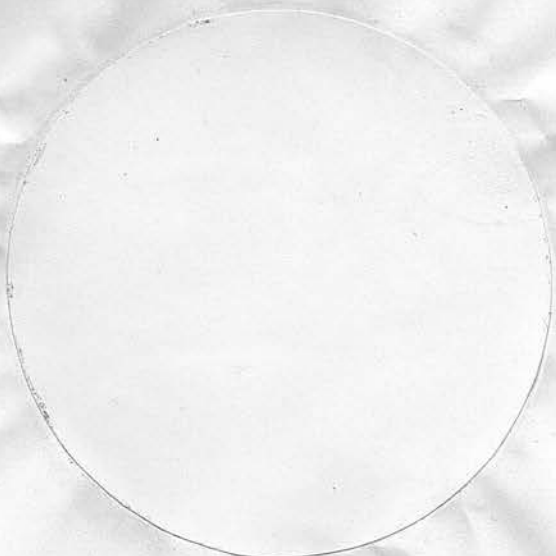


FIG. 158. Middle of ingot.

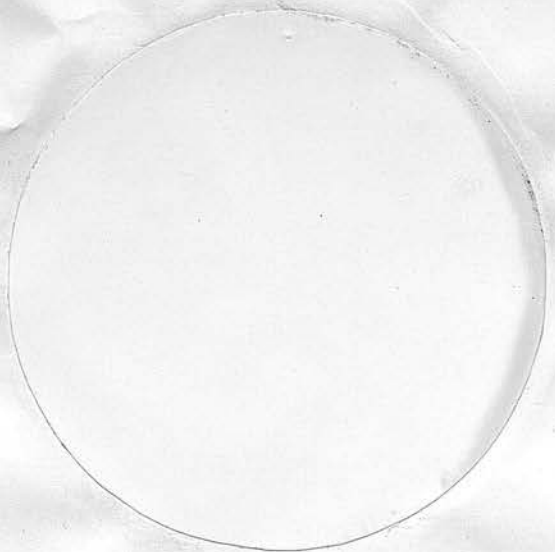


FIG. 159. Edge of ingot.

Chill cast from  $300^{\circ}$

Bismuth 50, tin 50 per cent.; all etched with ferric chloride, and magnified 100 diameters

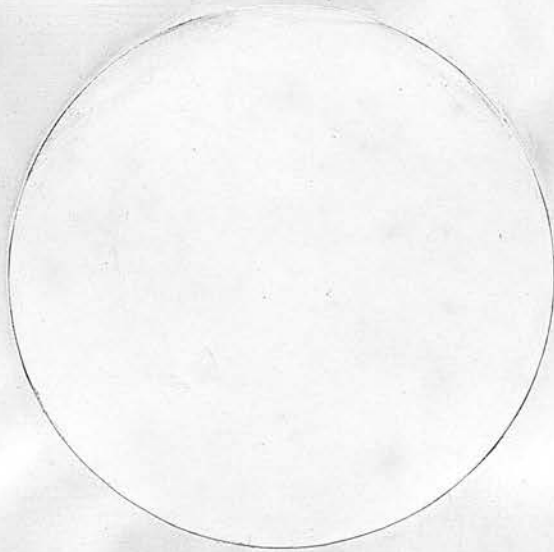


FIG. 160. Antimony 55, tin 45 percent; chill cast; etched with ferric chloride; magnified 100 diameters.

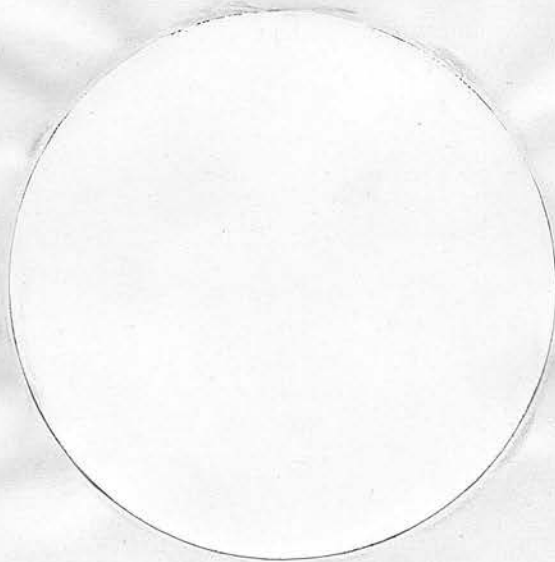


FIG. 161. Antimony 55, tin 45 percent.; slowly cooled; etched with caustic potash; magnified 100 diameters.

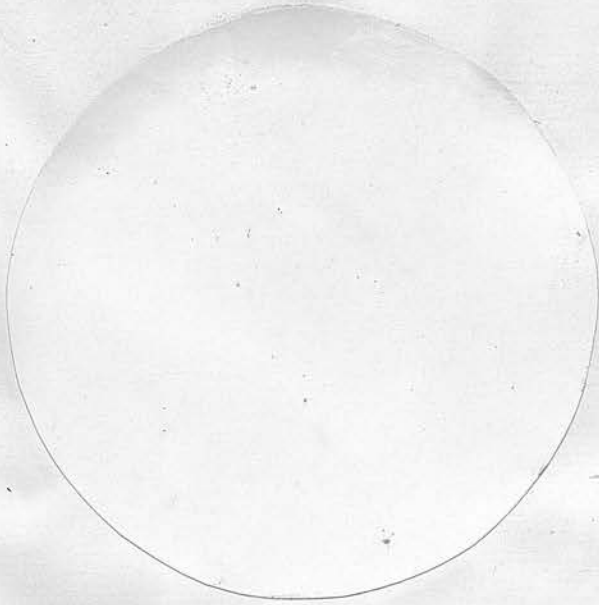


FIG. 162. Chill cast.

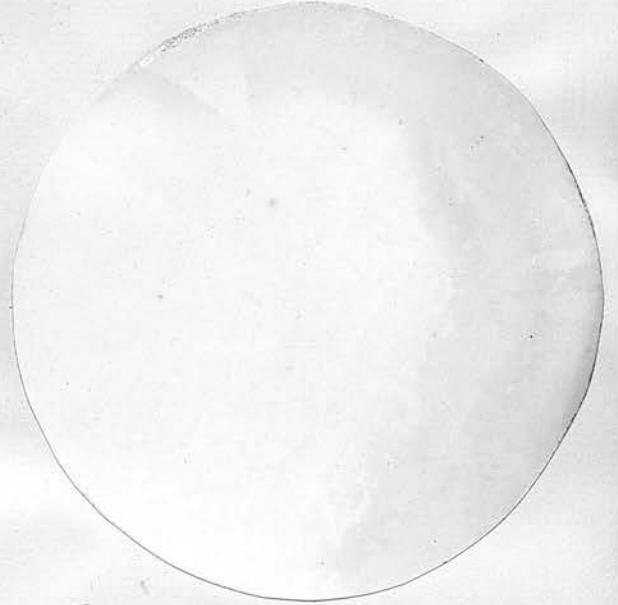


FIG. 163. Annealed at 140° for 100 hours.

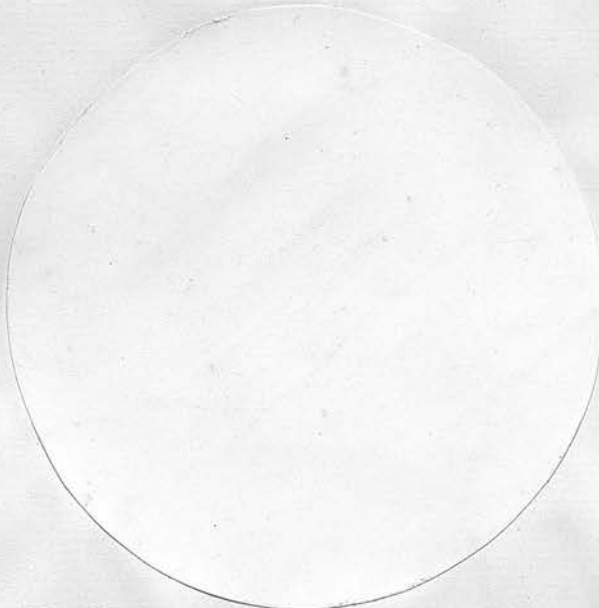


FIG. 164. Annealed at 140° for 200 hours

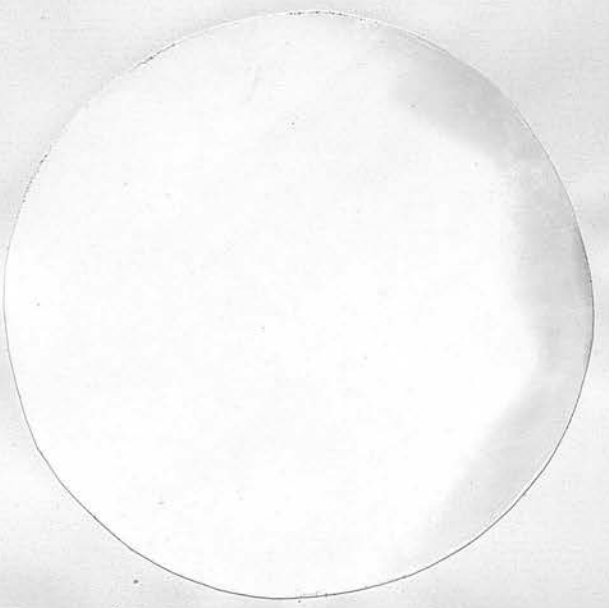


FIG. 165. Annealed at 140° for 400 hours.

Bismuth, chill cast and annealed; all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

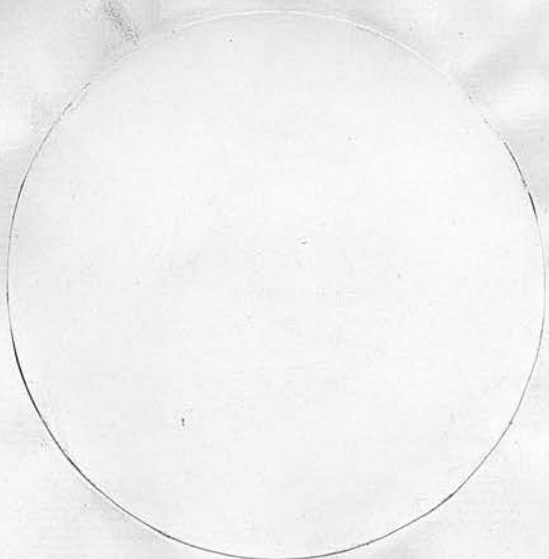


FIG. 166. Bismuth, showing recrystallized surface film; etched with nitric acid; magnified 100 diameters.

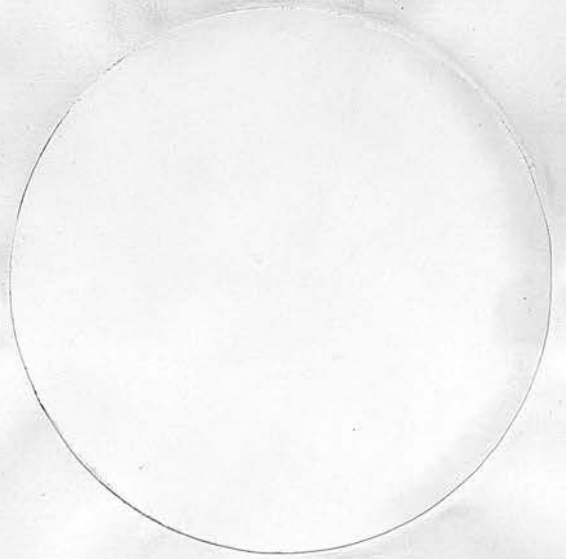


FIG. 167. Bismuth, with Surface film almost removed; etched with nitric acid; magnified 100 diameters.

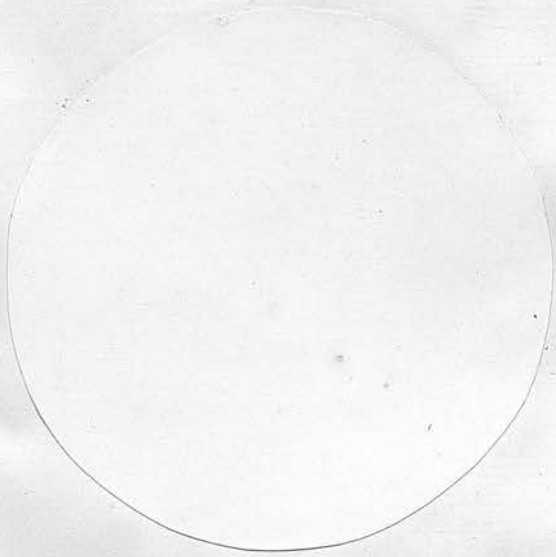


FIG. 168. Slowly cooled.

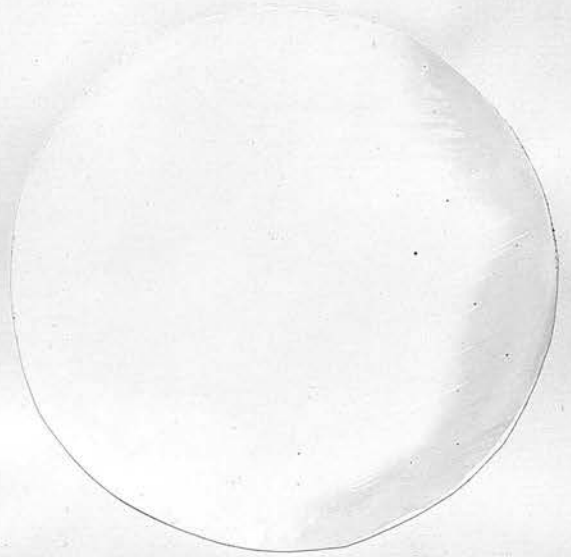


FIG. 169. Annealed at  $140^{\circ}$  for 100 hours

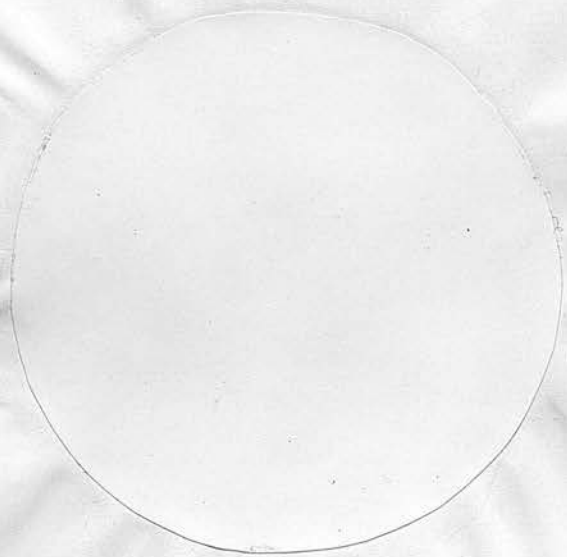


FIG. 170. Annealed at  $140^{\circ}$  for 200 hours.

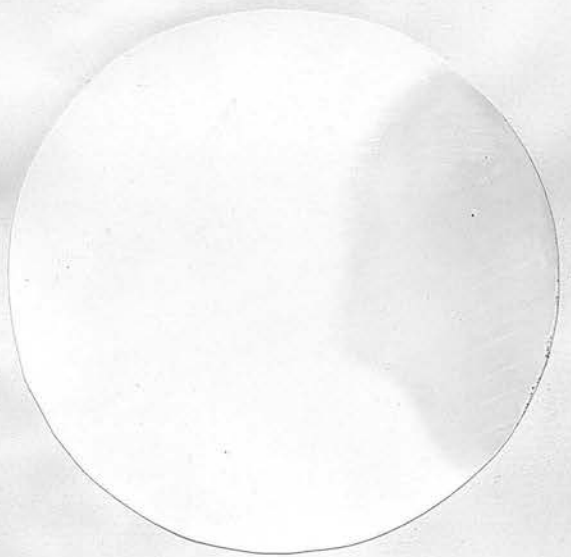


FIG. 171. Annealed at  $140^{\circ}$  for 400 hours.

Dismuth, slowly cooled and annealed; all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters

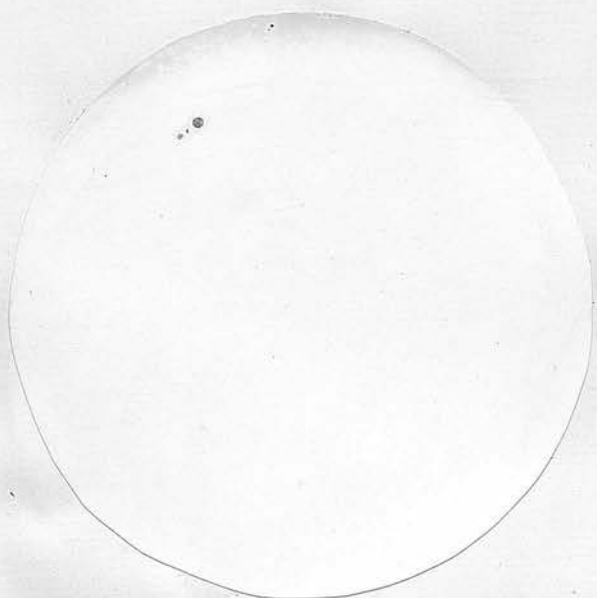


FIG. 172. Annealed at  $140^{\circ}$  for 100 hours

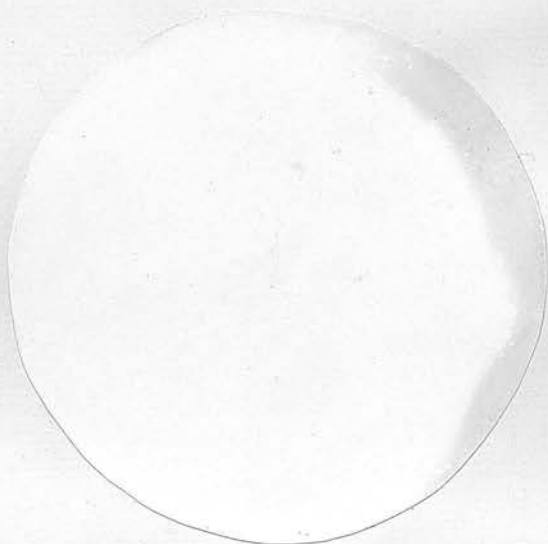


FIG. 175. Annealed at  $140^{\circ}$  for 100 hours

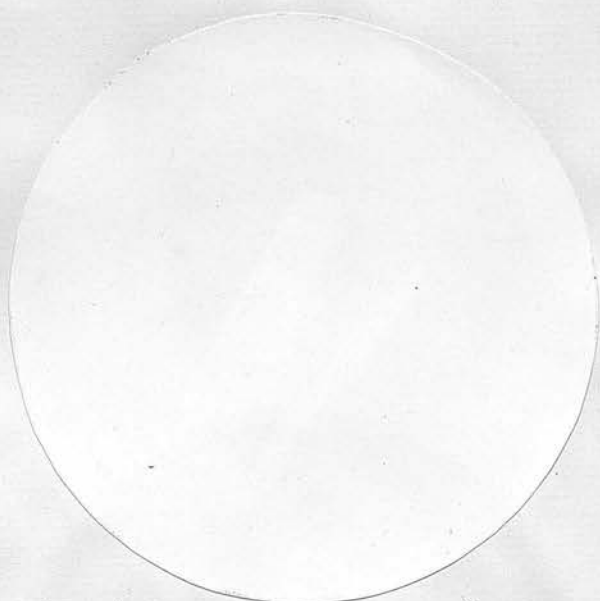


FIG. 173. Annealed at  $140^{\circ}$  for 200 hours

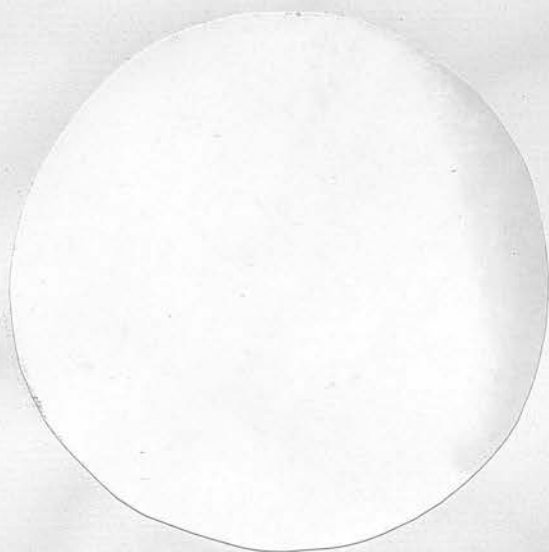


FIG. 176. Annealed at  $140^{\circ}$  for 200 hours

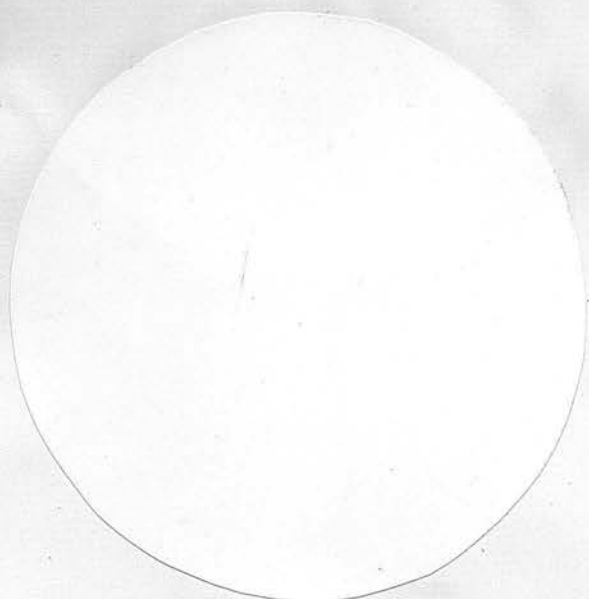


FIG. 174. Annealed at  $140^{\circ}$  for 400 hours.

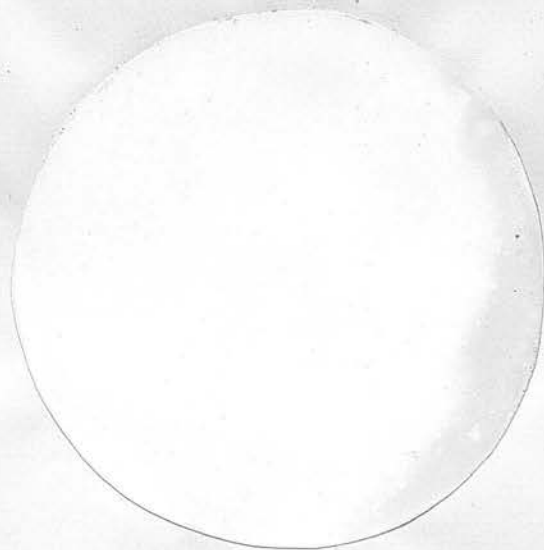


FIG. 177. Annealed at  $140^{\circ}$  for 400 hours.

Cadmium, etched with iodine, and magnified  $7\frac{1}{2}$  diameters  
 Chill cast slowly cooled.

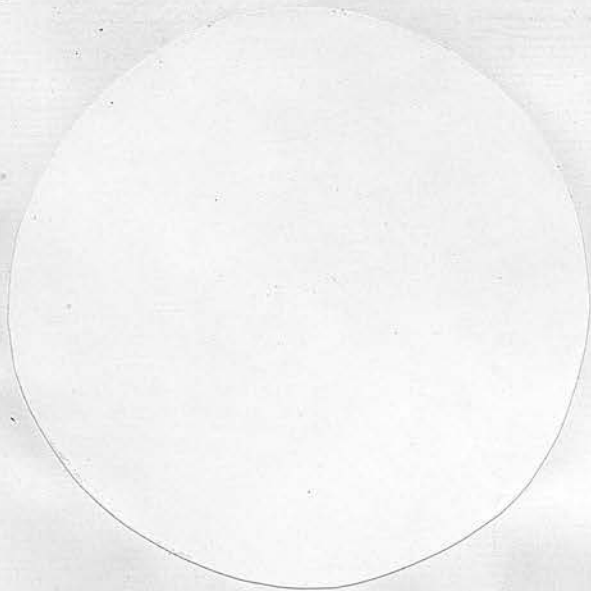


FIG. 178. Chill cast.

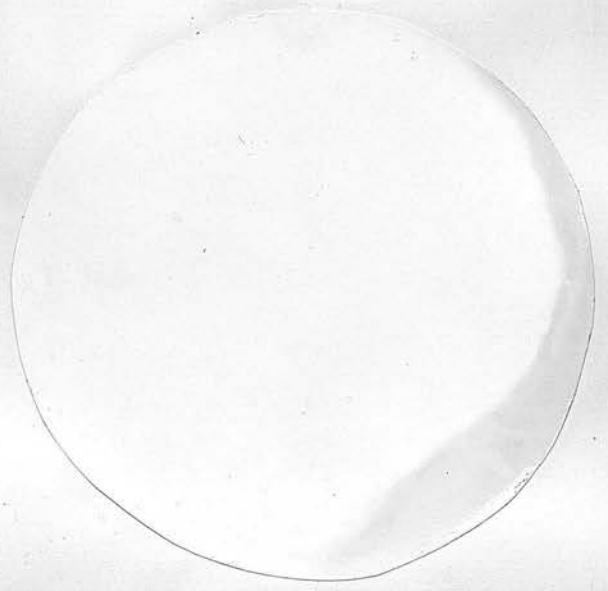


FIG. 179. Annealed at  $140^{\circ}$  for 100 hours

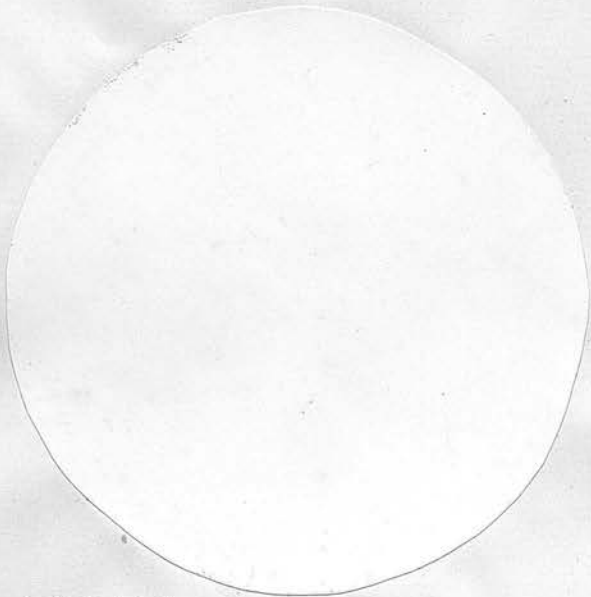


FIG. 180. Annealed at  $140^{\circ}$  for 200 hours.

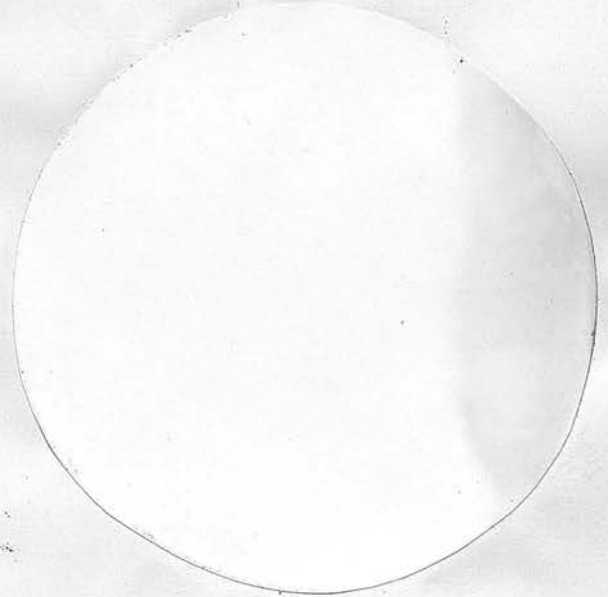


FIG. 181. Annealed at  $140^{\circ}$  for 400 hours.

*2 in.*, chill cast and annealed; all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters

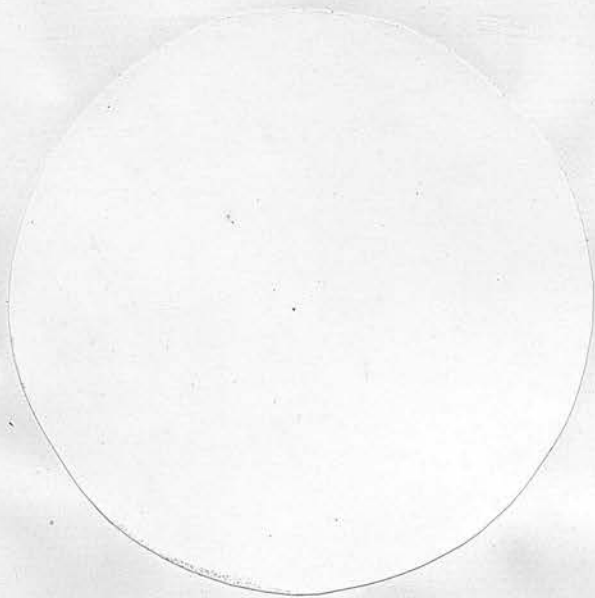


FIG. 182. Slowly cooled.

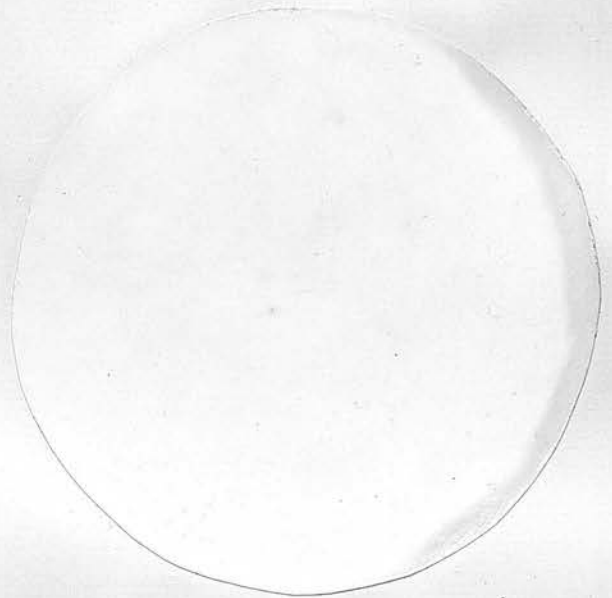


FIG. 183. Annealed at  $140^{\circ}$  for 100 hours

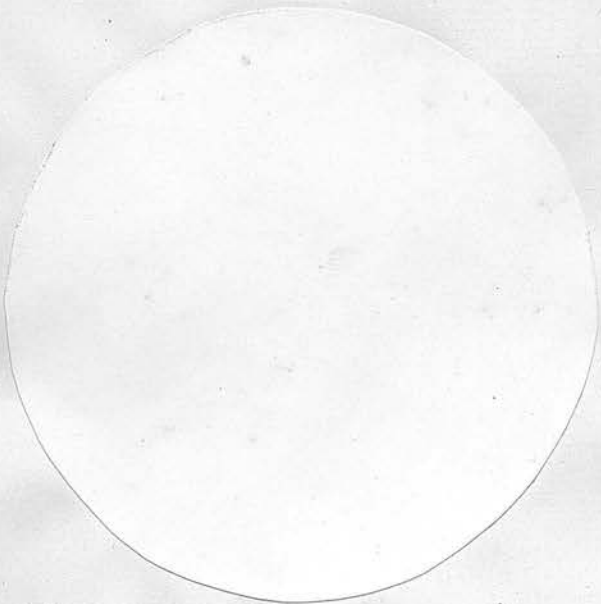


FIG. 184. Annealed at  $140^{\circ}$  for 200 hours.

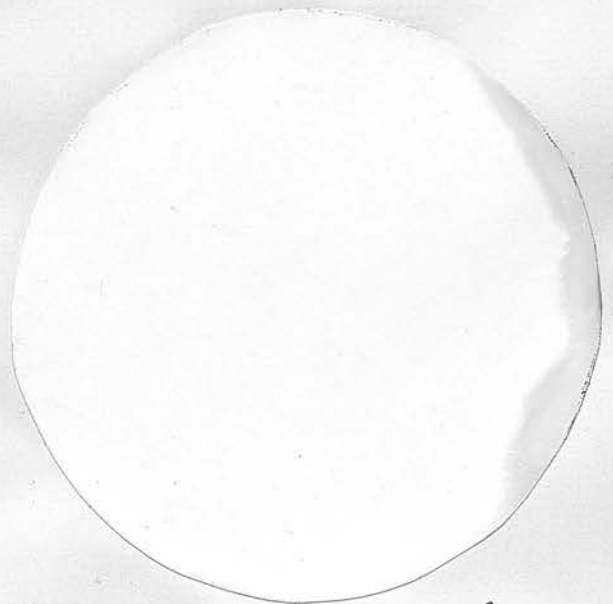


FIG. 185. Annealed at  $140^{\circ}$  for 400 hours.

2 in, slowly cooled and annealed; all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters

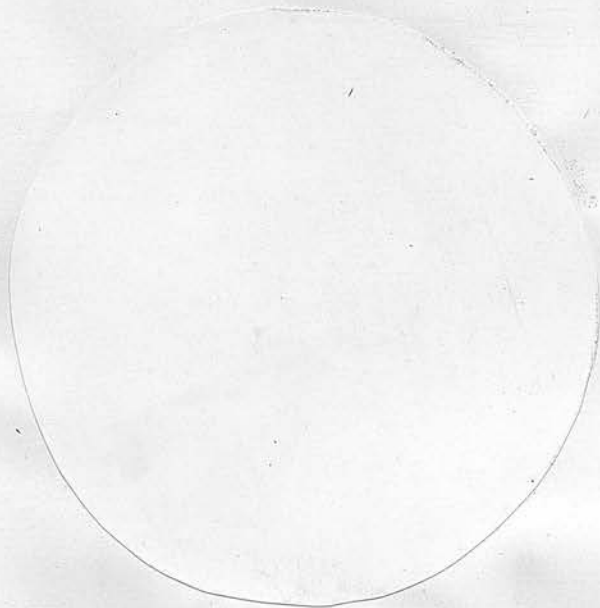


FIG. 186. Chill cast from  $750^{\circ}$ .

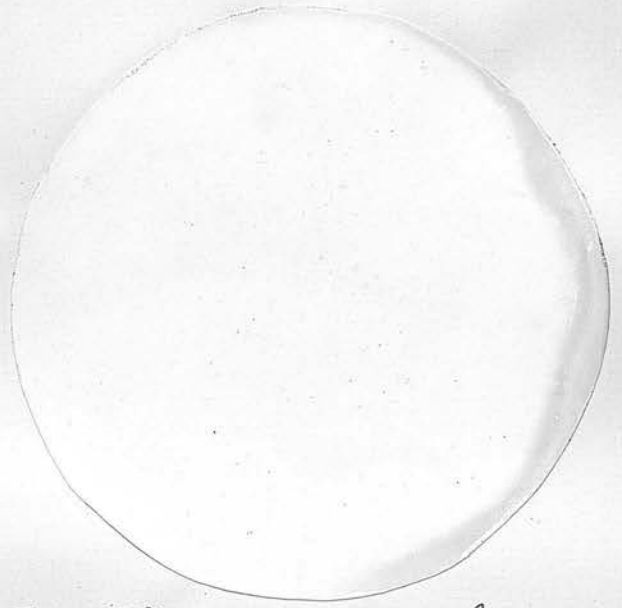


FIG. 187. Annealed at  $1440^{\circ}$  for 100 hours.

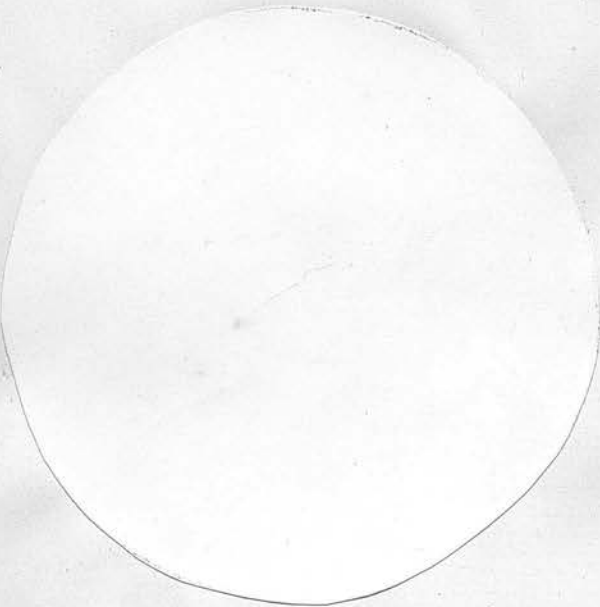


FIG. 188. Annealed at  $1440^{\circ}$  for 200 hours.

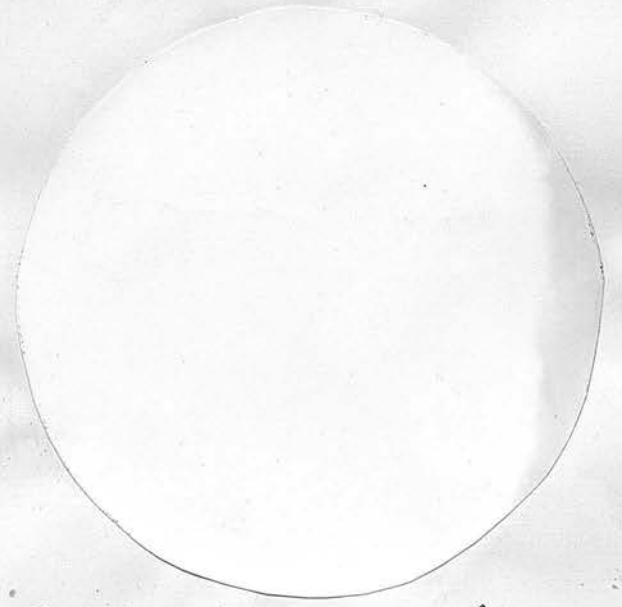


FIG. 189. Annealed at  $1440^{\circ}$  for 400 hours.

*In*, chill cast from  $750^{\circ}$  and annealed; all etched with ferric chloride, and magnified 100 diameters.

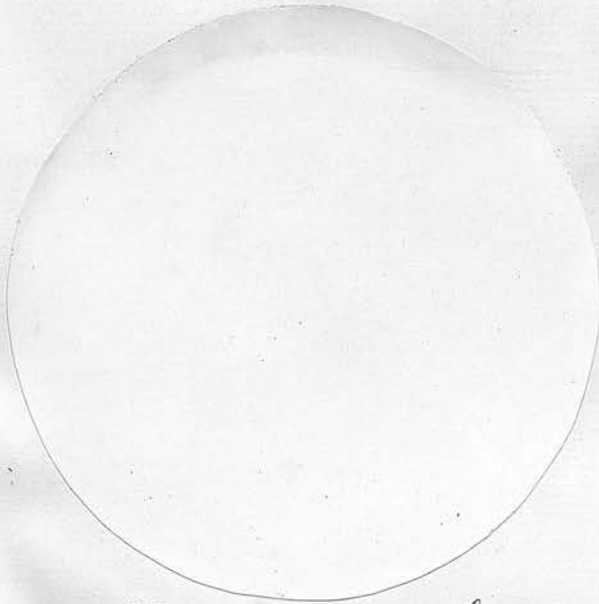


FIG. 190. Annealed at  $140^{\circ}$  for 100 hours.

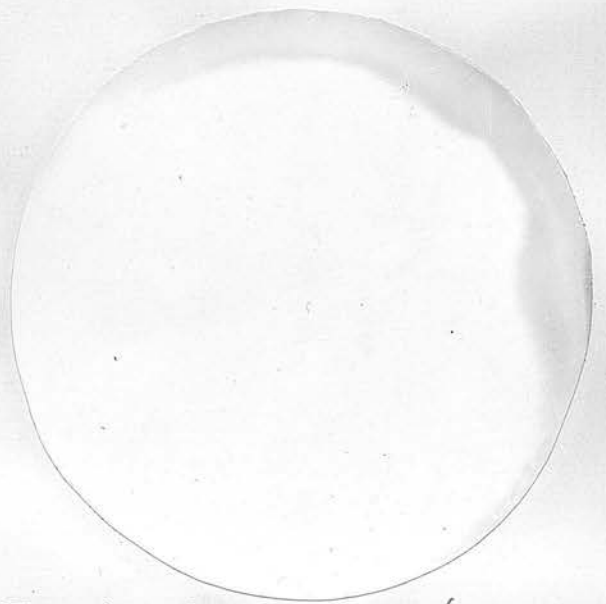


FIG. 191. Annealed at  $140^{\circ}$  for 400 hours.

Bismuth 98, antimony 2 per cent; chill cast and annealed; etched with ferric chloride, + magnified  $7\frac{1}{2}$  diameters.

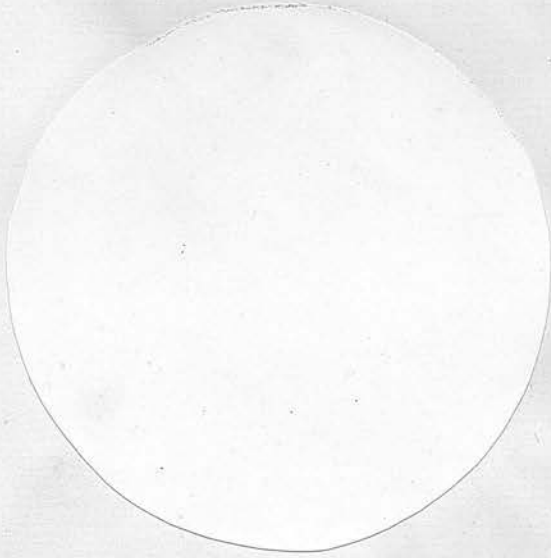


FIG. 192. Annealed at  $140^{\circ}$  for 100 hours.

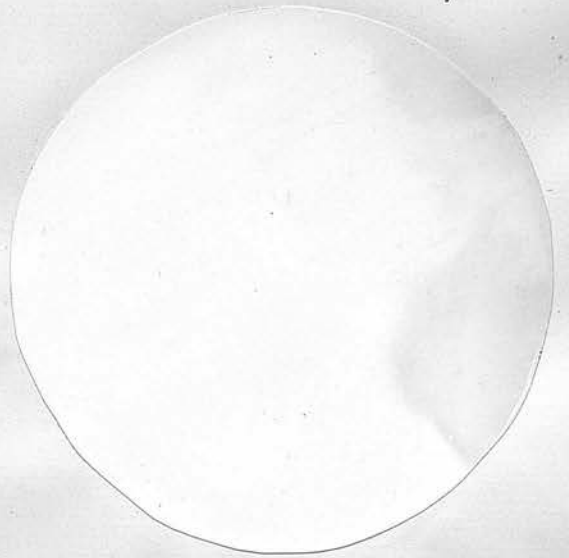


FIG. 193. Annealed at  $140^{\circ}$  for 400 hours.

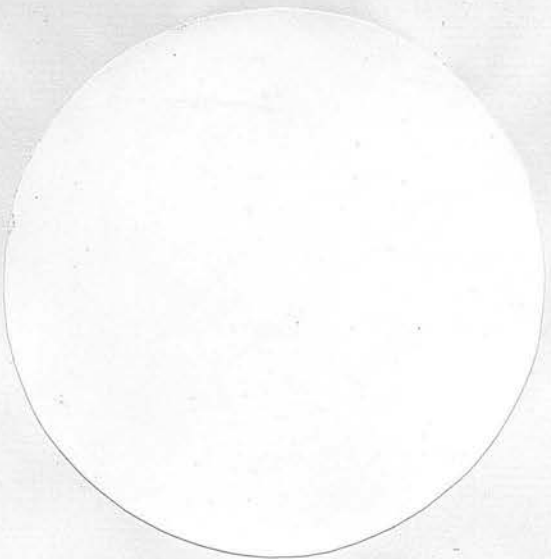


FIG. 194. Annealed 400 hours; film partly removed.

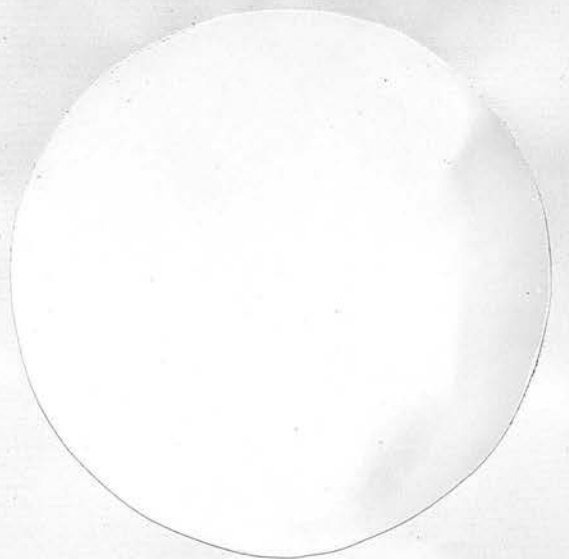


FIG. 195. Annealed 400 hours; film wholly removed.

Bismuth 98, antimony 2 per cent.; slowly cooled and annealed; etched with ferric chloride, + magnified  $7\frac{1}{2}$  diameters.

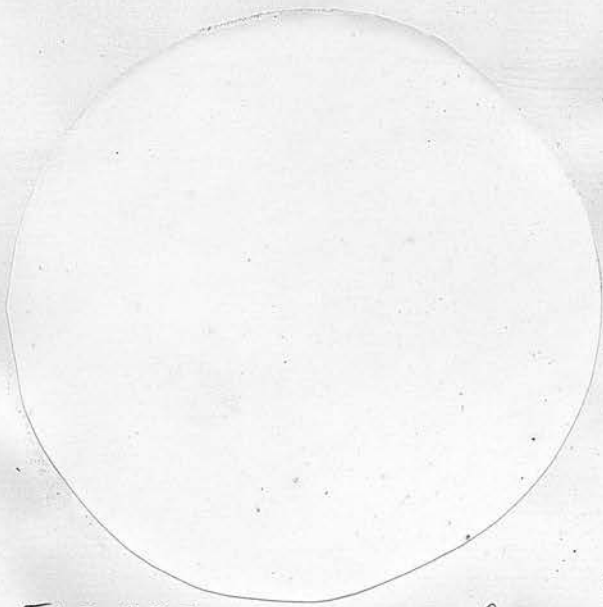


FIG. 196. Annealed at  $140^{\circ}$  for 100 hours.

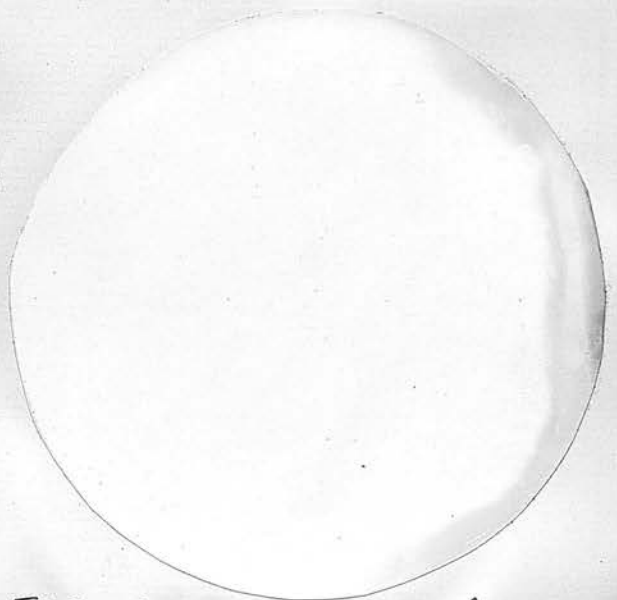


FIG. 197. Annealed at  $140^{\circ}$  for 200 hours.

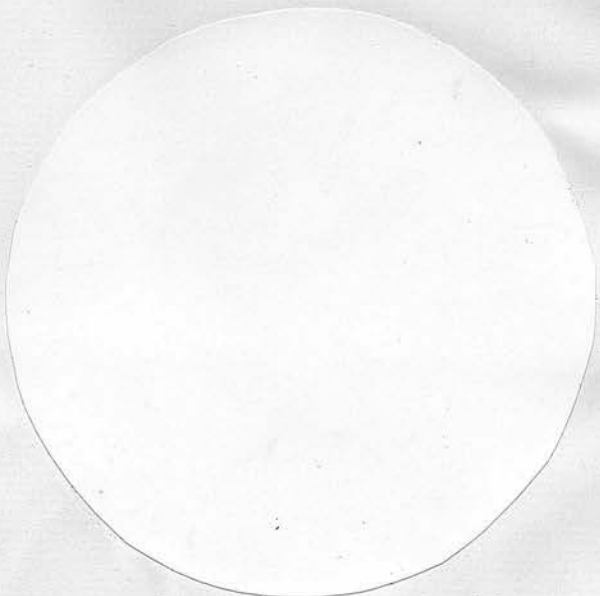


FIG. 198. Annealed at  $140^{\circ}$  for 400 hours.



FIG. 199. Annealed 400 hours; repolished.

Disinuth 98, Cadmium 2 percent.; chill cast and annealed; etched with ferric chloride, + magnified  $7\frac{1}{2}$  diameters

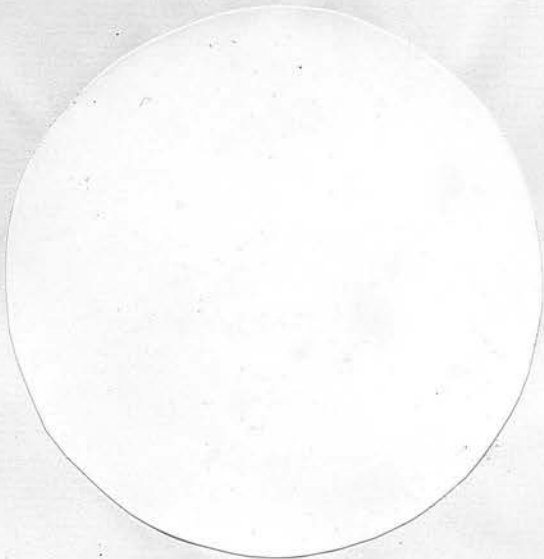


FIG. 200. Annealed at  $140^{\circ}$  for 100 hours.

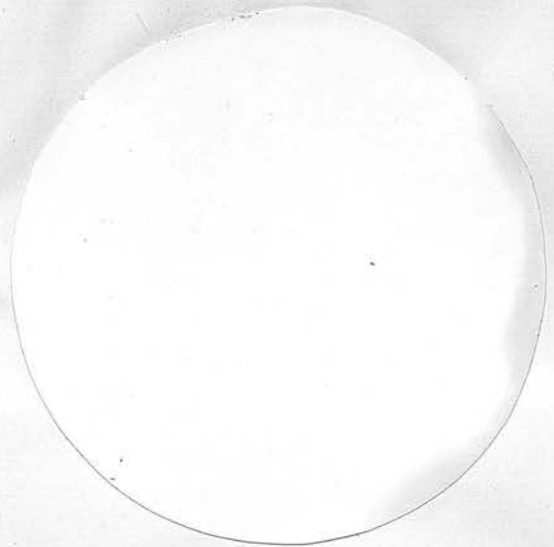


FIG. 201. Annealed at  $140^{\circ}$  for 400 hours.

Disinuth 98, Cadmium 2 percent.; slowly cooled and annealed; etched with ferric chloride, + magnified  $7\frac{1}{2}$  diameters

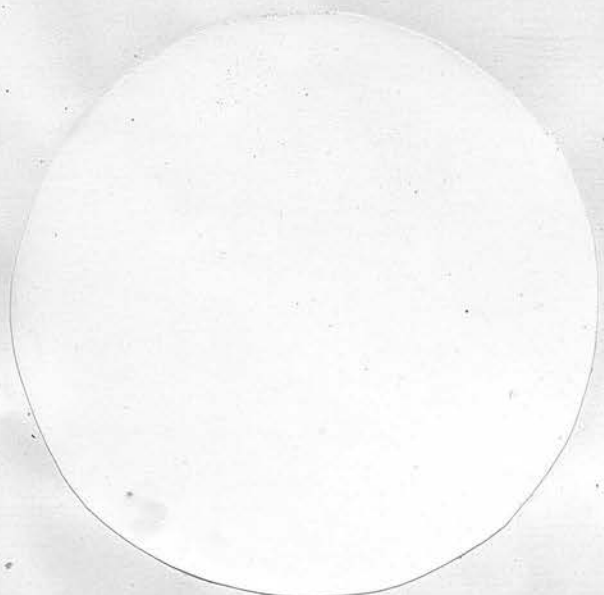


FIG. 202. Chill cast; annealed at 140° for 400 hours.

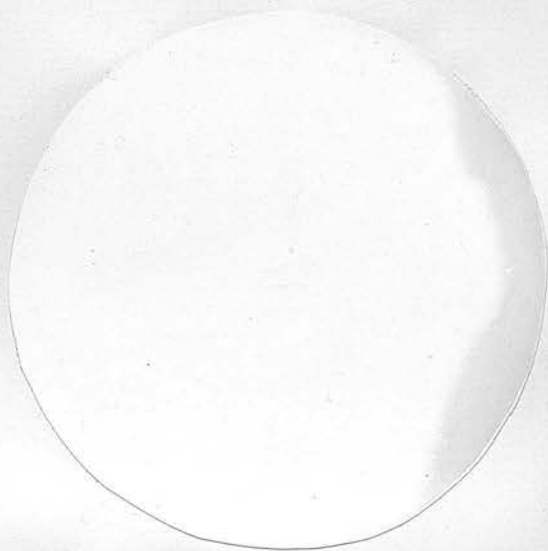


FIG. 203. Slowly cooled; annealed at 140° for 400 hours

Bismuth 98, tin 2 per cent.

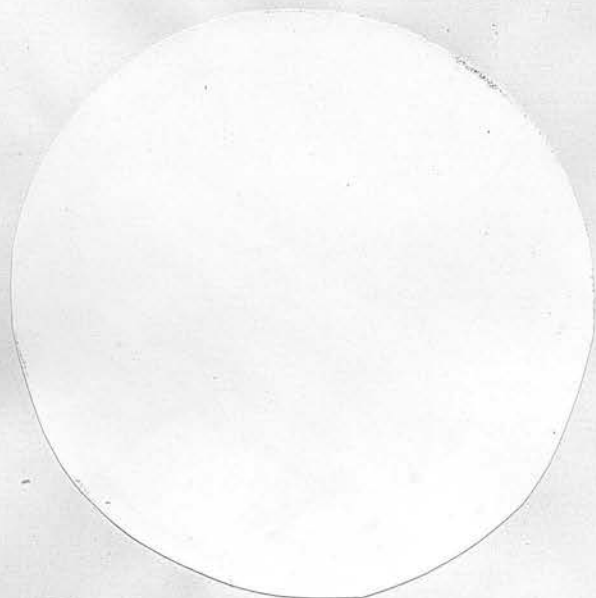


FIG. 204. Chill cast; annealed at 140° for 400 hours.

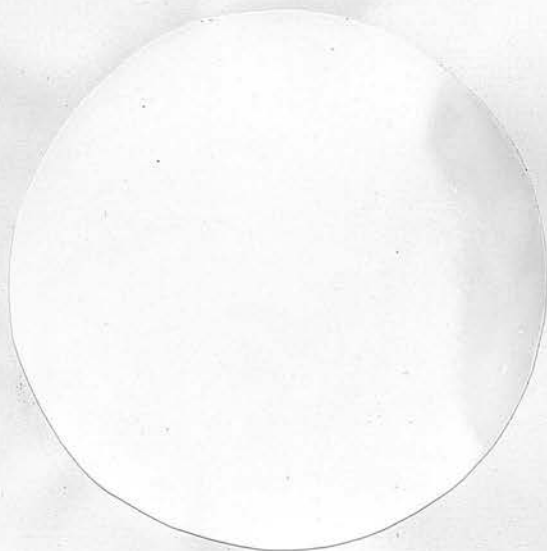


FIG. 205. Slowly cooled; annealed at 140° for 400 hours

Bismuth 98, zinc 2 per cent.

All etched with ferric chloride, and magnified 7½ diameters.

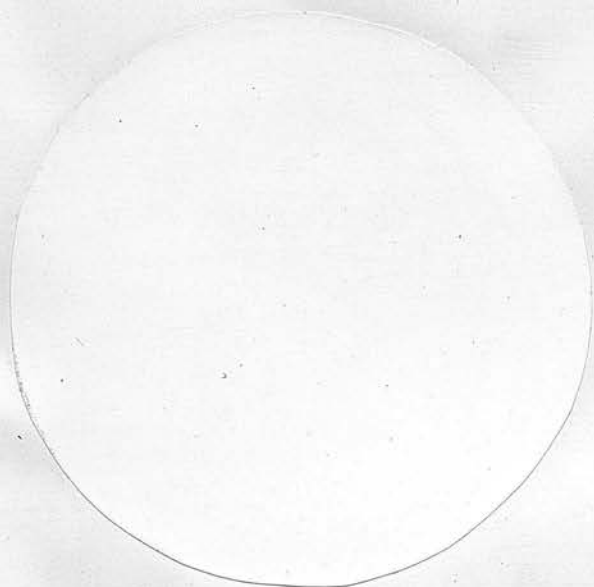


FIG. 206. Chill cast; annealed at 140° for 400 hours

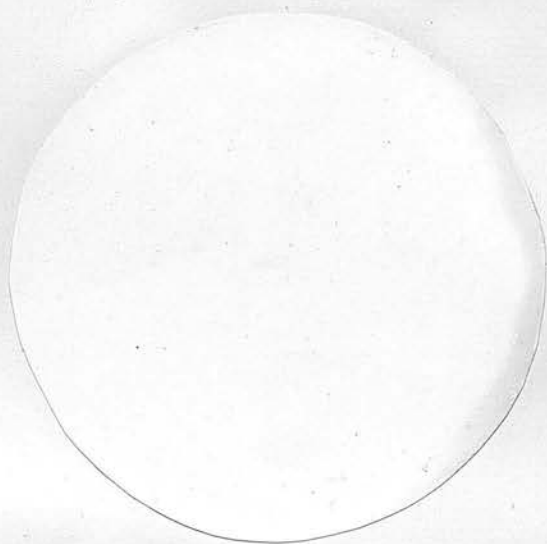


FIG. 207. Slowly cooled; annealed at 140° for 100 hours.

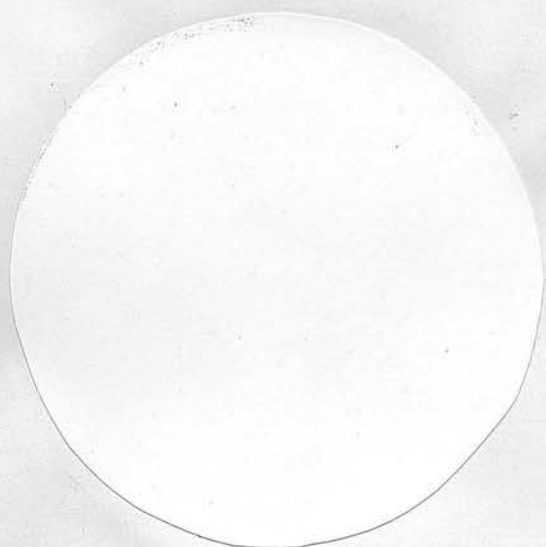


FIG. 208. Slowly cooled; annealed at 140° for 200 hours.

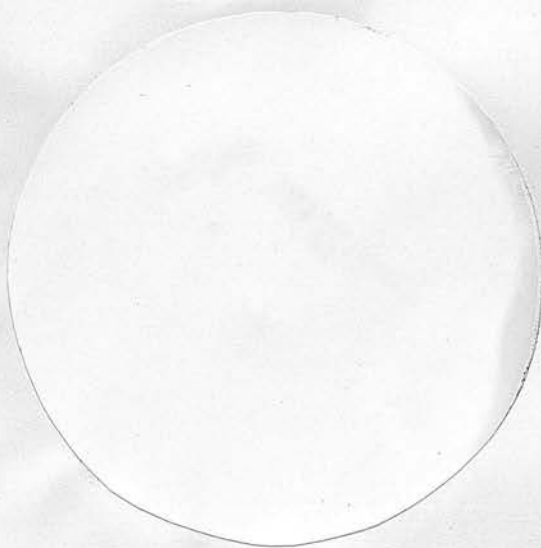


FIG. 209. Slowly cooled; annealed at 140° for 400 hours.

Cadmium 98, antimony 2 percent; all etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

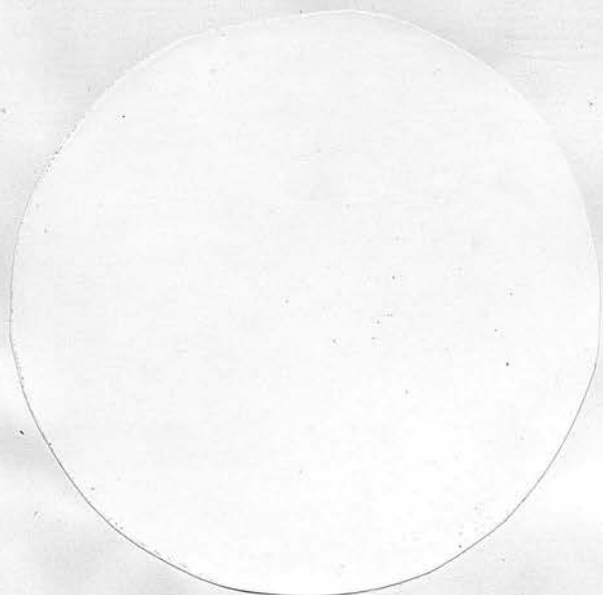


FIG. 210. Annealed at 140° for 100 hours

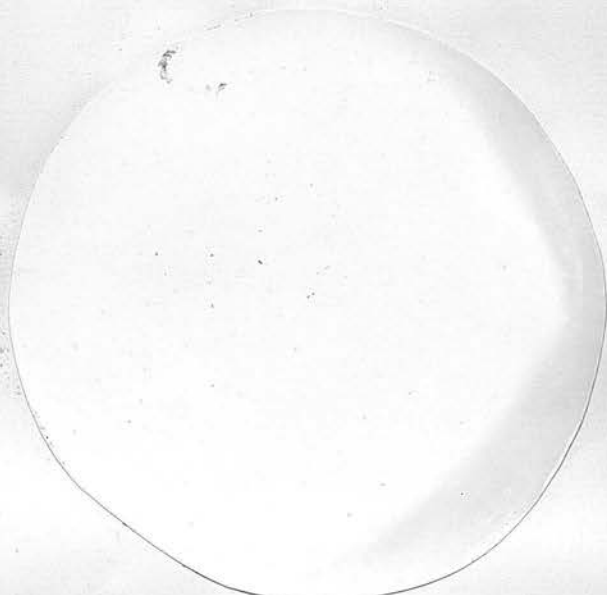


FIG. 211. Annealed at 140° for 200 hours.

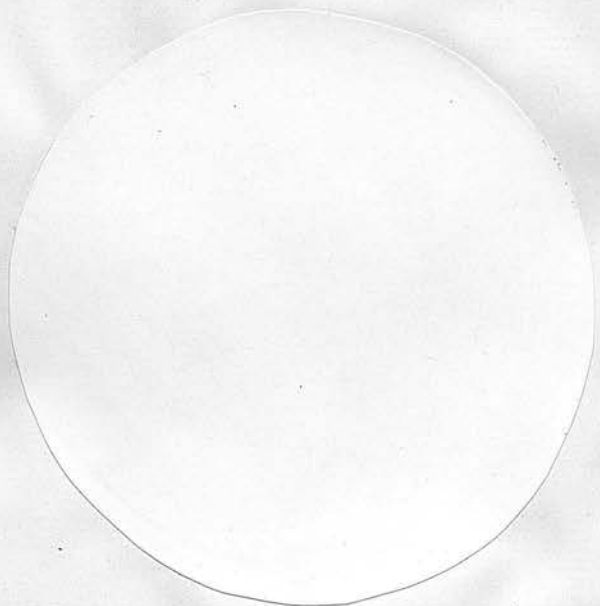


FIG. 212. Annealed at 140° for 400 hours.

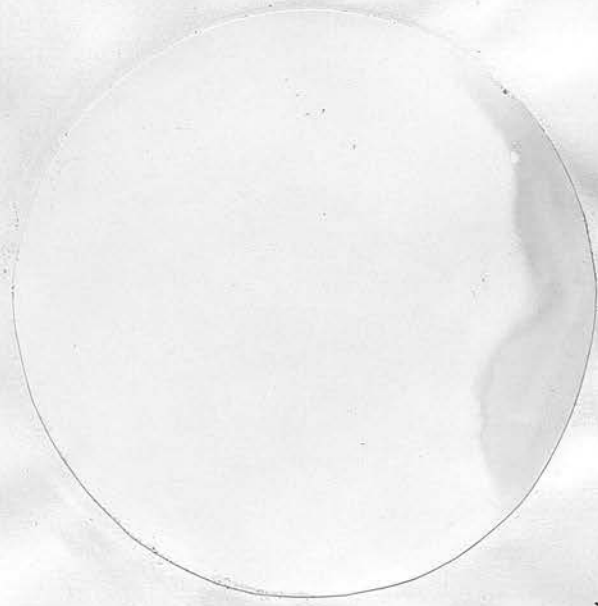


FIG. 213. Annealed 400 hours; repolished.

Cadmium 98, bismuth 2 percent.; chill cast and annealed; all etched with iodine, magnified  $7\frac{1}{2}$  diameters

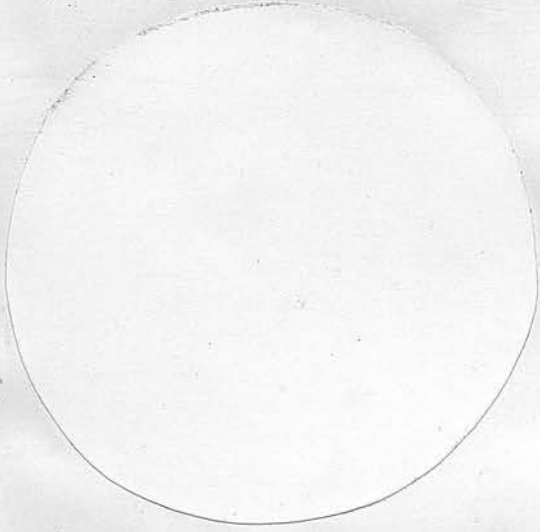


FIG. 214. Annealed at  $140^{\circ}$  for 100 hours.

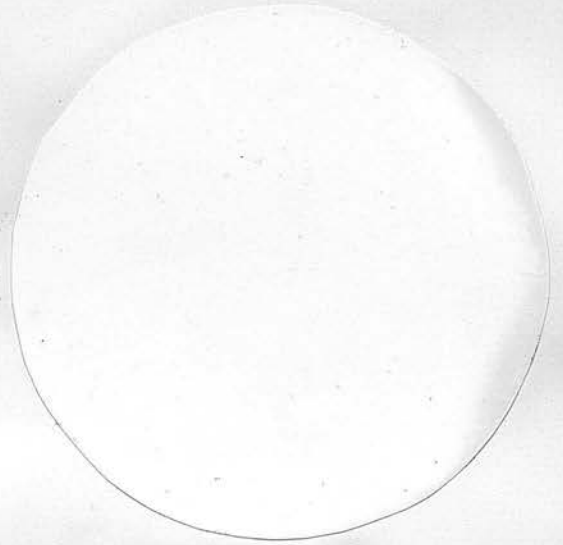


FIG. 215. Annealed at  $140^{\circ}$  for 200 hours.

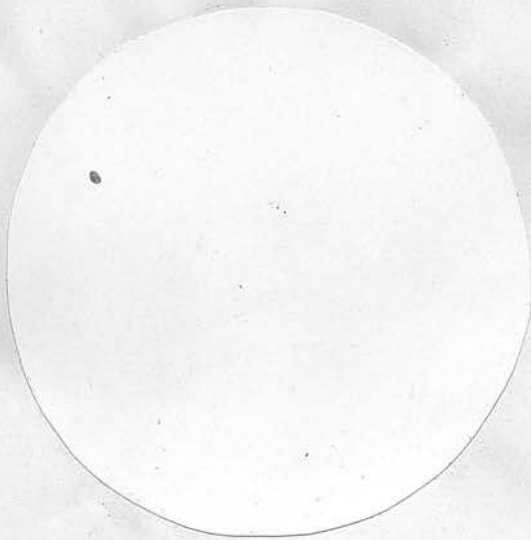


FIG. 216. Annealed at  $140^{\circ}$  for 400 hours.

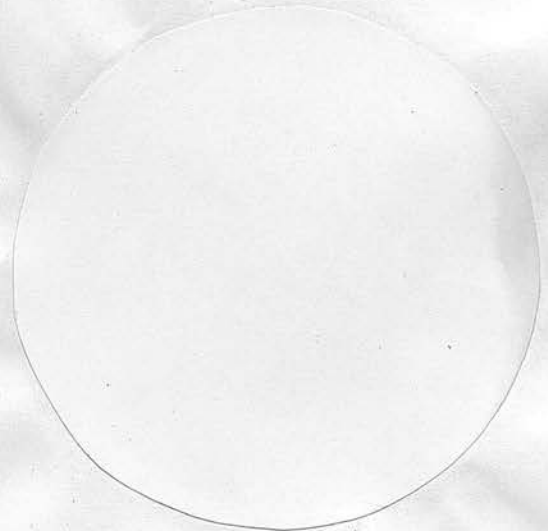


FIG. 217. Annealed 400 hours; repolished.

Cadmium 98, bismuth 2 percent.; slowly cooled and annealed; etched with iodine, & magnified  $7\frac{1}{2}$  diam.

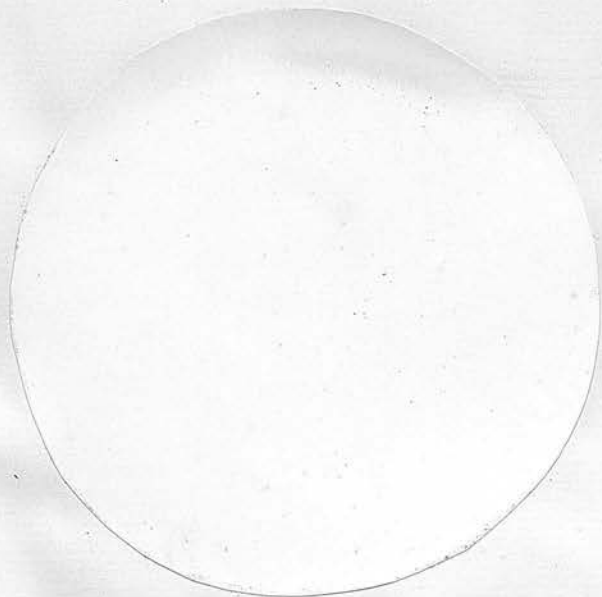


FIG. 218. Chill cast; annealed at  $140^{\circ}$  for 100 hours

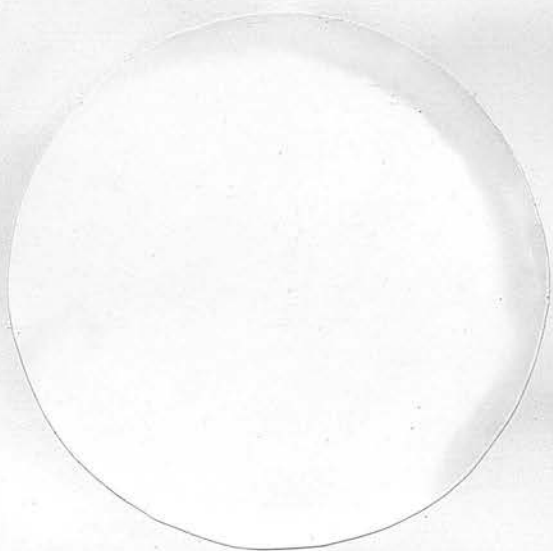


FIG. 221. Slowly cooled; annealed at  $140^{\circ}$  for 100 hours.

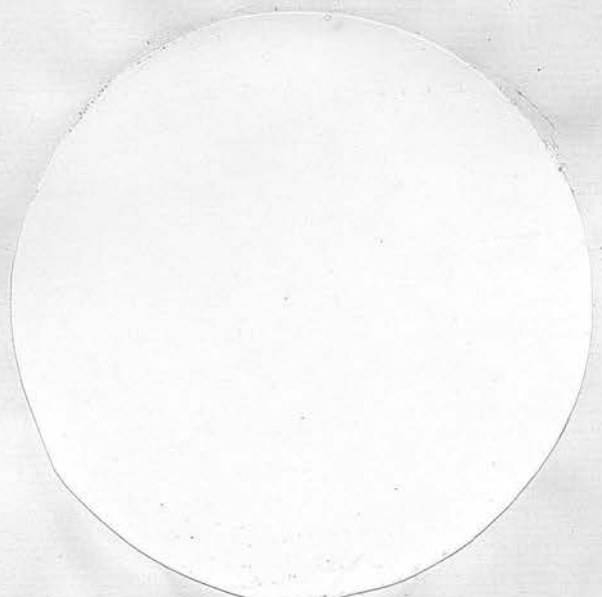


FIG. 219. Chill cast; annealed at  $140^{\circ}$  for 200 hours.

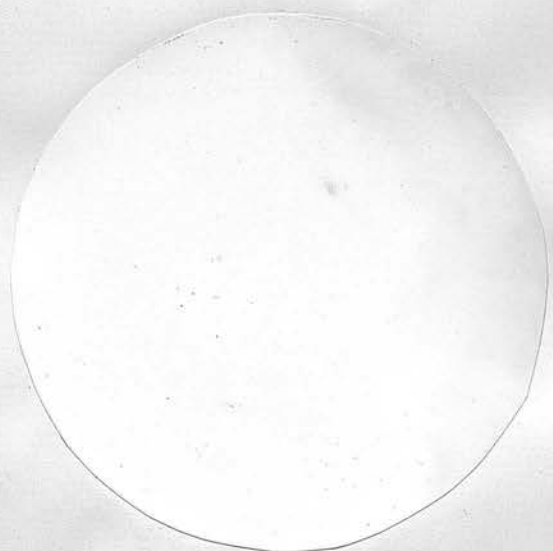


FIG. 222. Slowly Cooled; annealed at  $140^{\circ}$  for 200 hours.

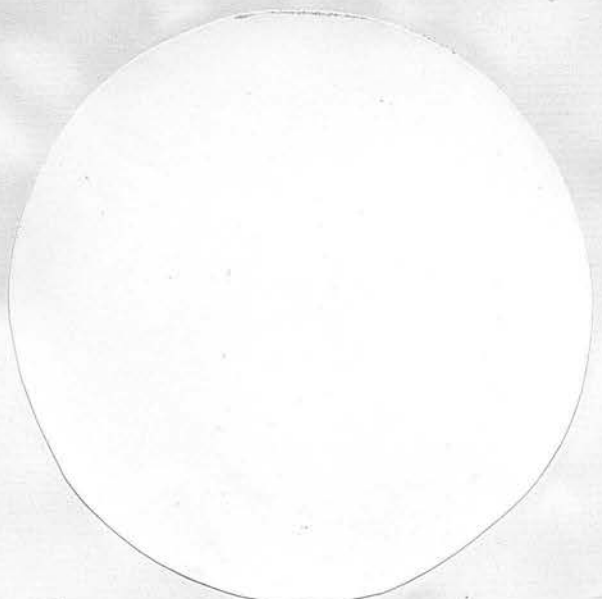


FIG. 220. Chill cast; annealed at  $140^{\circ}$  for 400 hours.

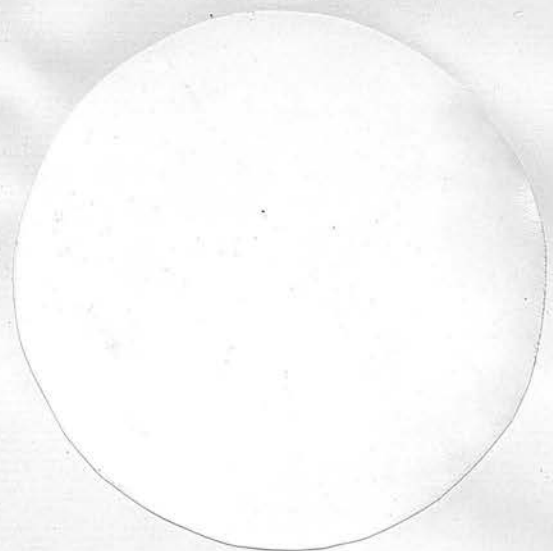


FIG. 223. Slowly cooled; annealed at  $140^{\circ}$  for 400 hours.

Cadmium 98, tin 2 per cent; all etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

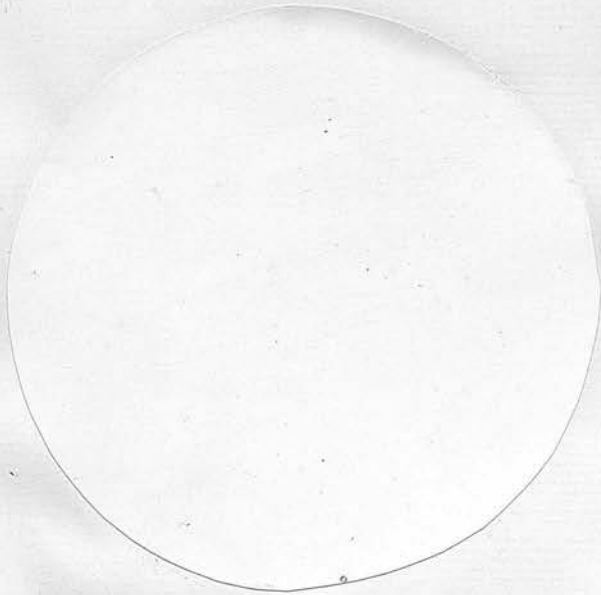


FIG. 224. Chill cast; annealed at  $140^{\circ}$  for 100 hours.

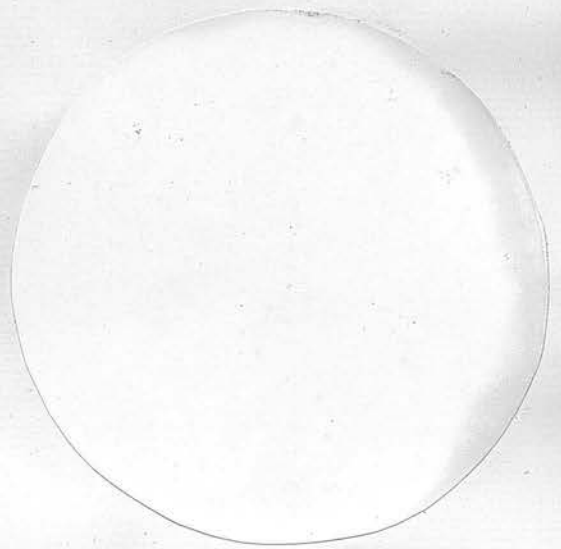


FIG. 227. Slowly cooled; annealed at  $140^{\circ}$  for 100 hours.

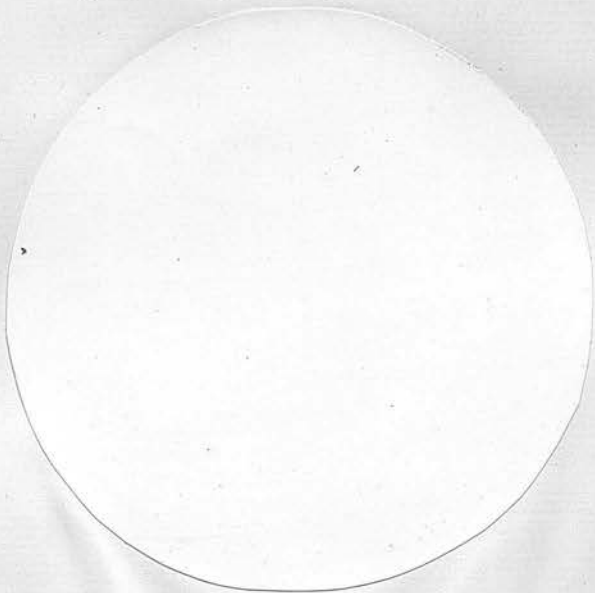


FIG. 225. Chill cast; annealed at  $140^{\circ}$  for 200 hours.

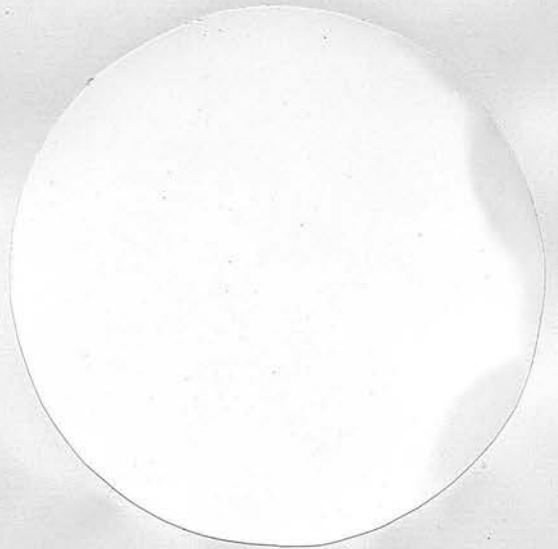


FIG. 228. Slowly cooled; annealed at  $140^{\circ}$  for 200 hours.

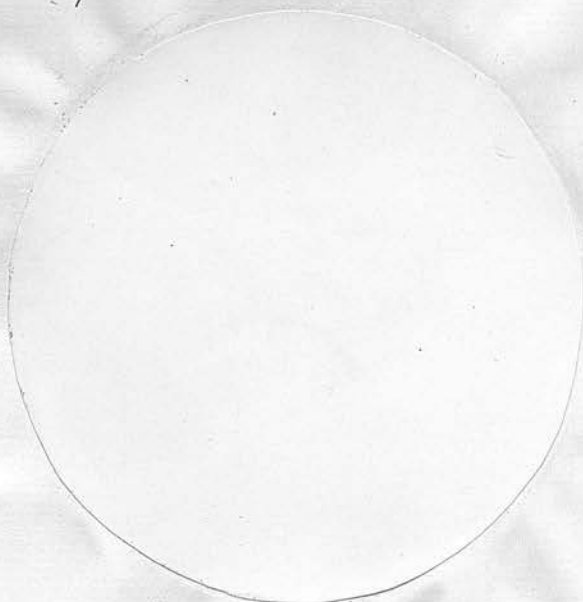


FIG. 226. Chill cast; annealed at  $140^{\circ}$  for 400 hours.

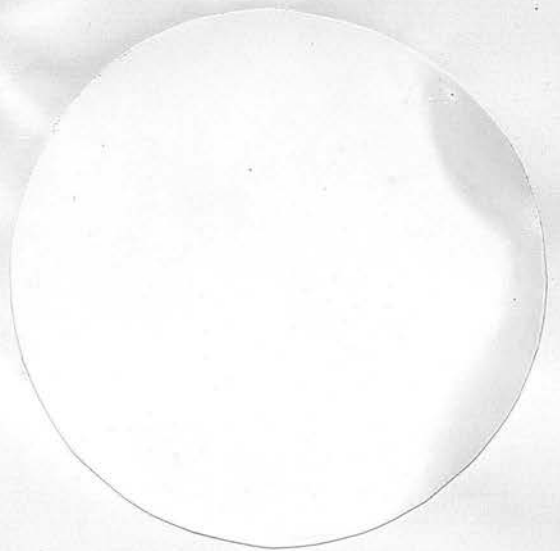


FIG. 229. Slowly cooled; annealed at  $140^{\circ}$  for 400 hours.

Cadmium 98, Zinc 2 percent.; all etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

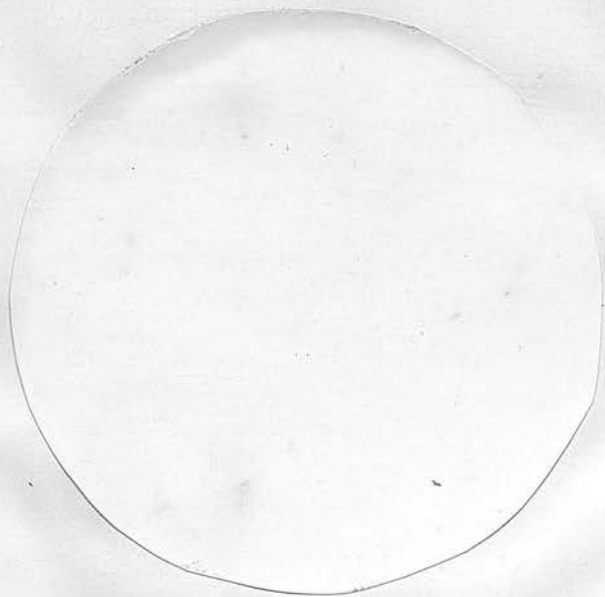


FIG. 230. Chill cast; annealed at  $140^{\circ}$  for 100 hours.

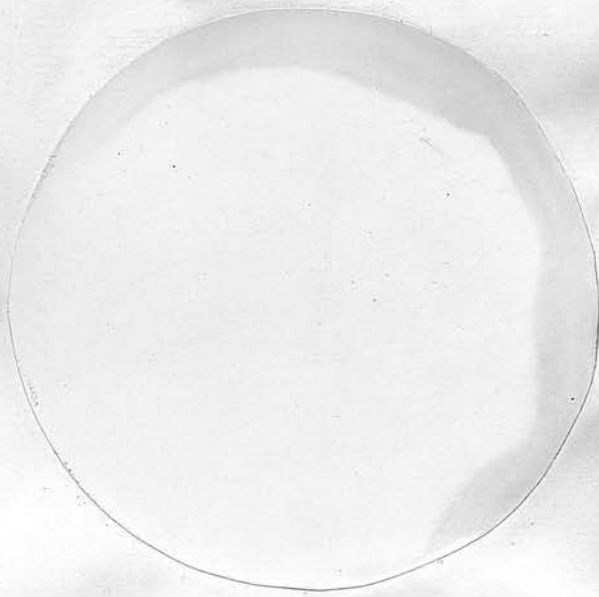


FIG. 231. Chill cast; annealed at  $140^{\circ}$  for 400 hours.

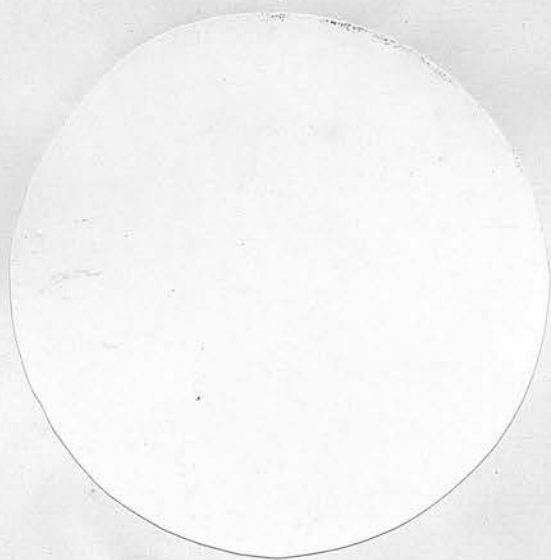


FIG. 232. Slowly cooled; annealed at  $140^{\circ}$  for 100 hours.

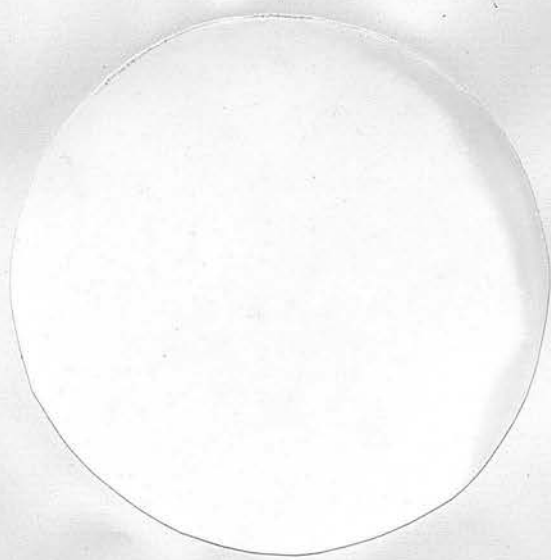


FIG. 233. Slowly cooled; annealed at  $140^{\circ}$  for 200 hours.

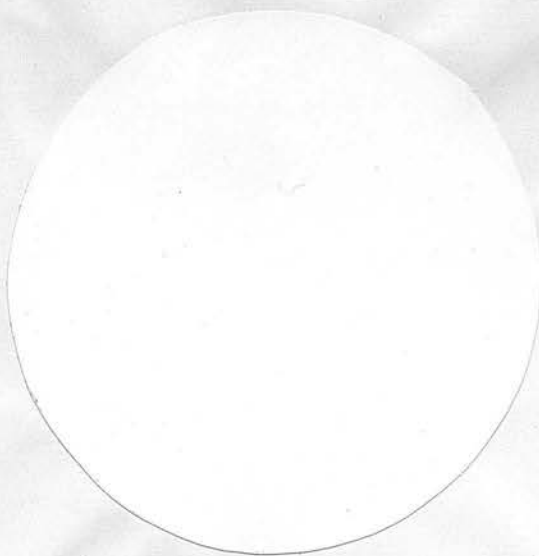


FIG. 234. Slowly cooled; annealed at  $140^{\circ}$  for 400 hours.

Iron 98, bismuth 2 per cent.; all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diams.

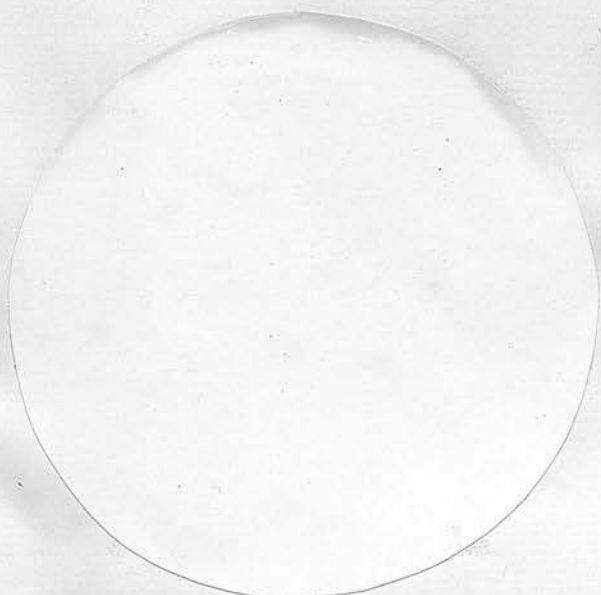


FIG. 235. Chill cast; annealed at  $140^{\circ}$  for 100 hours.

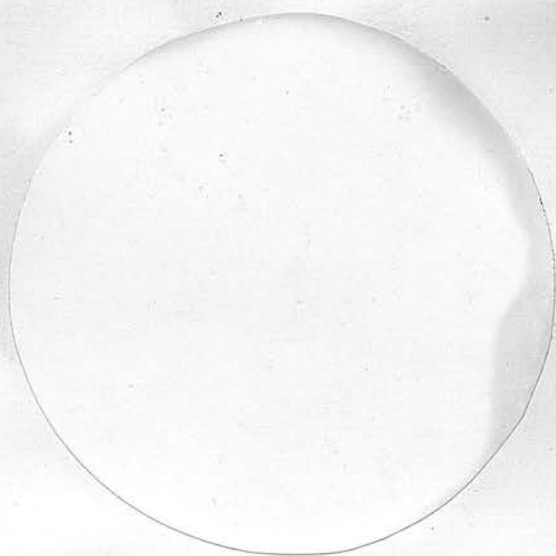


FIG. 238. Slowly cooled; annealed at  $140^{\circ}$  for 100 hours.

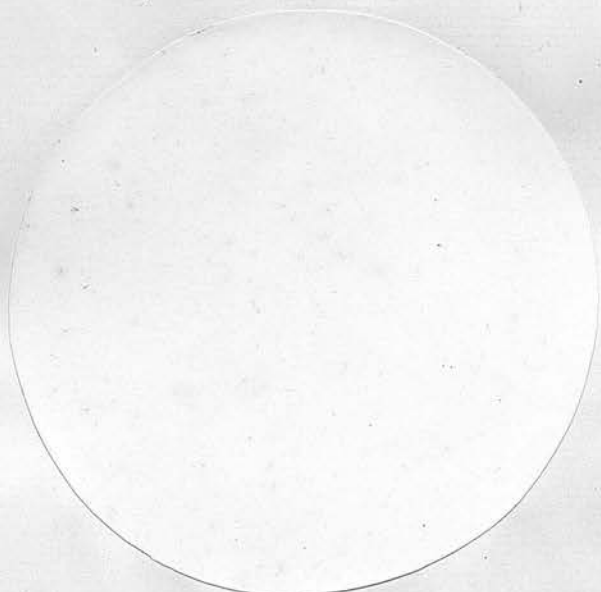


FIG. 236. Chill cast; annealed at  $140^{\circ}$  for 200 hours.

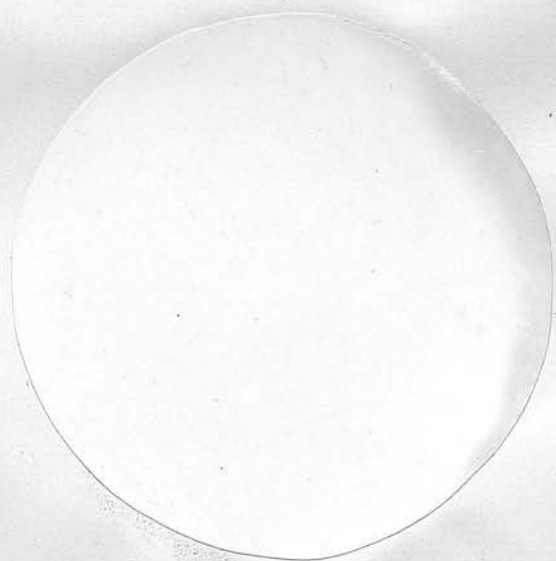


FIG. 239. Slowly cooled; annealed at  $140^{\circ}$  for 200 hours.

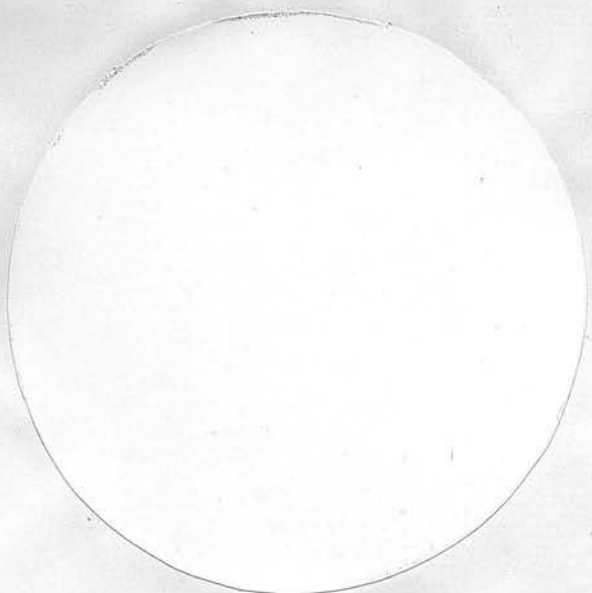


FIG. 237. Chill cast; annealed at  $140^{\circ}$  for 400 hours.

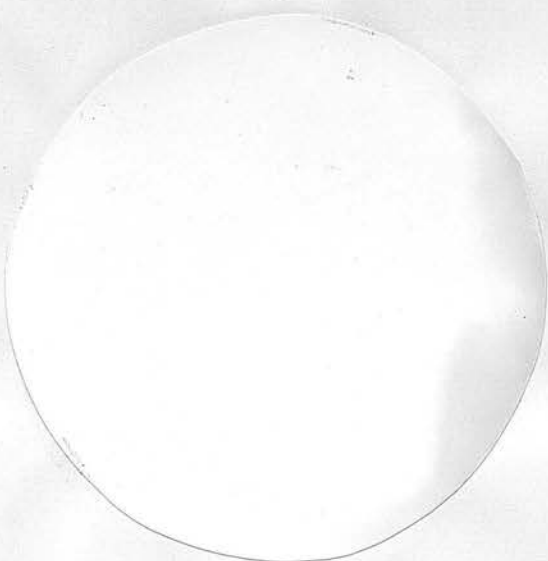


FIG. 240. Slowly cooled; annealed at  $140^{\circ}$  for 400 hours.

in 98, Cadmium 2 per cent.; all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diams

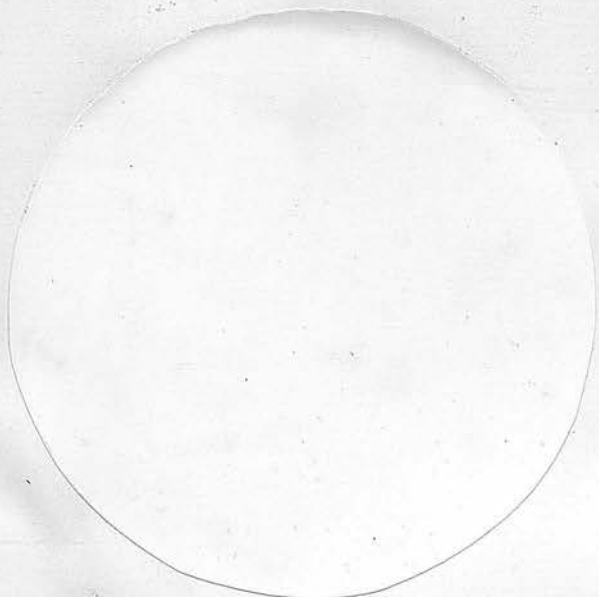


FIG. 241. Chill cast; annealed at  $140^{\circ}$  for 100 hours.

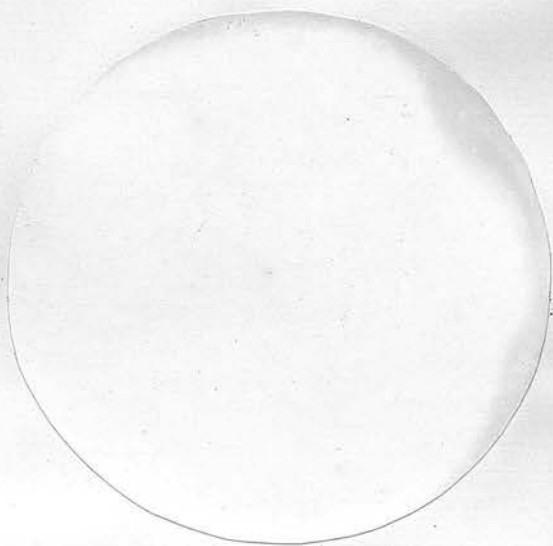


FIG. 244. Slowly cooled; annealed at  $140^{\circ}$  for 100 hours.

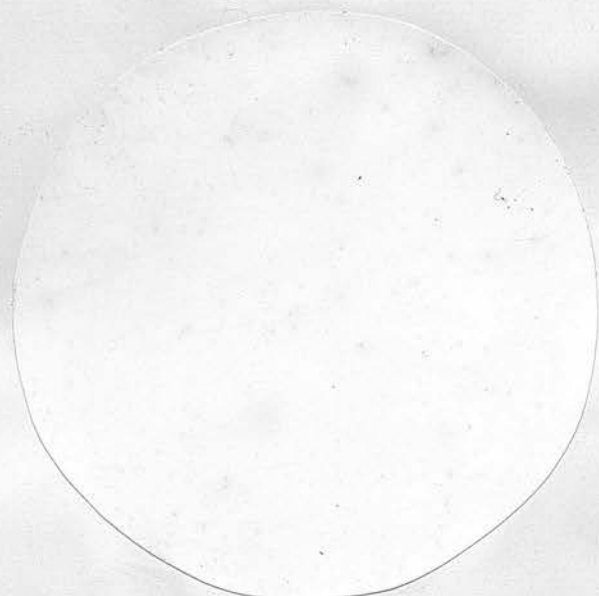


FIG. 242. Chill cast; annealed at  $140^{\circ}$  for 200 hours.

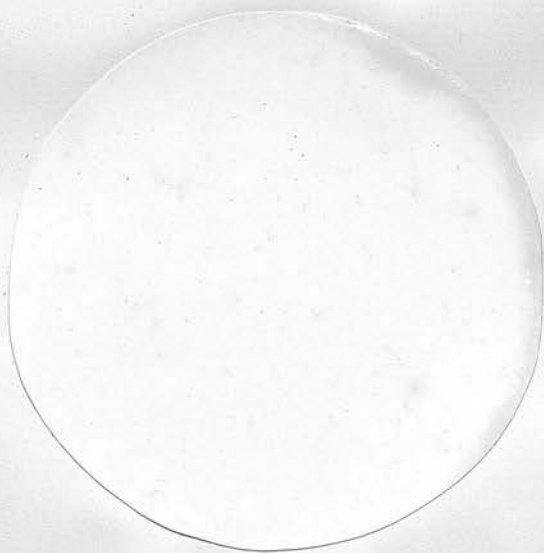


FIG. 245. Slowly cooled; annealed at  $140^{\circ}$  for 200 hours.

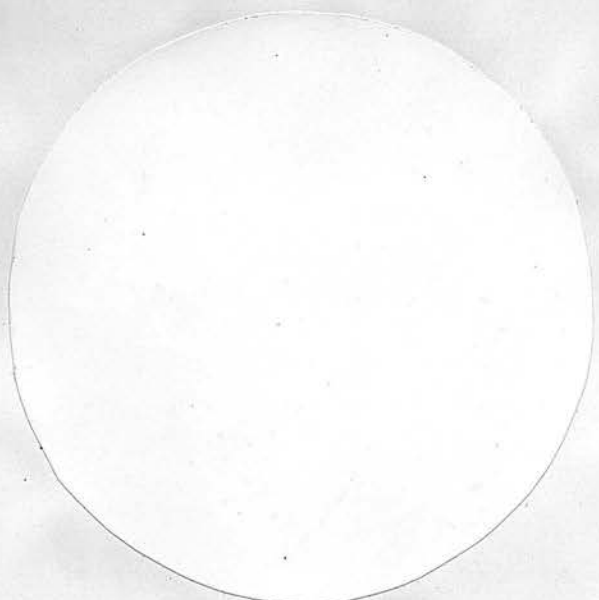


FIG. 243. Chill cast; annealed at  $140^{\circ}$  for 400 hours.

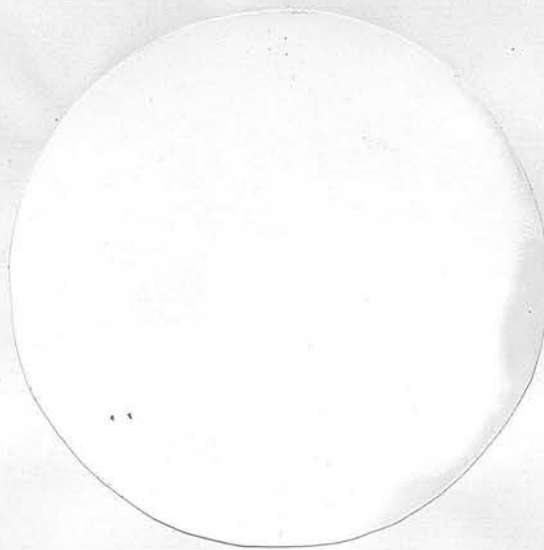


FIG. 246. Slowly cooled; annealed at  $140^{\circ}$  for 400 hours.

Iron 98, Zinc 2 percent.; all etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

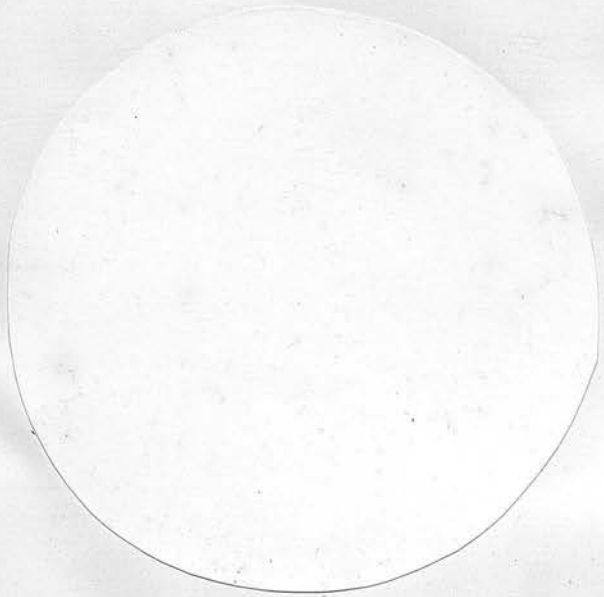


FIG. 247. Chill cast.

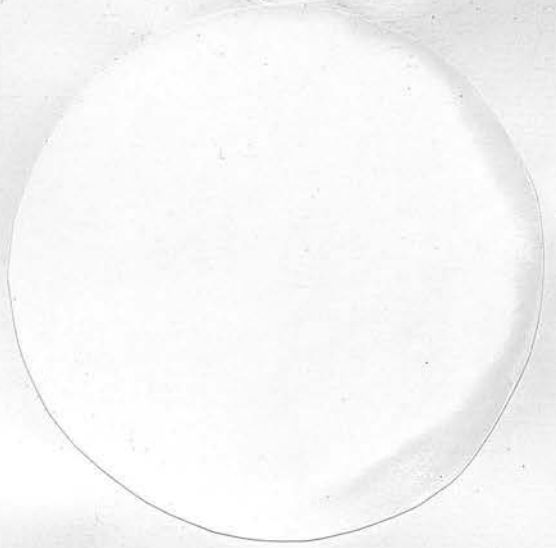


FIG. 249. Slowly cooled.

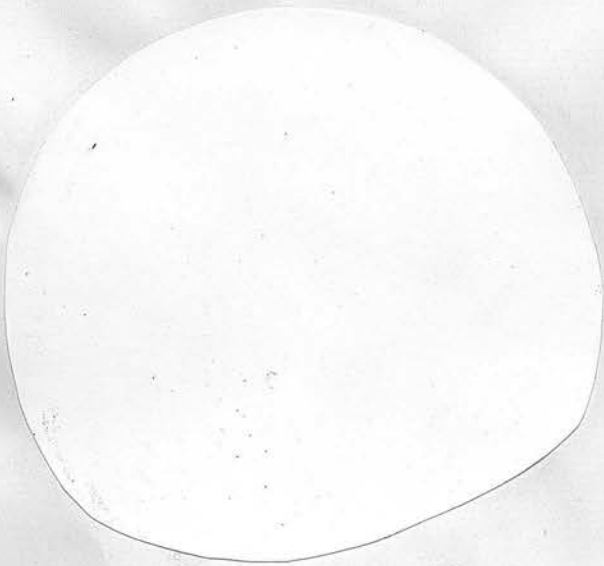


FIG. 248. Heated to incipient melting

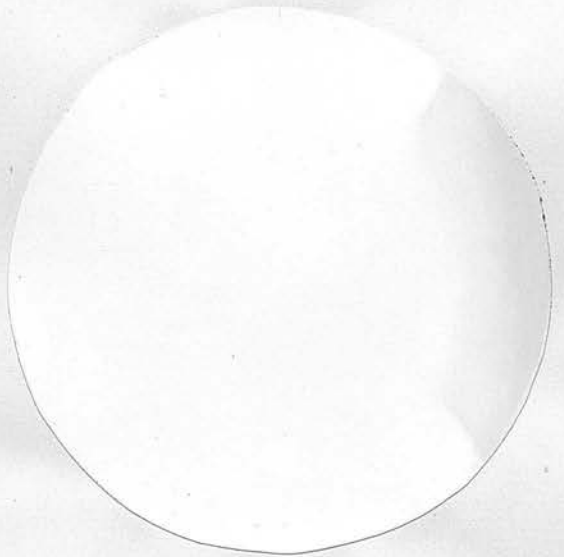


FIG. 250. Heated to incipient melting

Bismuth 98, Cadmium 2 per cent.; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diams.

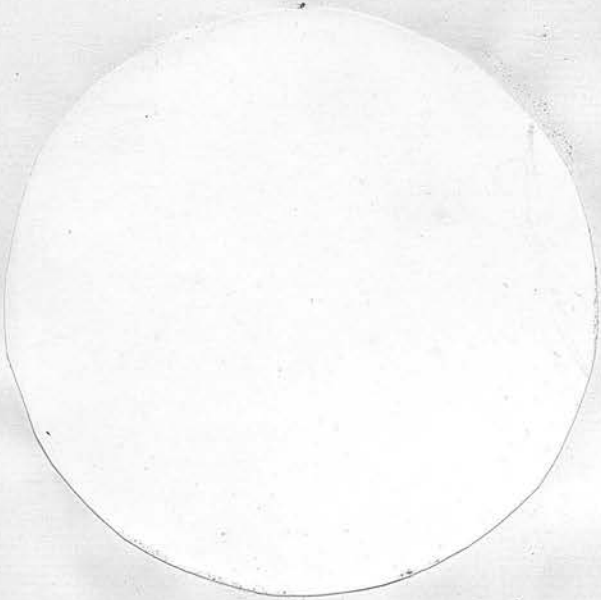


FIG. 251. Chill cast.

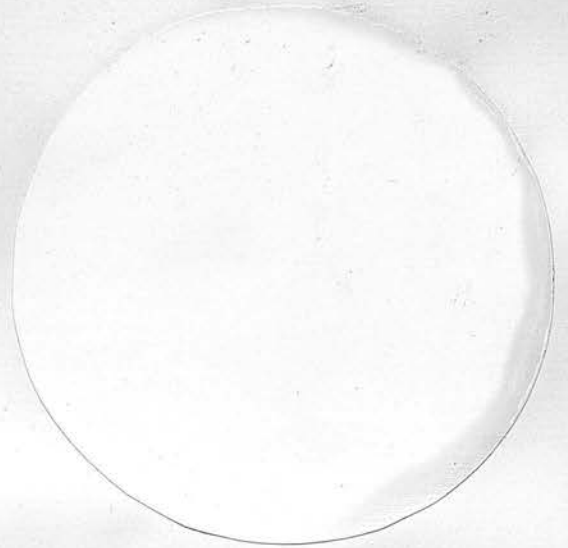


FIG. 253. Slowly cooled.

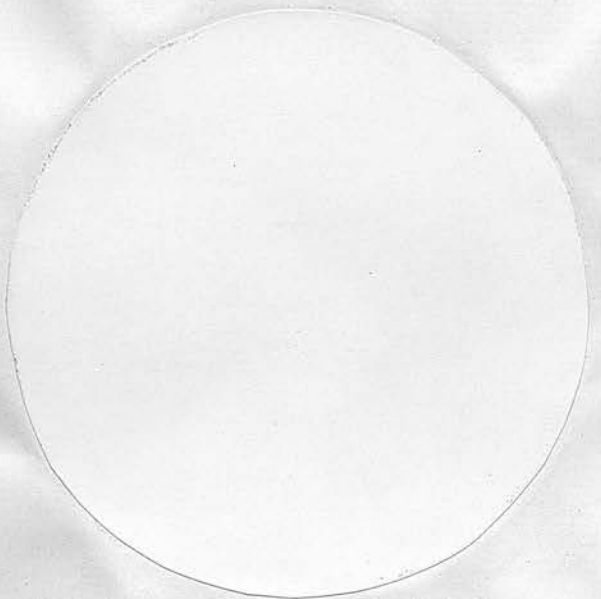


FIG. 252. Heated to incipient melting.

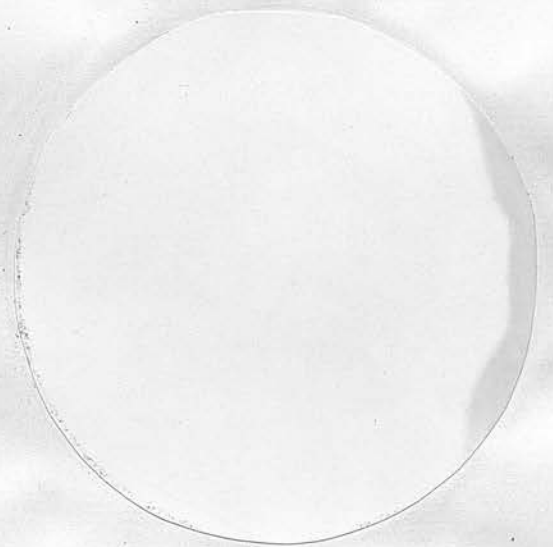


FIG. 254. Heated to incipient melting.

Cadmium 98, bismuth 2 percent; etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

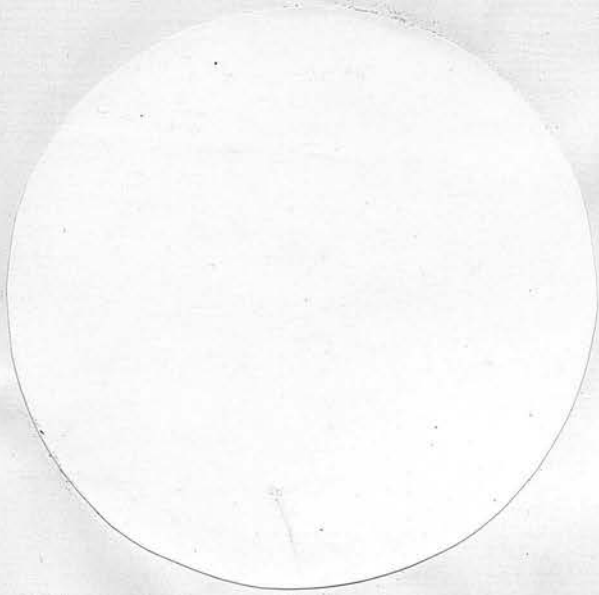


FIG. 255. Chill cast.

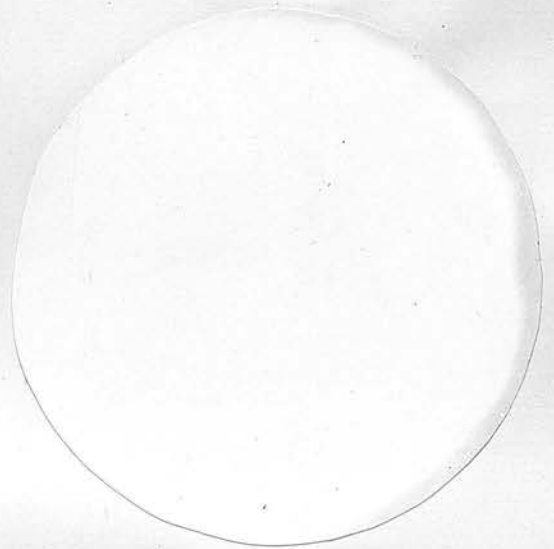


FIG. 257. Slowly cooled.

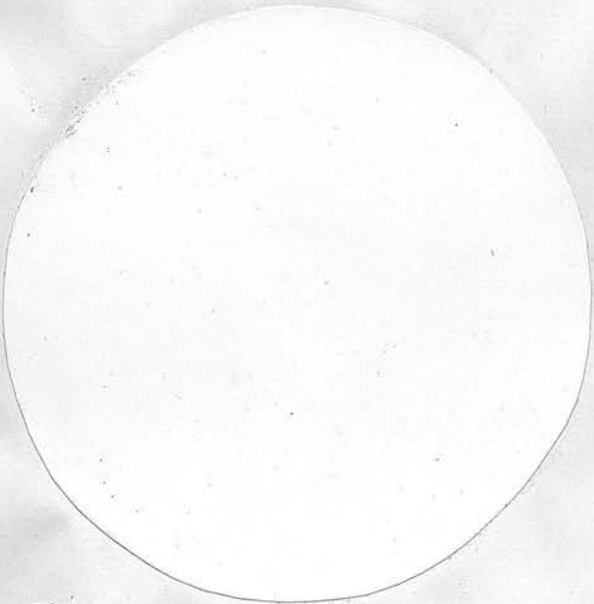


FIG. 256. Heated to incipient melting.

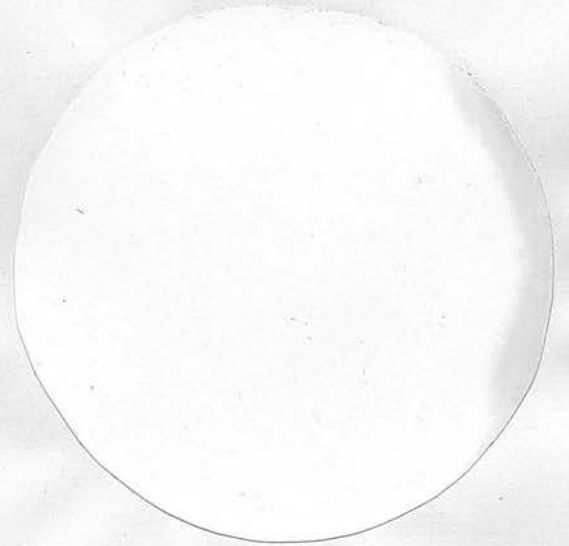


FIG. 258. Heated to incipient melting.

Cadmium 98, tin 2 percent.; etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

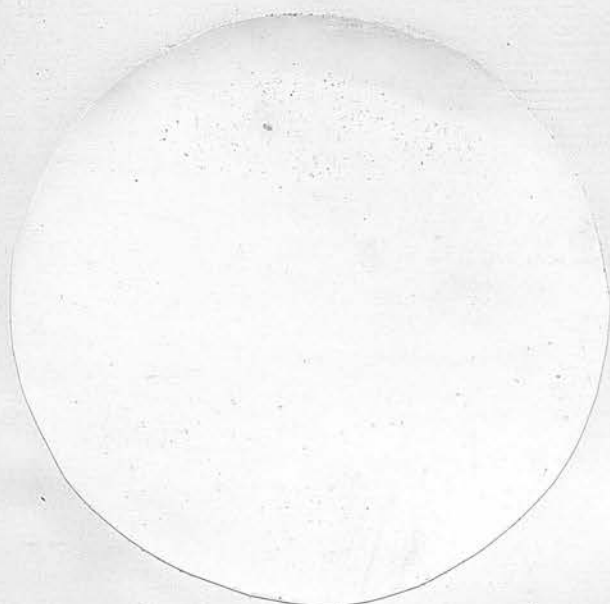


FIG. 259. Chill cast

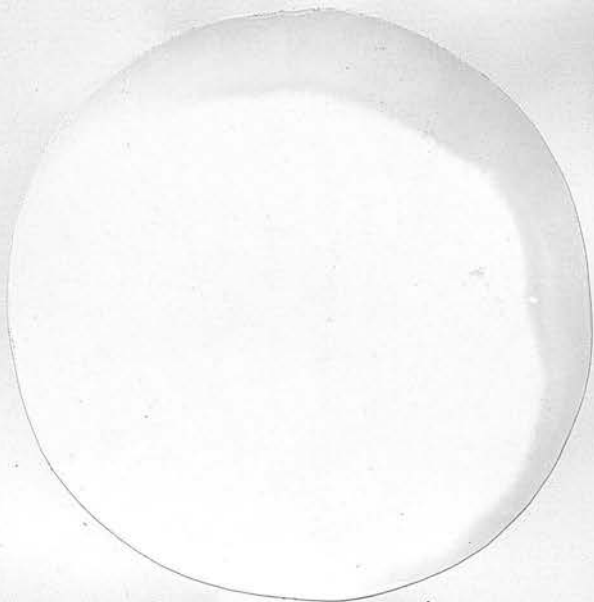


FIG. 260. Heated to incipient melting.

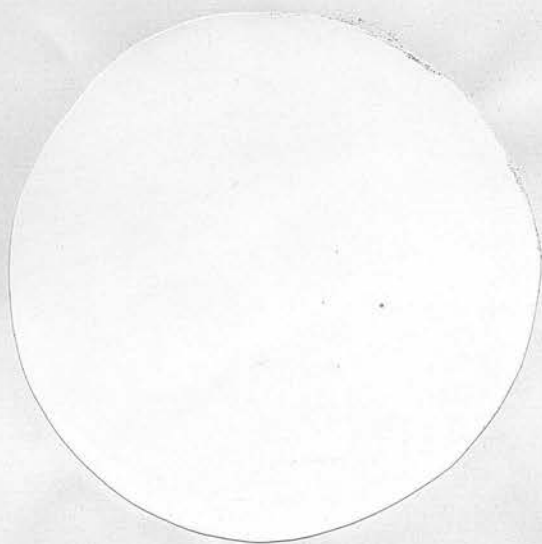


FIG. 261. Slowly cooled.

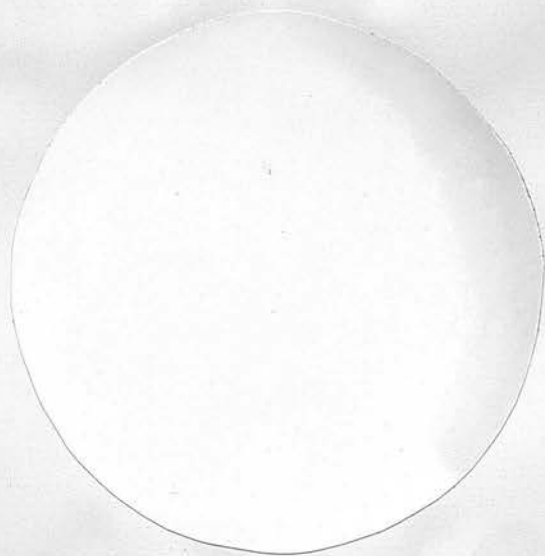


FIG. 262. Heated to incipient melting.

In 98, bismuth 2 per cent.

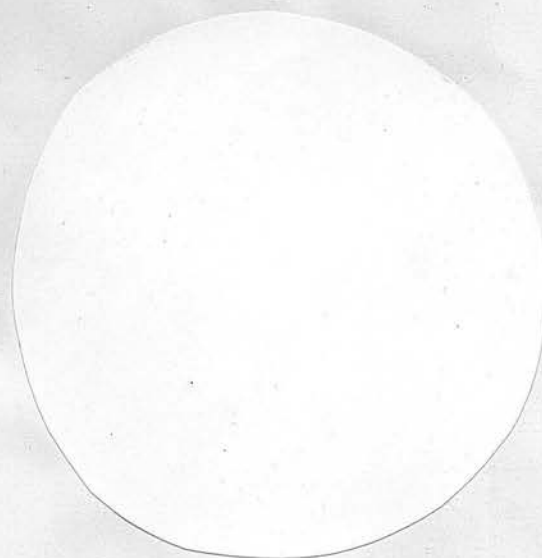


FIG. 263. Slowly cooled.

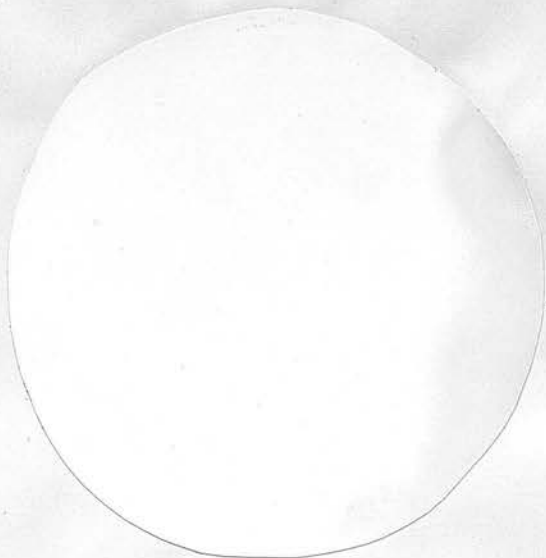


FIG. 264. Heated to incipient melting.

In 98, Cadmium 2 per cent.

All etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

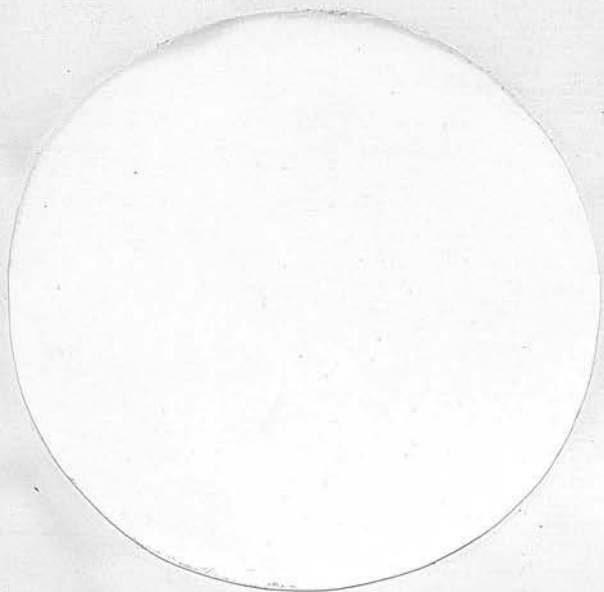


FIG. 265. Chill cast.

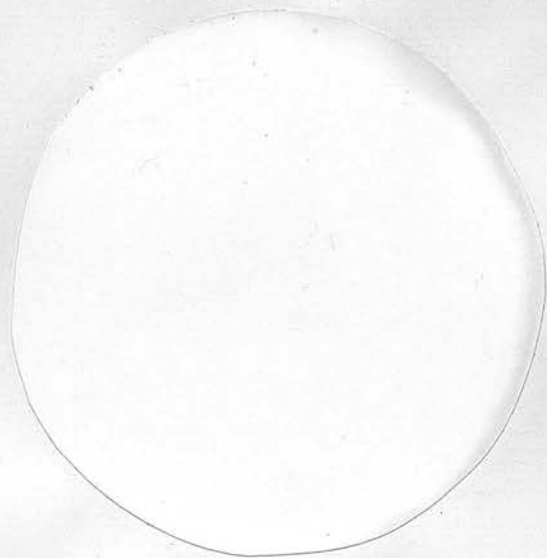


FIG. 268. Slowly cooled.

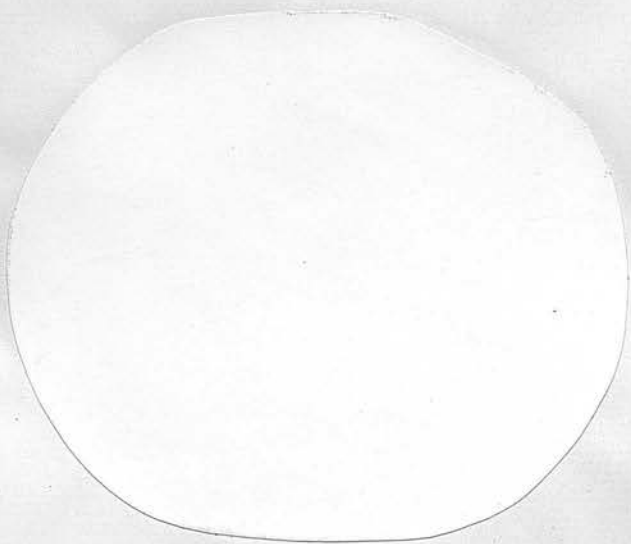


FIG. 266. Chill cast; squeezed in vice.

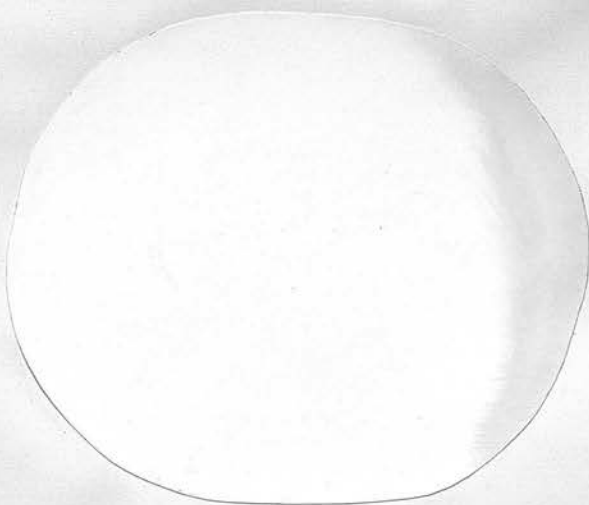


FIG. 269. Slowly cooled; squeezed in vice.

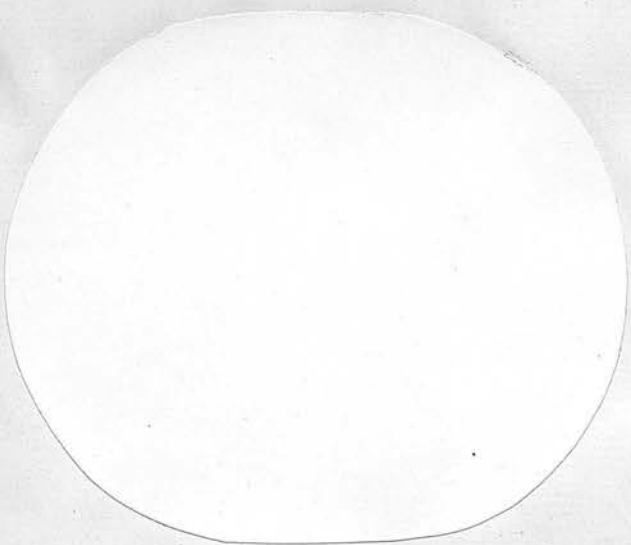


FIG. 267. Chill cast; squeezed in vice; annealed at  $140^{\circ}$  for 100 hours.

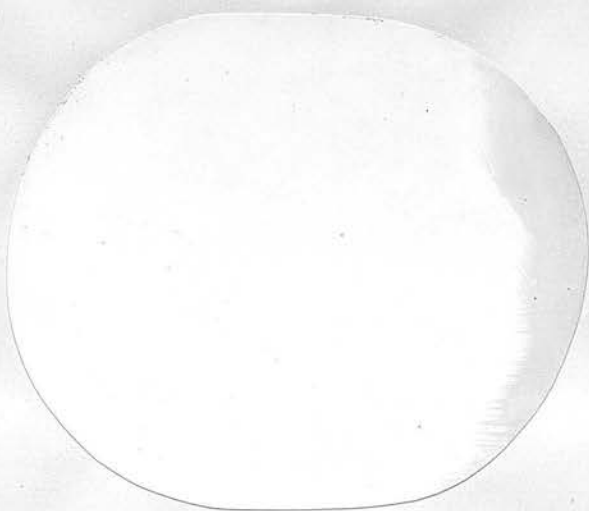


FIG. 270. Slowly cooled; squeezed in vice; annealed at  $140^{\circ}$  for 1 hour.

Bismuth, etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

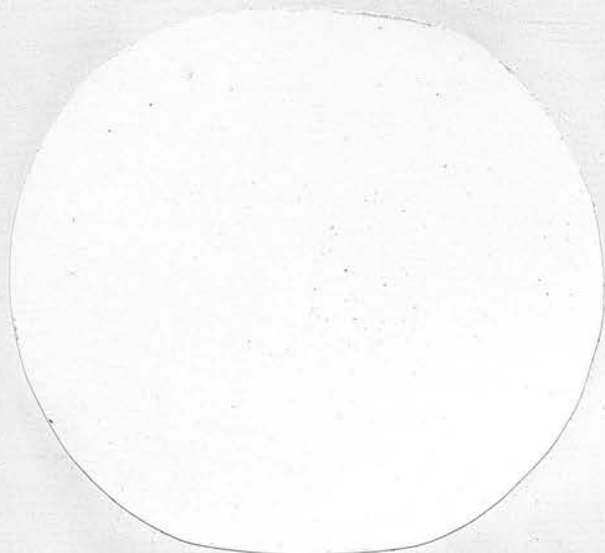


FIG. 271. Chill cast.

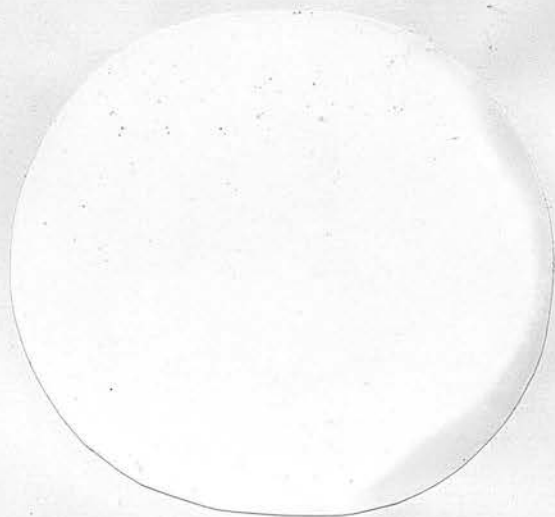


FIG. 273. Slowly cooled.

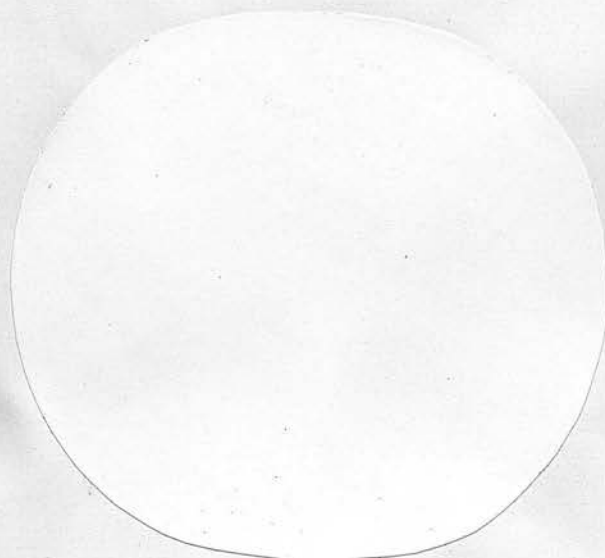


FIG. 272. Chill cast; annealed at 140° for 100 hours

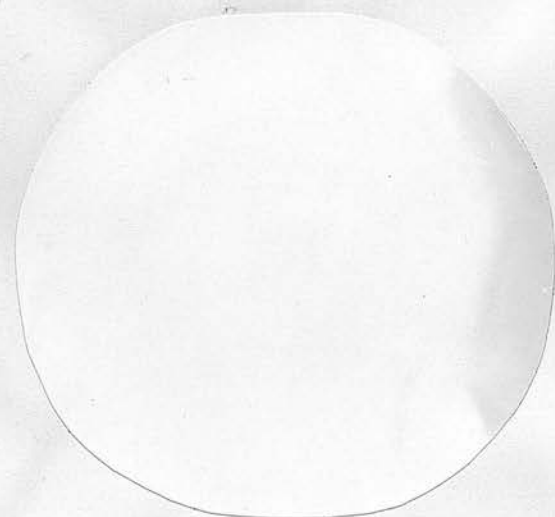


FIG. 274. Slowly cooled; annealed at 140° for 100 hours.

Cadmium, squeezed in vice; etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

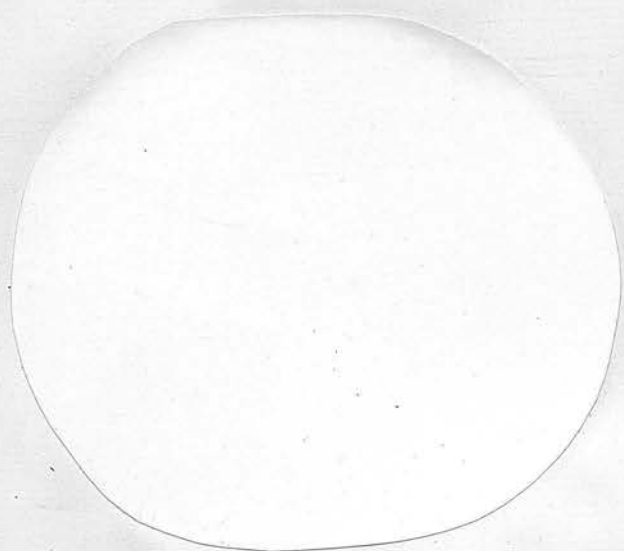


FIG. 275. Chill cast.

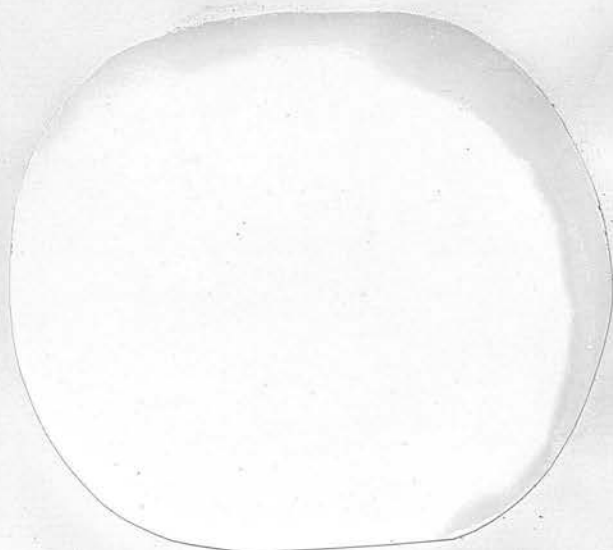


FIG. 278. Slowly cooled.

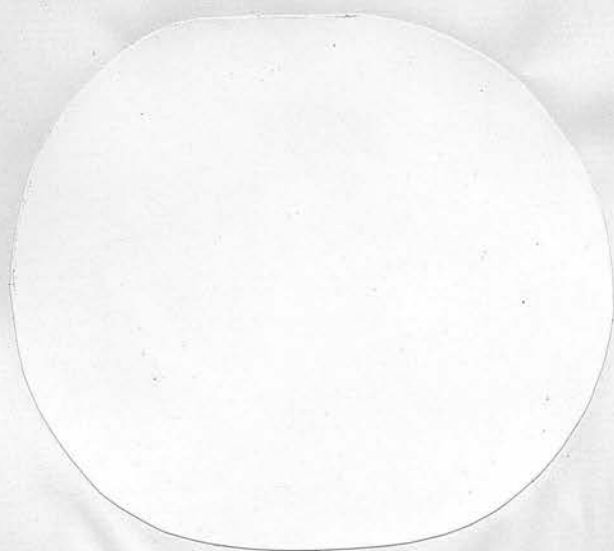


FIG. 276. Chill cast; annealed at 140° for 2 hours.

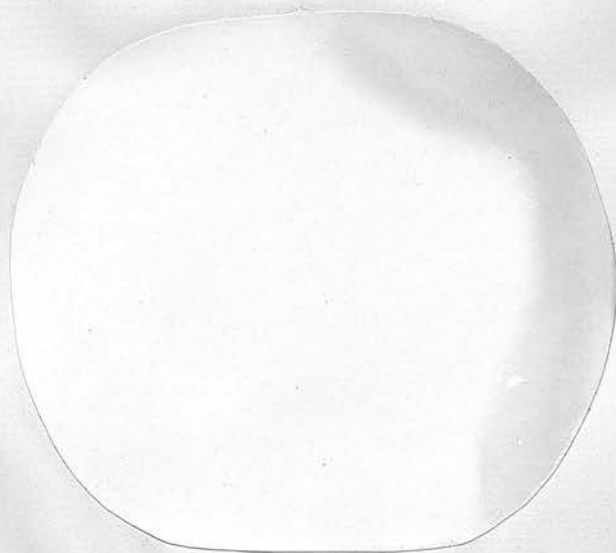


FIG. 279. Slowly cooled; annealed at 140° for 1 hour

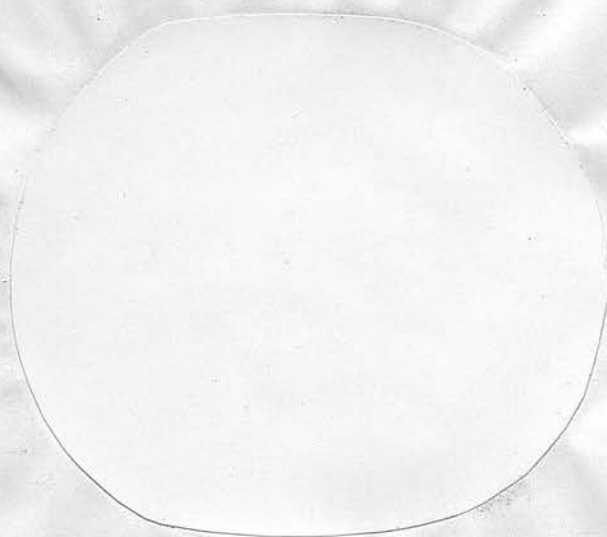


FIG. 277. Chill cast; annealed at 140° for 100 hours.

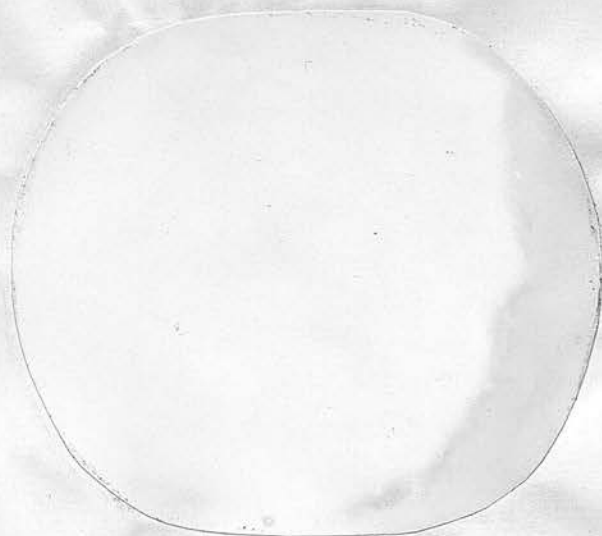


FIG. 280. Slowly cooled; annealed at 140° for 100 hours.

2 in., squeezed in vice; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters

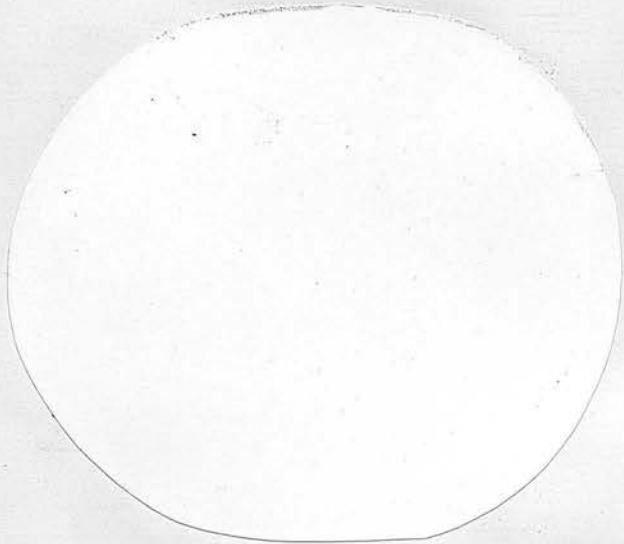


FIG. 281. Chill cast from  $750^{\circ}$ .

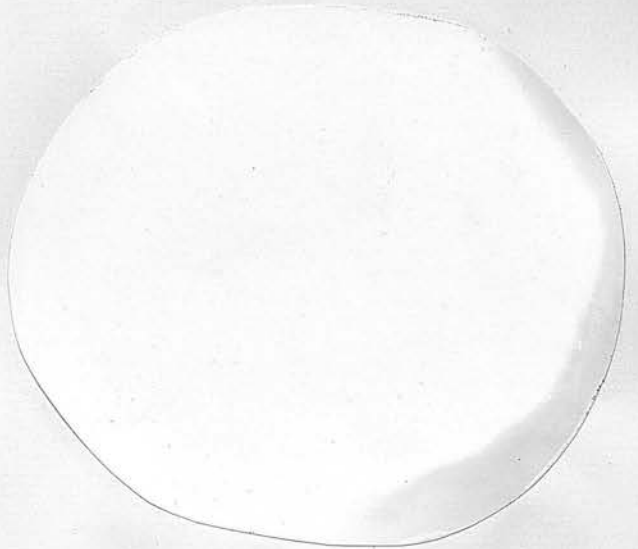


FIG. 282. Annealed at  $140^{\circ}$  for 1 hour.

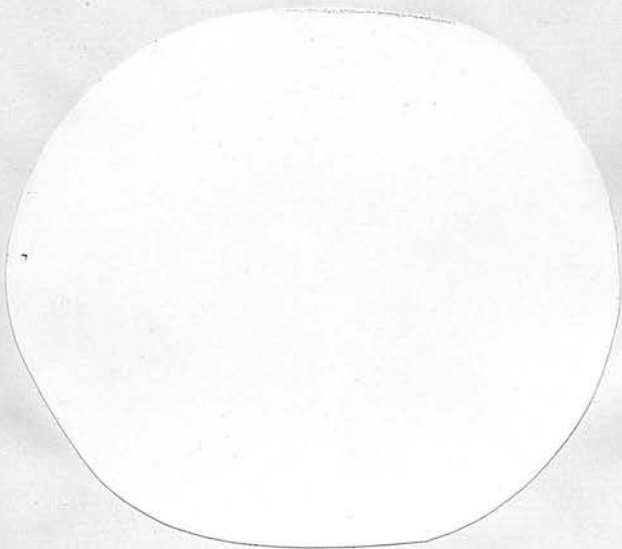


FIG. 283. Annealed at  $140^{\circ}$  for 2 hours.

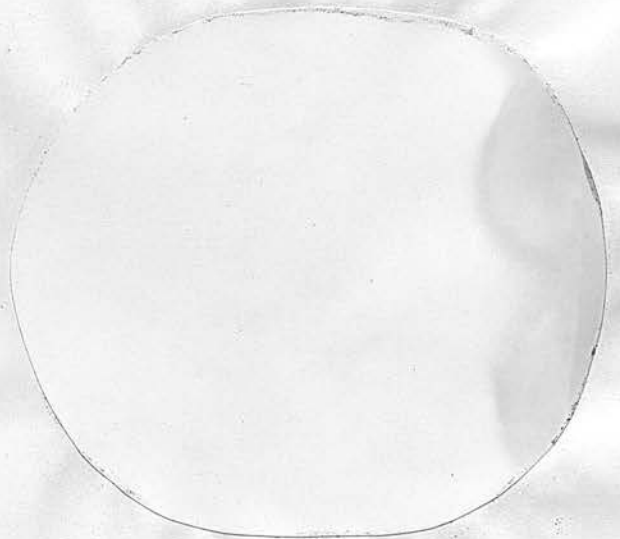


FIG. 284. Annealed at  $140^{\circ}$  for 100 hours.

3 in., squeezed in vice; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

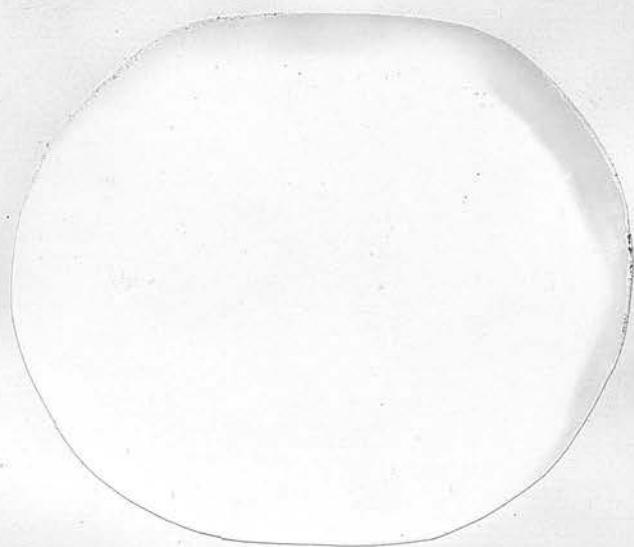
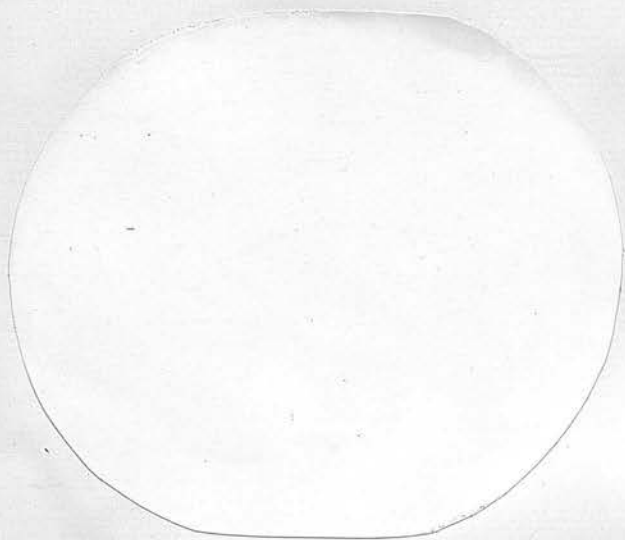


FIG. 285. Chill cast; squeezed in vice. FIG. 286. Annealed at  $140^{\circ}$  for 1 hour.

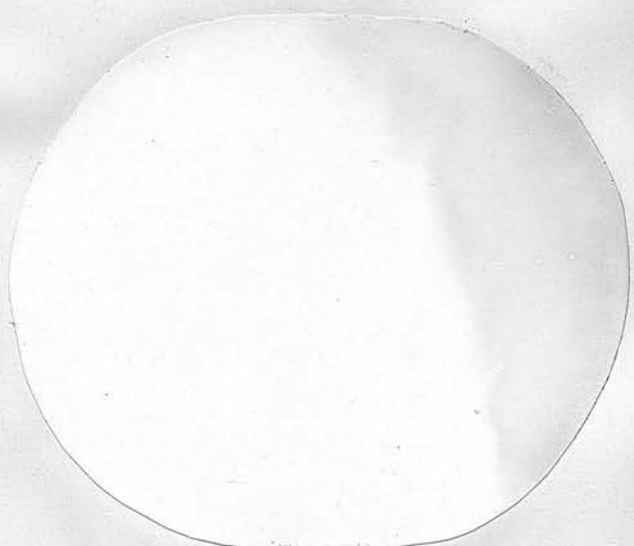
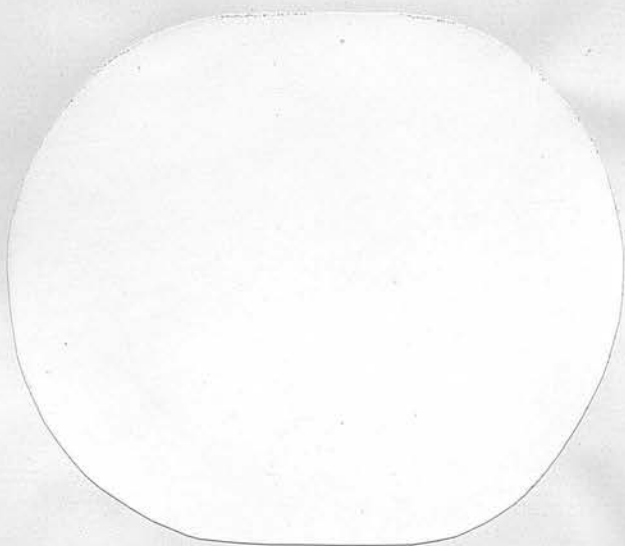


FIG. 287. Annealed at  $140^{\circ}$  for 2 hours. FIG. 288. Annealed at  $140^{\circ}$  for 5 hours.

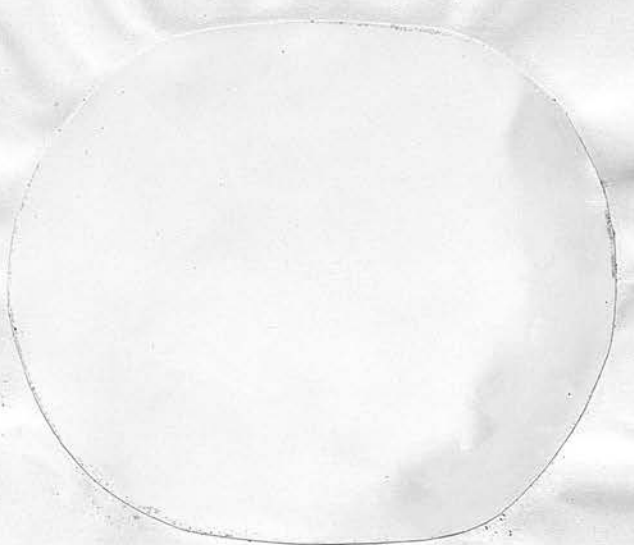
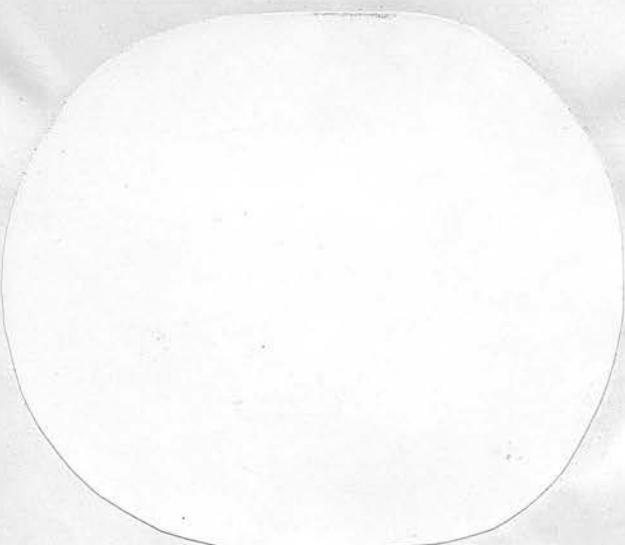


FIG. 289. Annealed at  $140^{\circ}$  for 20 hours. FIG. 290. Annealed at  $140^{\circ}$  for 100 hours.

Bismuth 98, Cadmium 2 per cent.; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

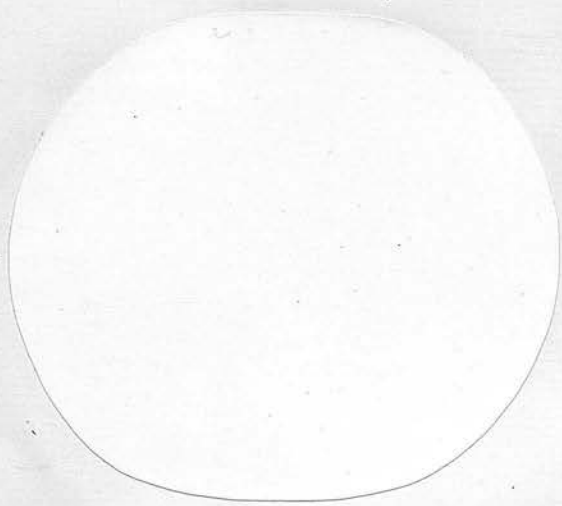


FIG. 291. Slowly cooled; squeezed in vice.

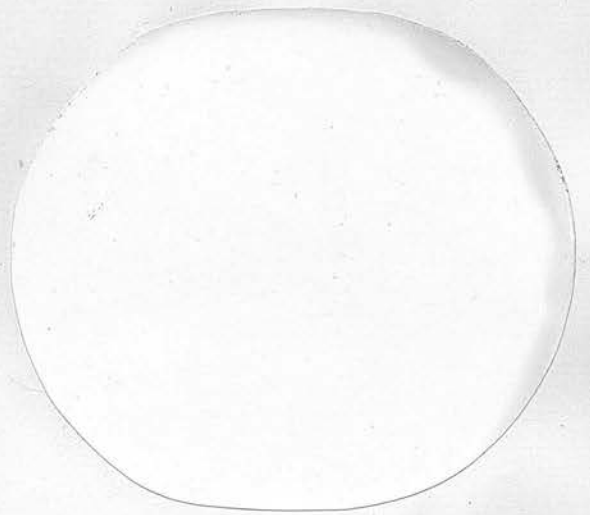


FIG. 292. Annealed at 140° for 1 hour

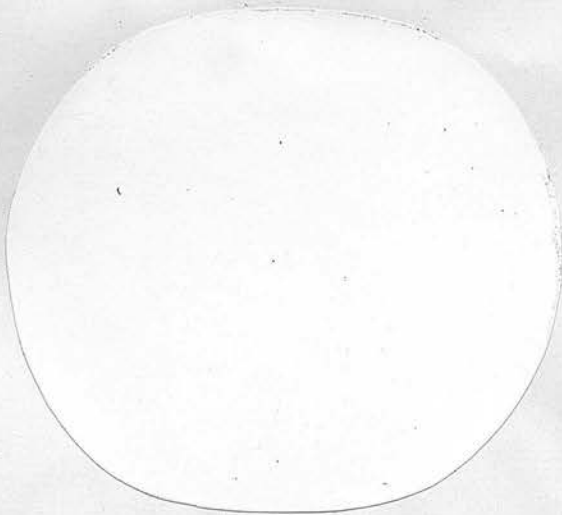


FIG. 293. Annealed at 140° for 5 hours.

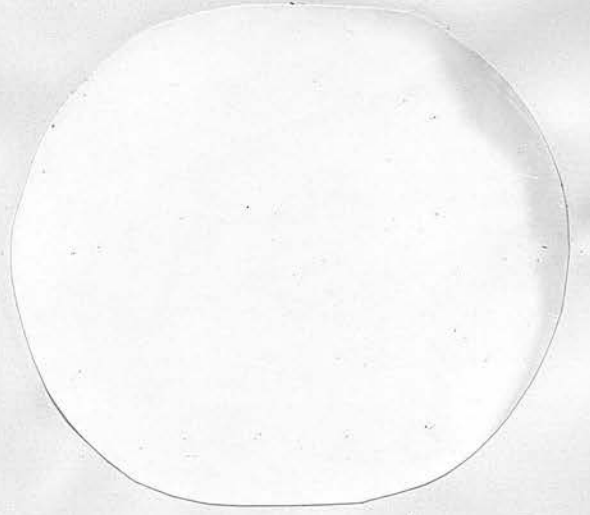


FIG. 294. Annealed at 140° for 20 hours

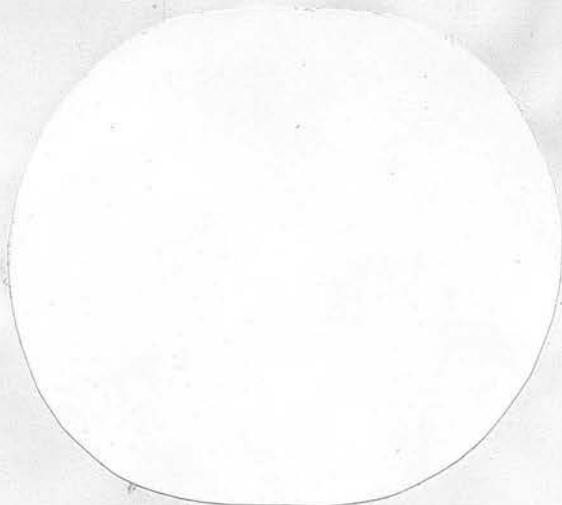


FIG. 295. Annealed at 140° for 100 hours.

Bismuth 98, Cadmium 2 percent.; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diams.

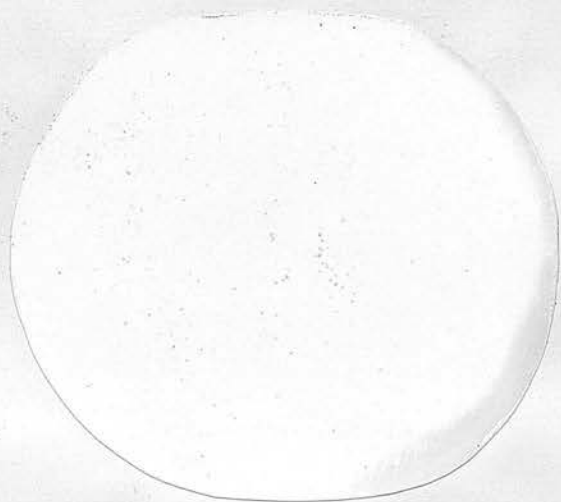
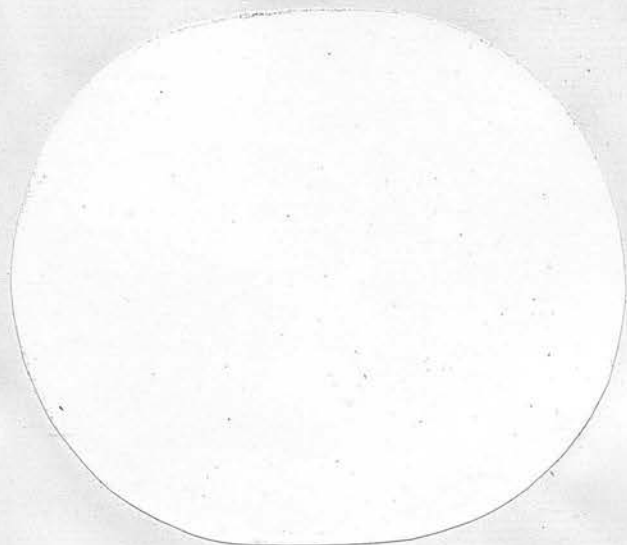


FIG. 296. Chill cast; squeezed in vice.

FIG. 298. Slowly Cooled; squeezed in vice.

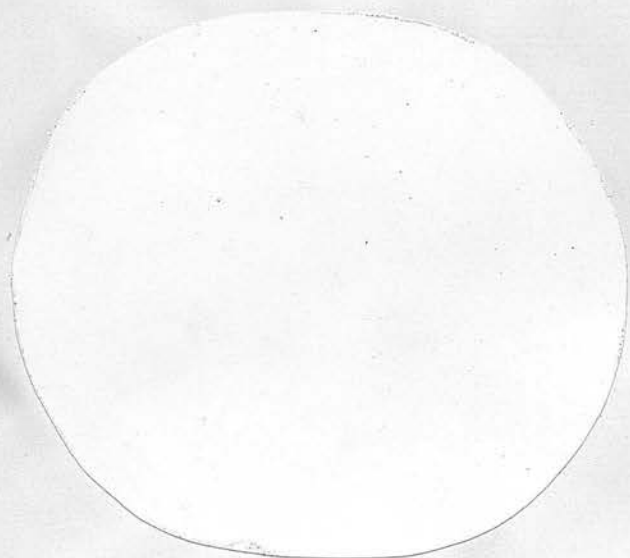


FIG. 297. Chill cast; squeezed in vice; annealed at  $140^{\circ}$  for 100 hours.

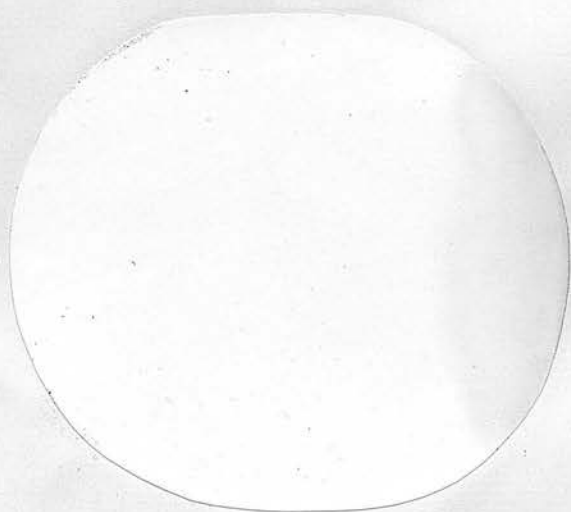


FIG. 299. Slowly Cooled; squeezed in vice; annealed at  $140^{\circ}$  for 100 hours.

Bismuth 98, tin 2 per cent.; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters

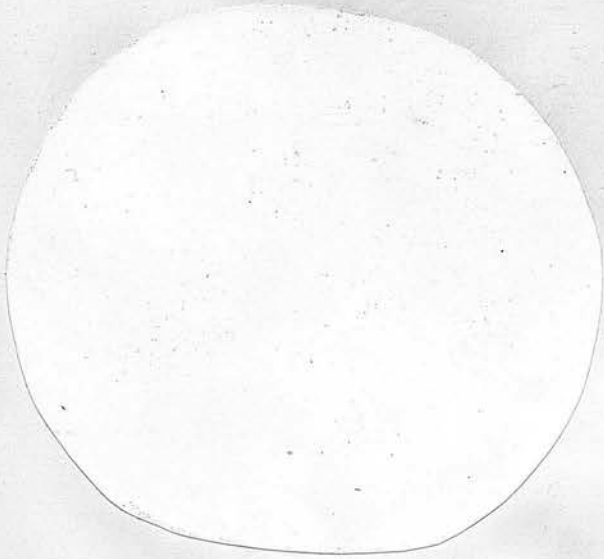


FIG. 300. Chill cast, squeezed in vice.

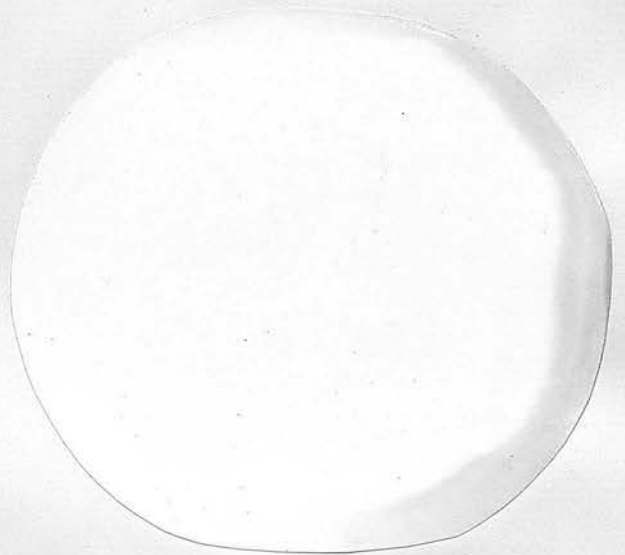


FIG. 301. Annealed at  $140^{\circ}$  for 1 hour.

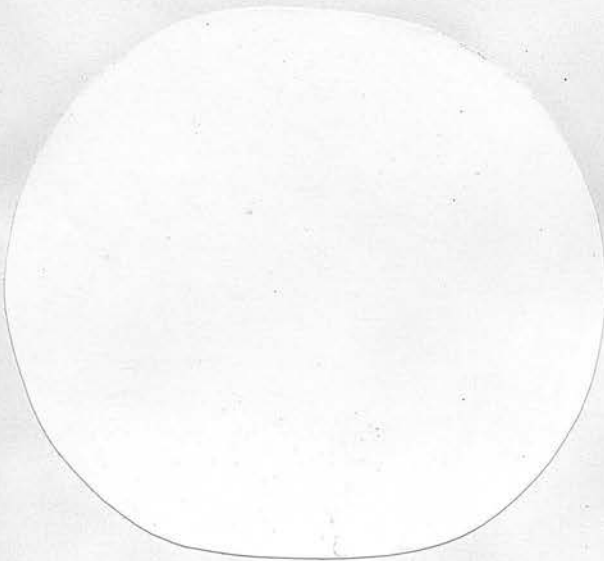


FIG. 302. Annealed at  $140^{\circ}$  for 2 hours.

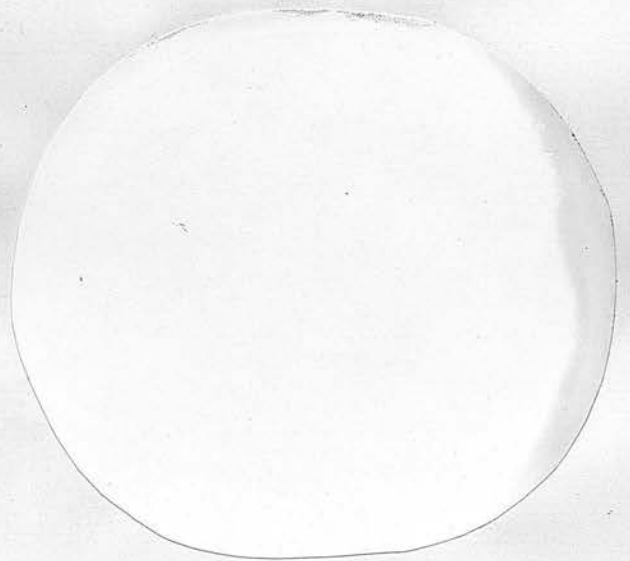


FIG. 303. Annealed at  $140^{\circ}$  for 100 hours.

Cadmium 98, bismuth 2 per cent.; etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

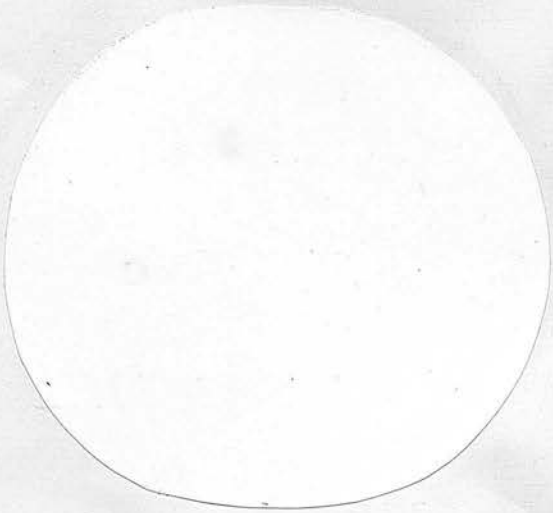


FIG. 304. Slowly cooled; squeezed in vice.

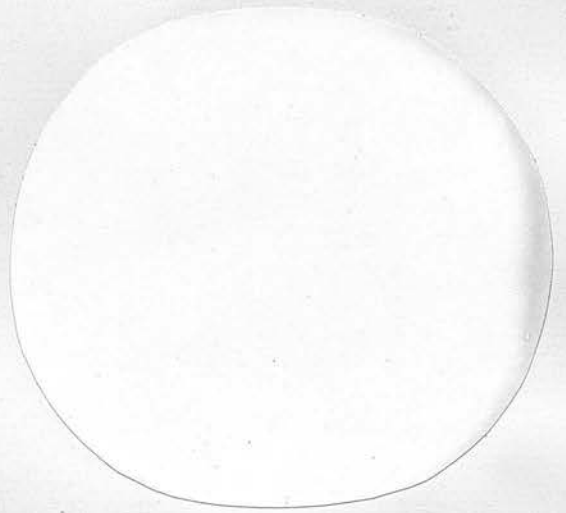


FIG. 305. Annealed at  $140^{\circ}$  for 1 hour.

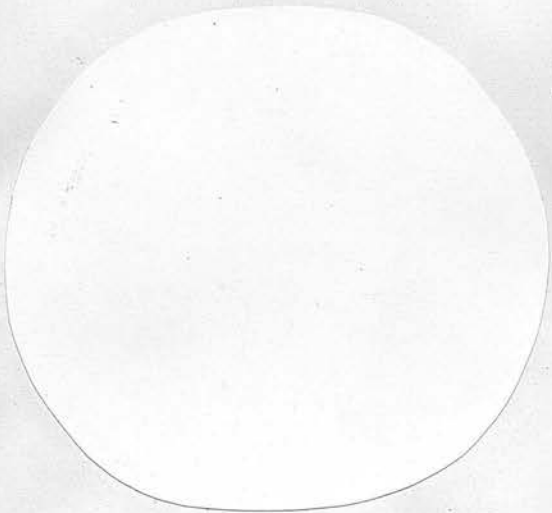


FIG. 306. Annealed at  $140^{\circ}$  for 2 hours.

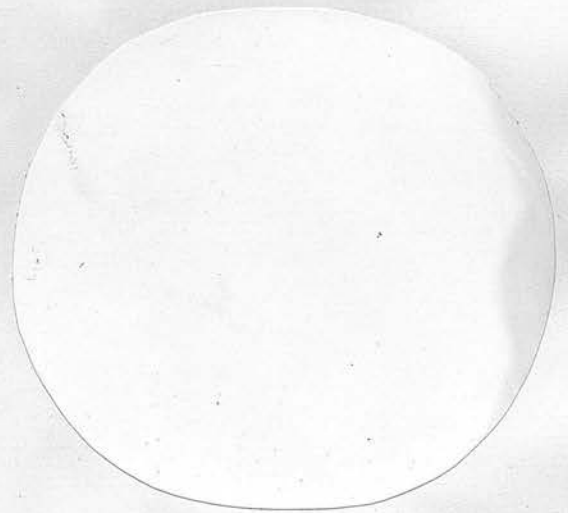


FIG. 307. Annealed at  $140^{\circ}$  for 100 hours.

Cadmium 98, bismuth 2 percent.; etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

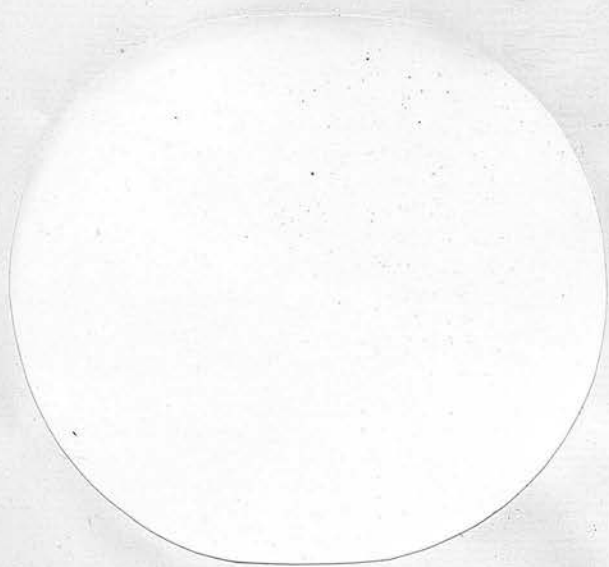


FIG. 308. Chill cast; squeezed in vice.

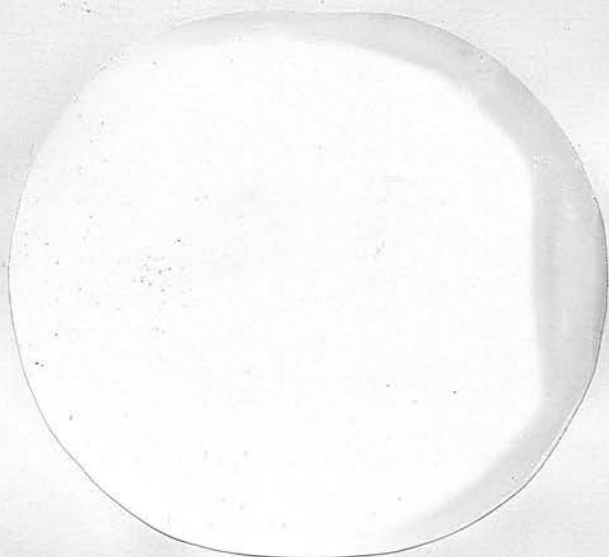


FIG. 309. Annealed at  $140^{\circ}$  for 1 hour

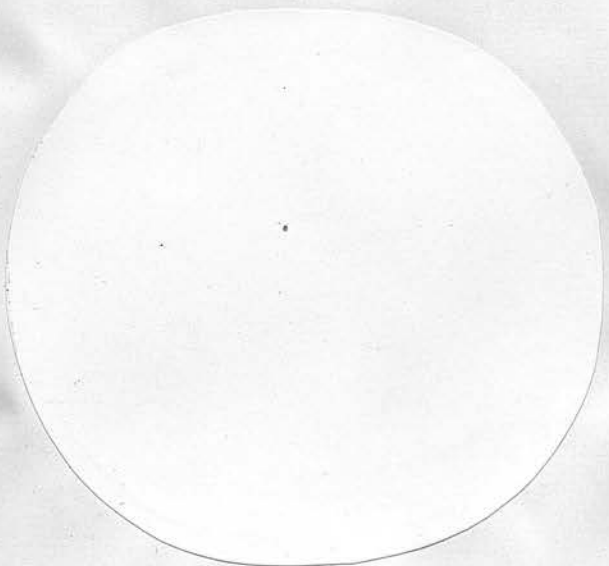


FIG. 310. Annealed at  $140^{\circ}$  for 2 hours.

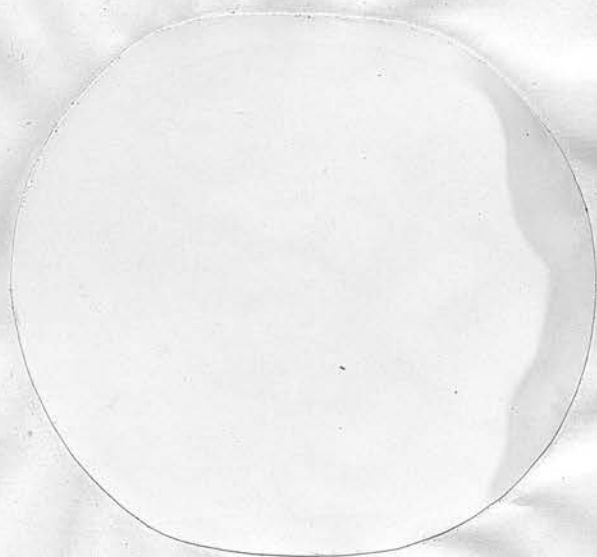


FIG. 311. Annealed at  $140^{\circ}$  for 100 hours.

Cadmium 98, tin 2 per cent; etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

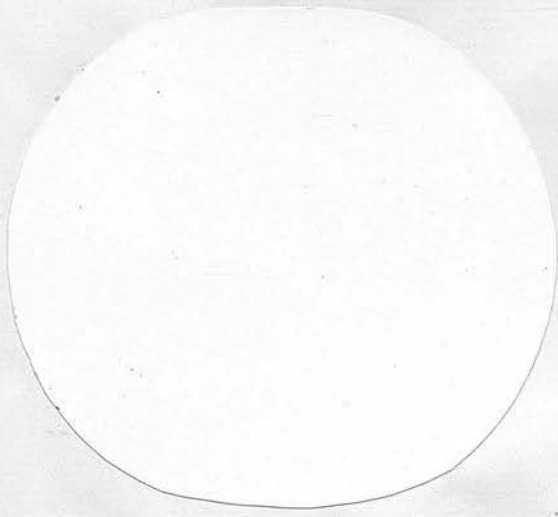


FIG. 312. Slowly cooled; squeezed in vice.

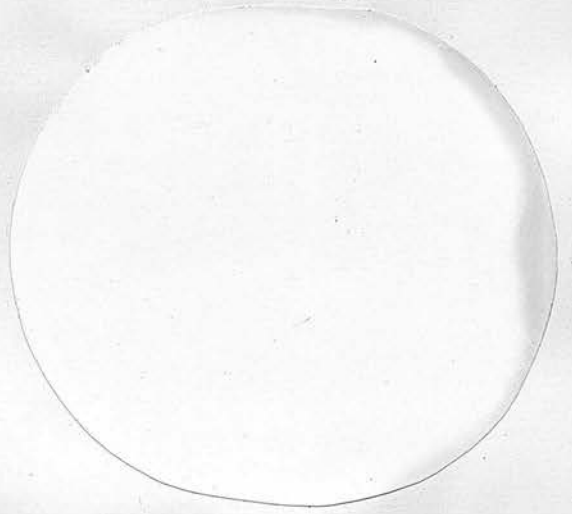


FIG. 313. Annealed at  $140^{\circ}$  for 1 hour.

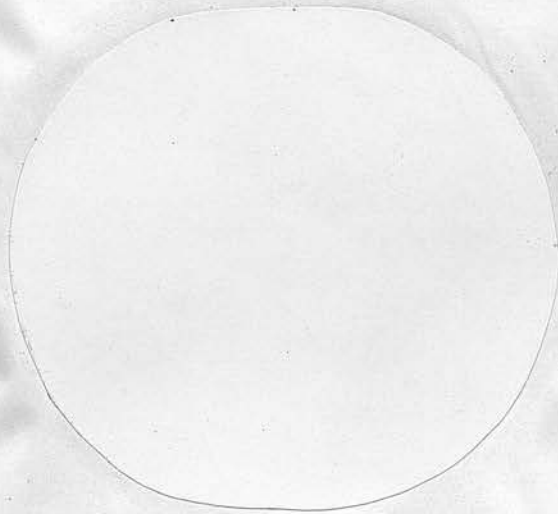


FIG. 314. Annealed at  $140^{\circ}$  for 2 hours.

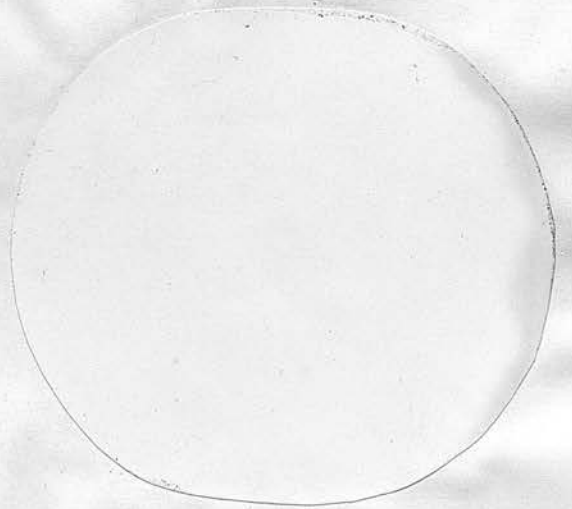


FIG. 315. Annealed at  $140^{\circ}$  for 100 hours.

Cadmium 98, tin 2 percent.; etched with iodine, and magnified  $7\frac{1}{2}$  diameters.

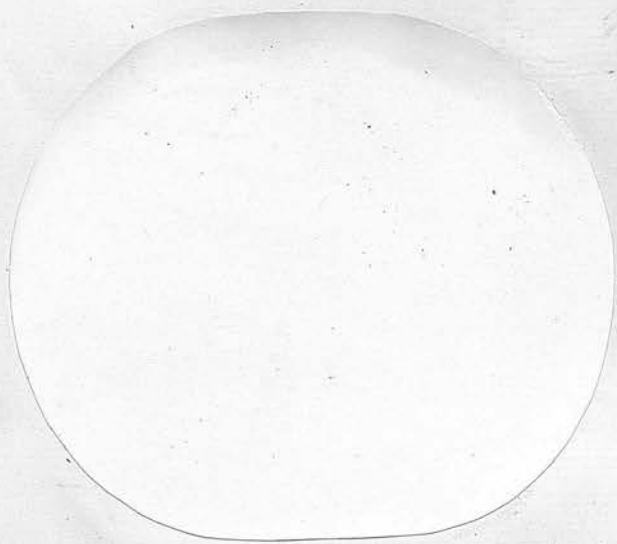


FIG. 316. Chill cast; squeezed in vice.

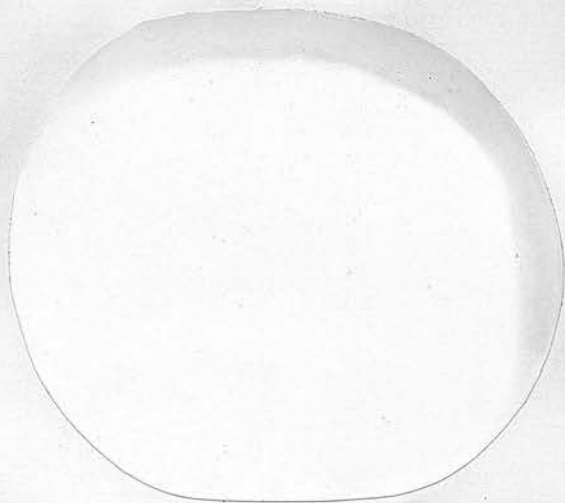


FIG. 319. Slowly cooled; squeezed in vice

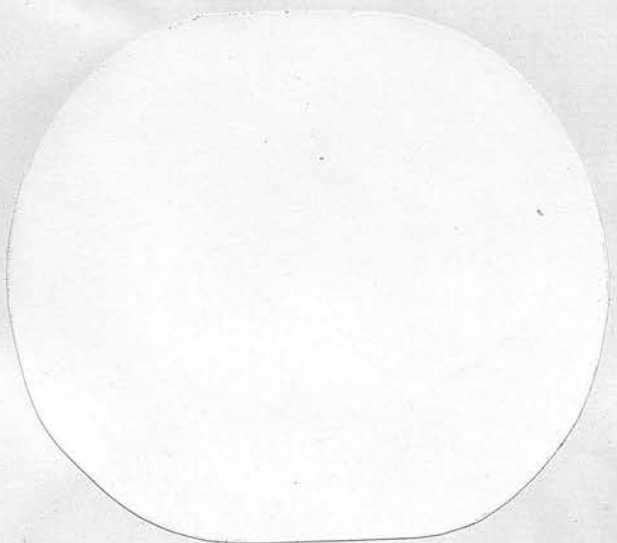


FIG. 317. Chill cast; squeezed in vice;  
annealed at  $140^{\circ}$  for 1 hour.

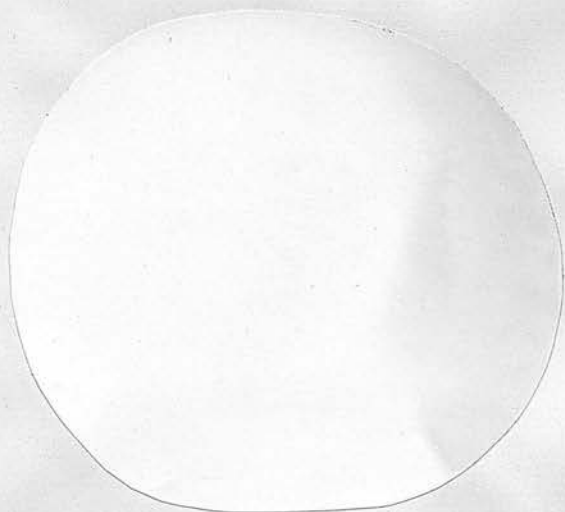


FIG 320. Slowly Cooled; squeezed in vice;  
annealed at  $140^{\circ}$  for 2 hours.

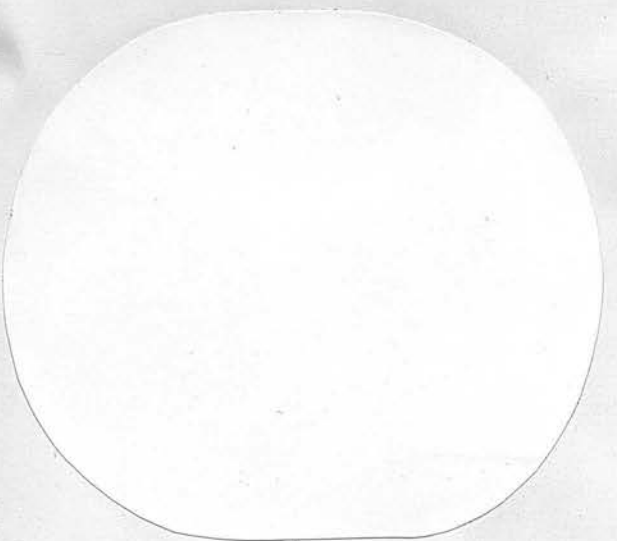


FIG. 318. Chill cast; squeezed in vice;  
annealed at  $140^{\circ}$  for 100 hours.

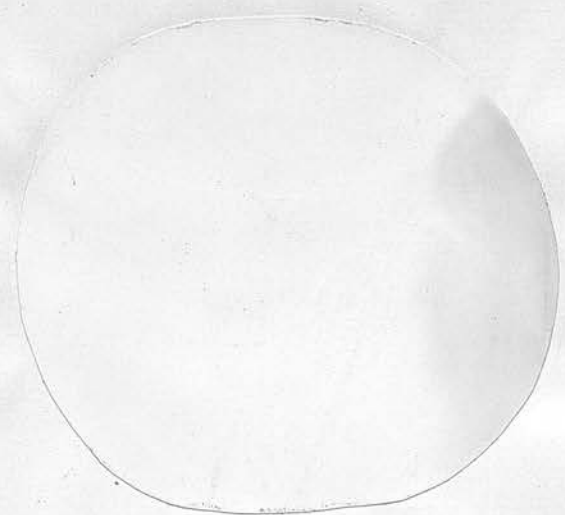


FIG. 321. Slowly Cooled; squeezed in vice;  
annealed at  $140^{\circ}$  for 100 hours.

2 in 98, bismuth 2 per cent.; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

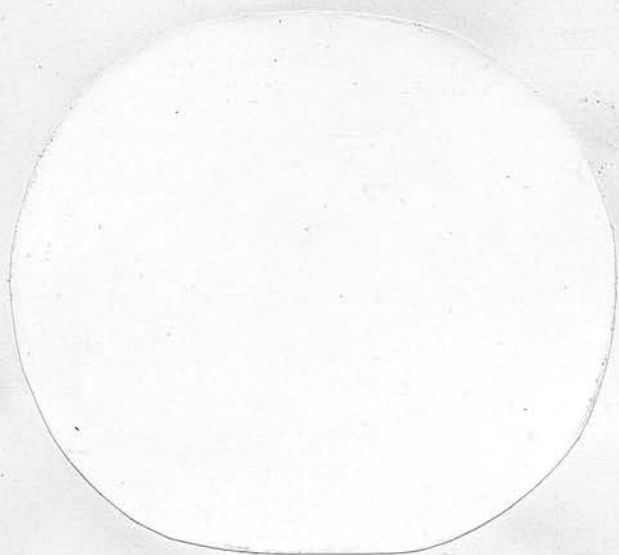


FIG. 322. Chill cast; squeezed in vice.

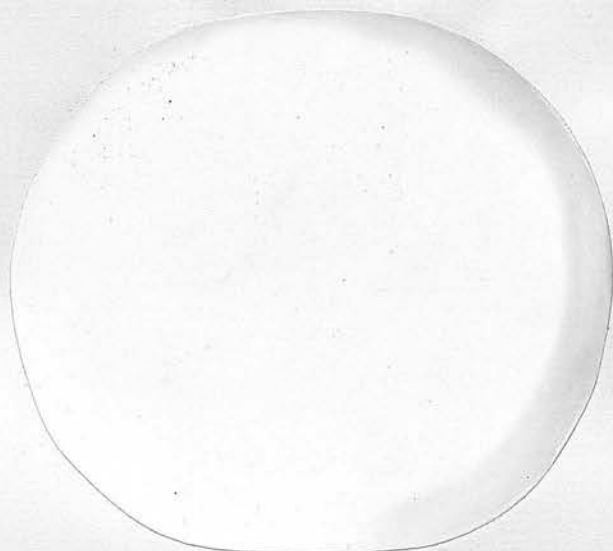


FIG. 323. Annealed at 140° for 1 hour

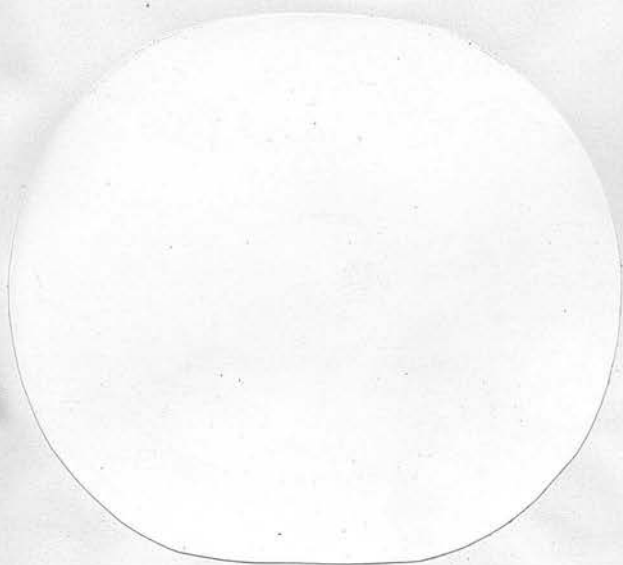


FIG. 324. Annealed at 140° for 2 hours.

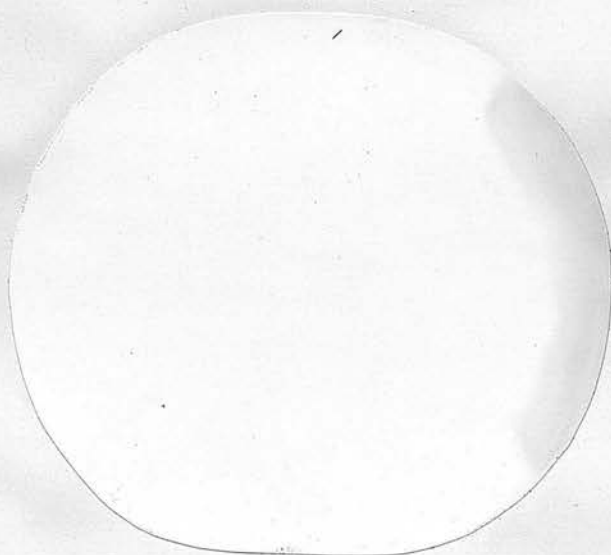


FIG. 325. Annealed at 140° for 100 hours.

In 98, Cadmium 2 per cent.; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters.

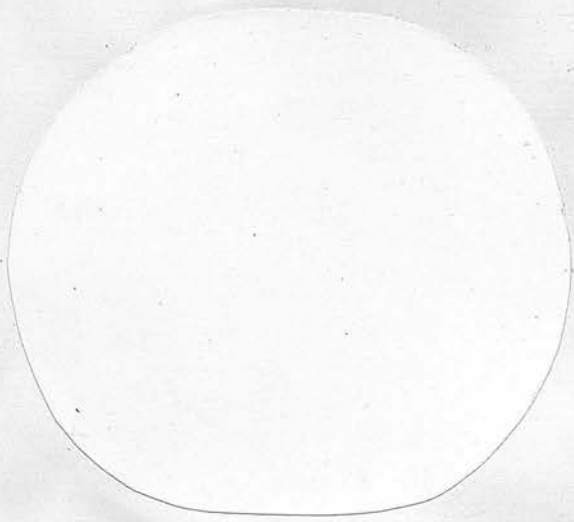


FIG. 326. Slowly cooled; squeezed in vice.

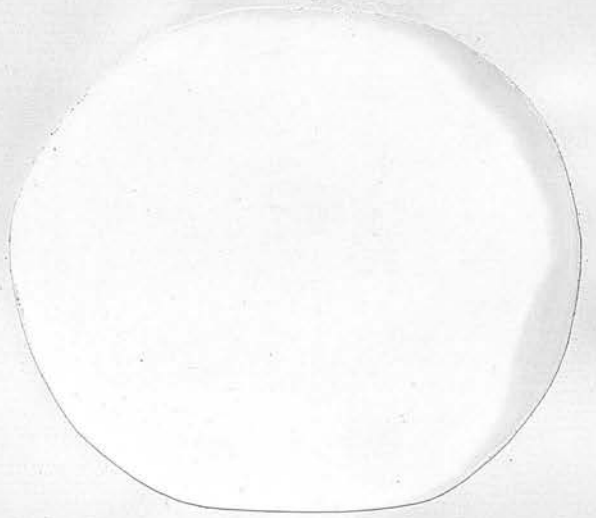


FIG. 327. Annealed at 140° for 2 hours.

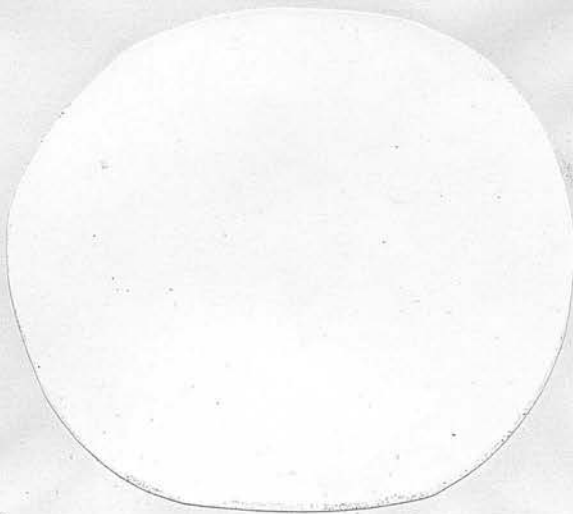


FIG. 328. Annealed at 140° for 100 hours.

Sim 98, Cadmium 2 percent.; etched with ferric chloride, and magnified  $7\frac{1}{2}$  diameters

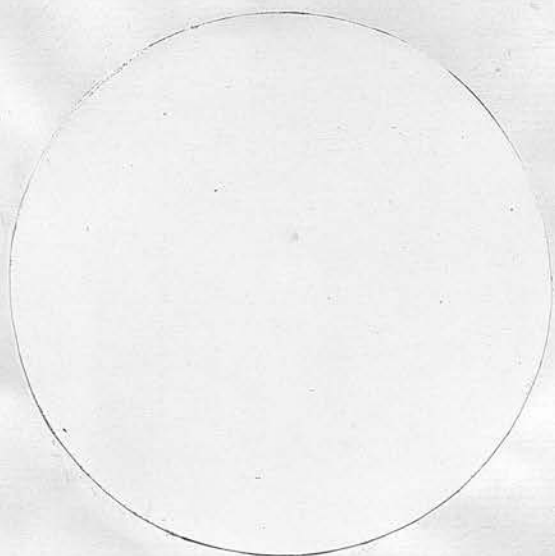


FIG. 329. Middle of ingot.

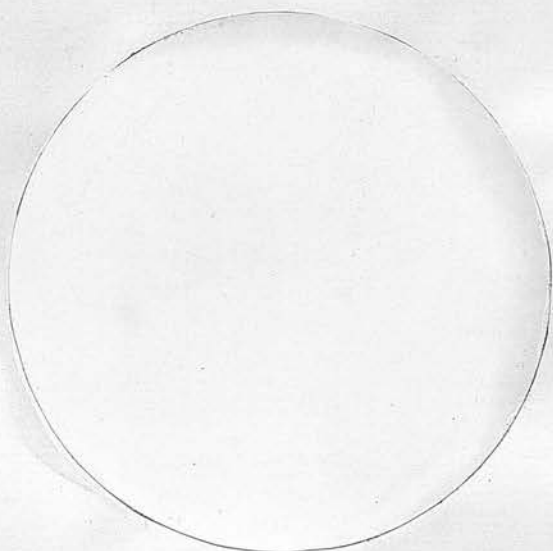


FIG. 330. Edge of ingot.

*Bismuth-tin eutectic, chill cast from 160°; etched with nitric acid, and magnified 100 diameters.*

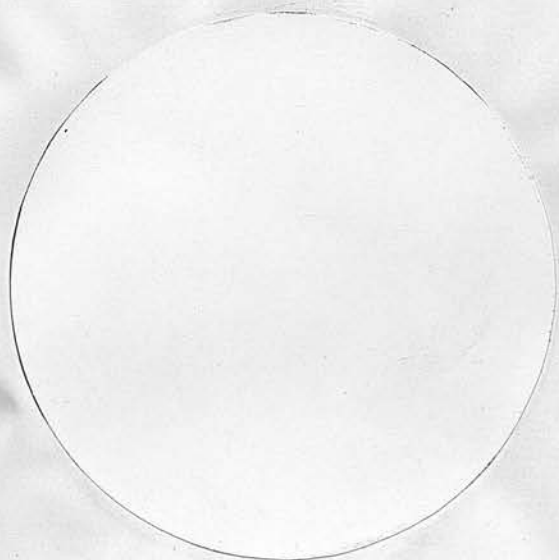


FIG. 331. Middle of ingot.

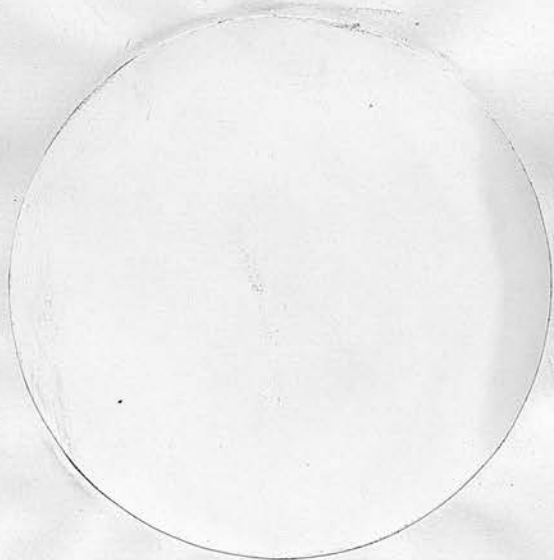


FIG. 332. Edge of ingot.

*Bismuth 55, tin 45 percent., chill cast from 300°; etched with nitric acid, and magnified 100 diameters.*

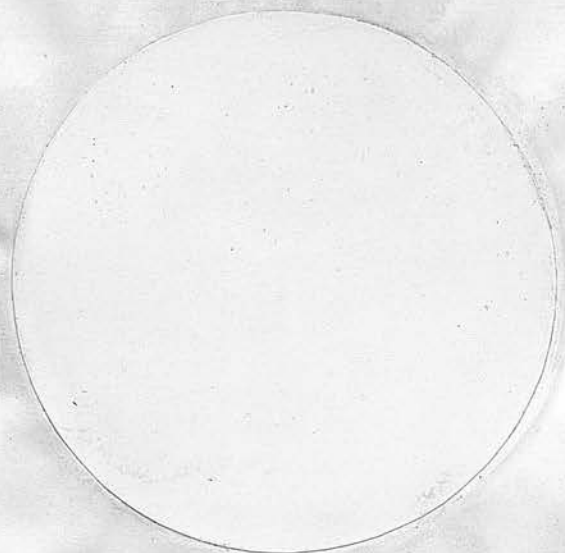


FIG. 333. Middle of ingot.

Chill cast from  $160^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours

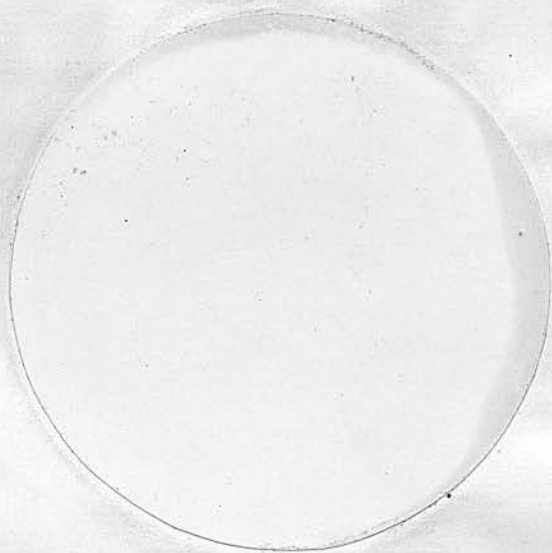


FIG. 334. Edge of ingot

Chill cast from  $160^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours

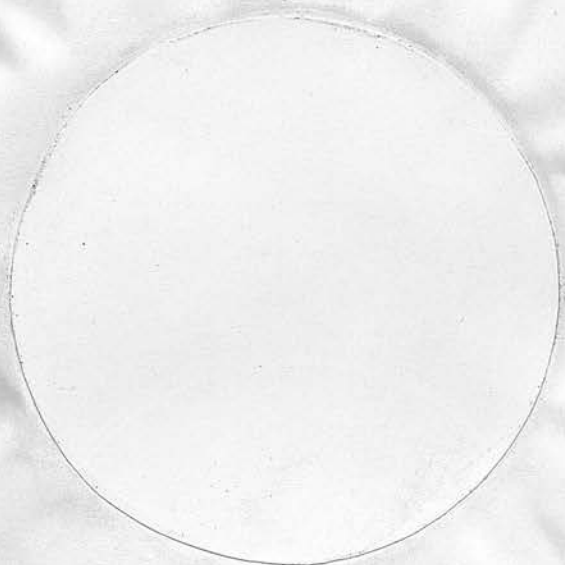


FIG. 335. Middle of ingot.

Chill cast from  $300^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours.

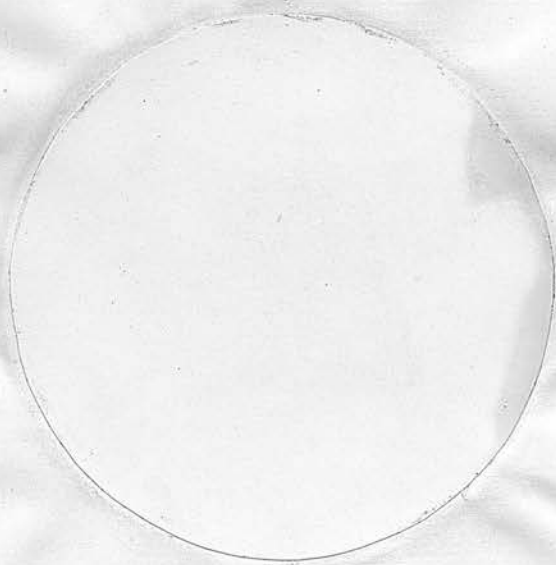


FIG. 336. Edge of ingot.

Chill cast from  $300^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours.

Bismuth 60, tin 40 percent; etched with ferric chloride, and magnified 100 diameters.

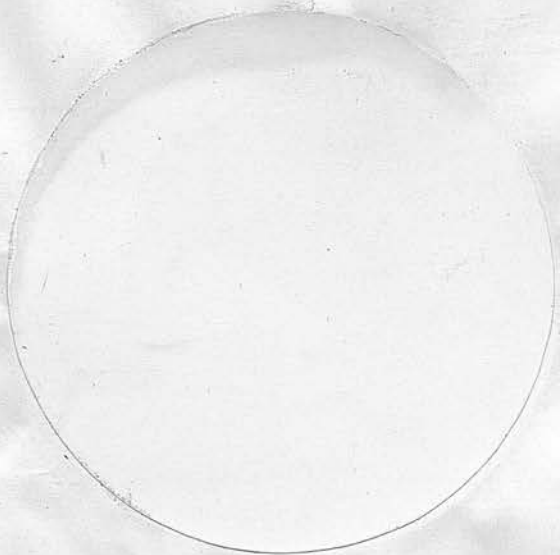


FIG. 337. Middle of ingot.

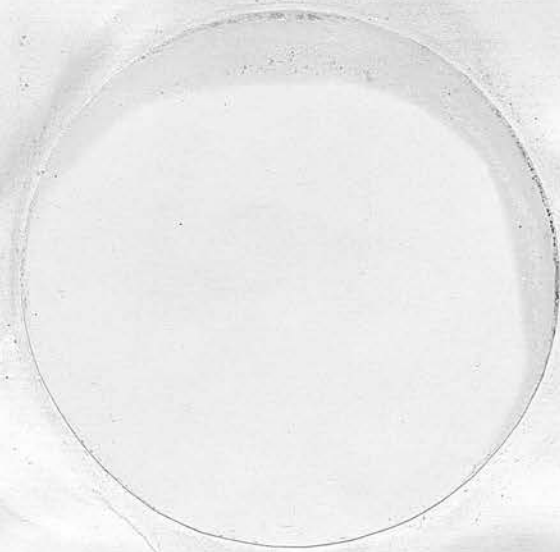


FIG. 338. Edge of ingot.

Chill cast from  $160^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours.

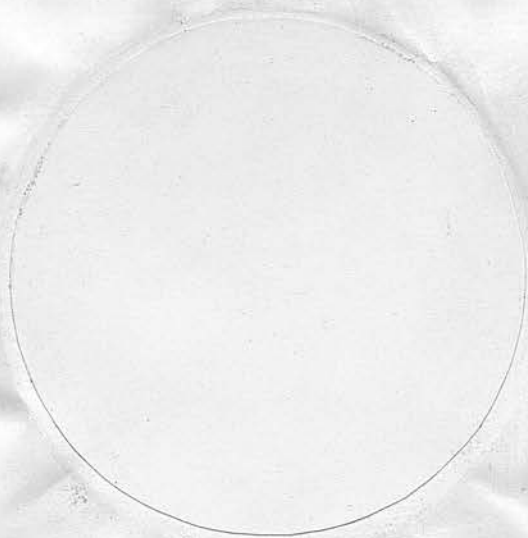


FIG. 339. Middle of ingot.

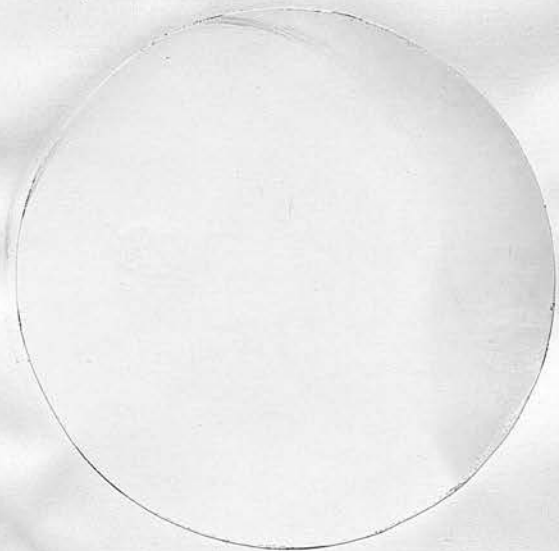


FIG. 340. Edge of ingot.

Chill cast from  $300^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours.

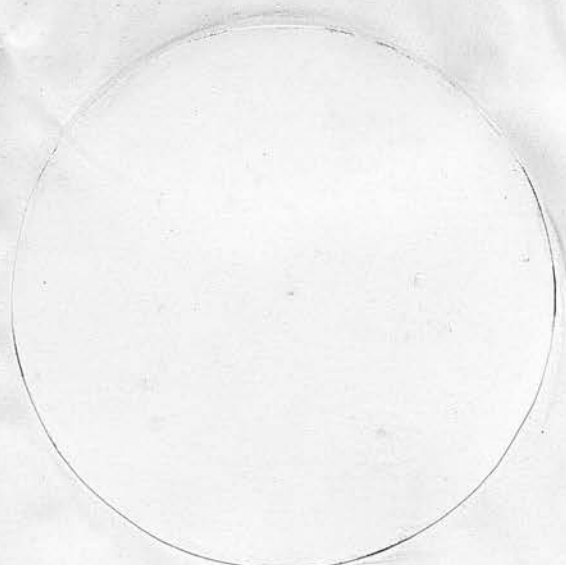


FIG. 341. Middle of ingot.

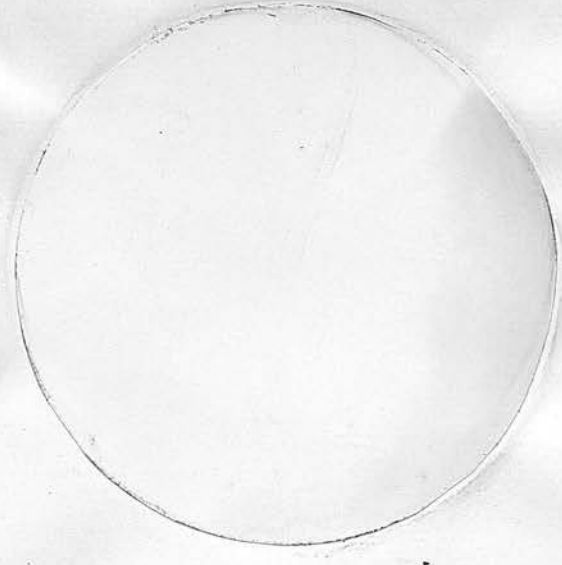


FIG. 342. Edge of ingot.

Chill cast from  $750^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours.

Bismuth-tin eutectic; etched with ferric chloride, and magnified 100 diameters.

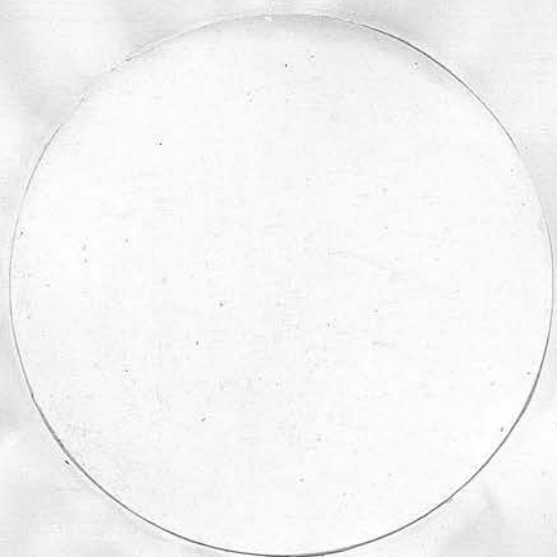


FIG. 343. Middle of ingot.

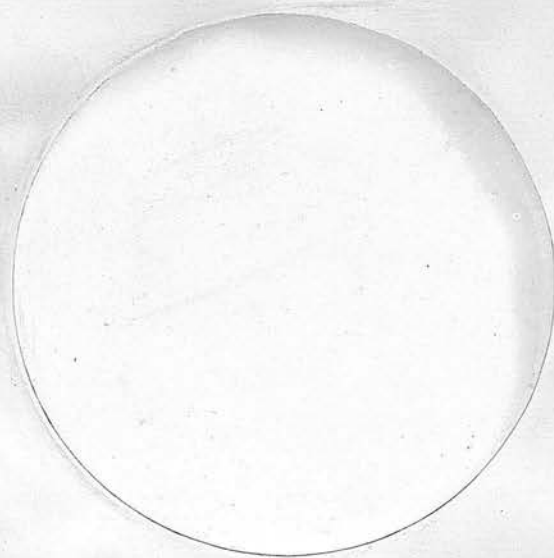


FIG. 344. Edge of ingot.

Chill cast from  $160^{\circ}$ , and annealed at  $100^{\circ}$  for 200 hours.

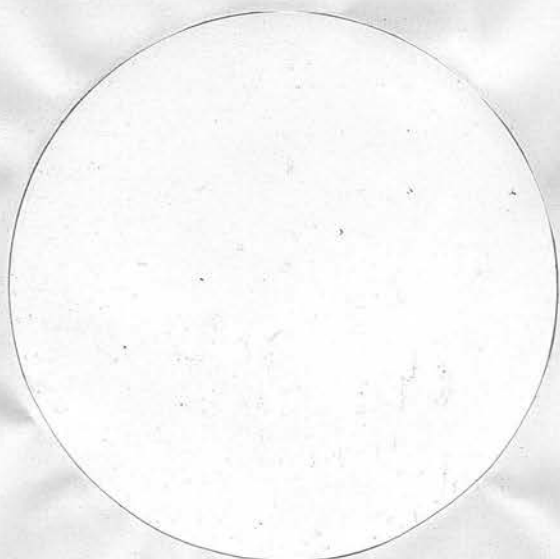


FIG. 345. Middle of ingot.

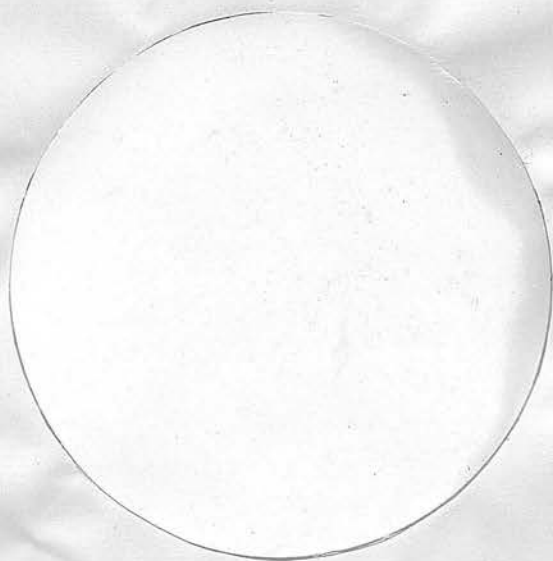


FIG. 346. Edge of ingot.

Chill cast from  $300^{\circ}$ , and annealed at  $100^{\circ}$  for 200 hours.

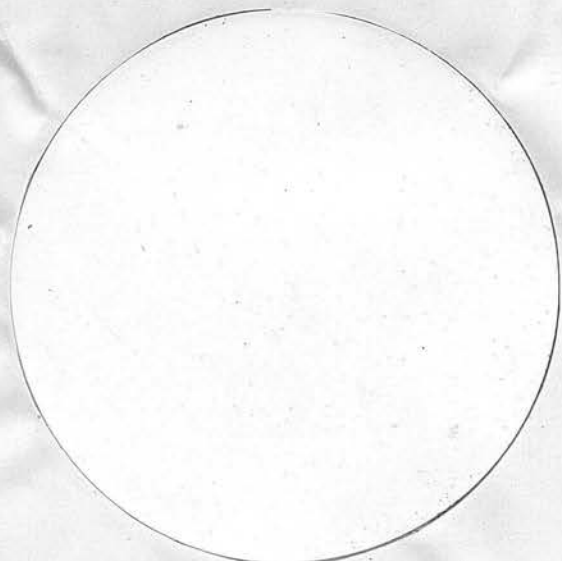


FIG. 347. Middle of ingot.

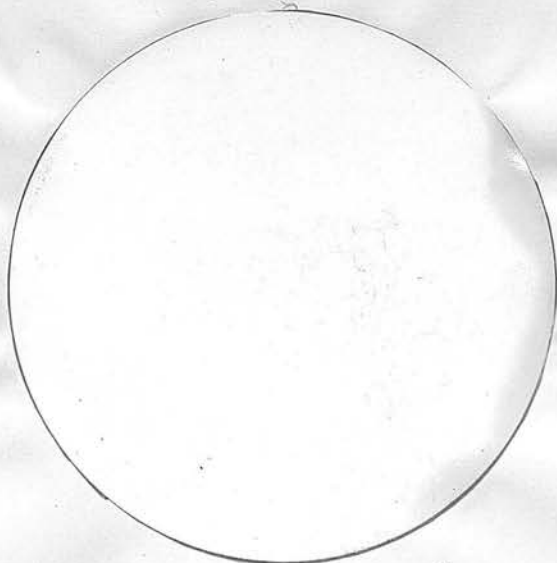


FIG. 348. Edge of ingot.

Chill cast from  $750^{\circ}$ , and annealed at  $100^{\circ}$  for 200 hours.

Bismuth 55, tin 45 percent.; etched with ferric chloride, and magnified 100 diameters.

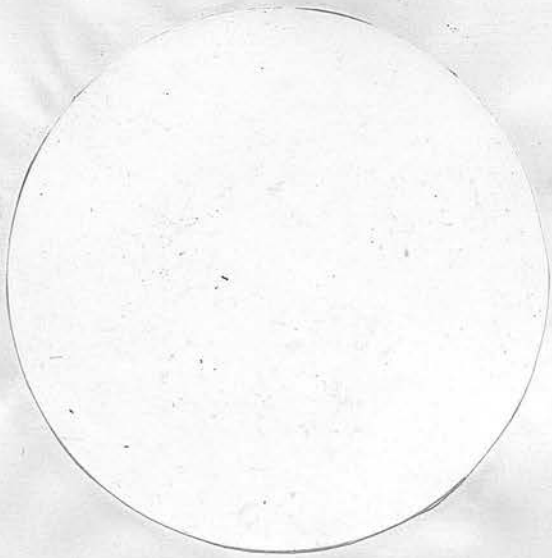


FIG. 349. Middle of ingot.

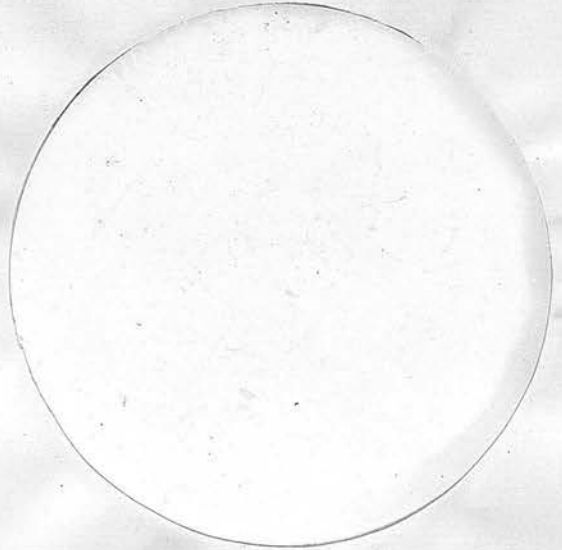


FIG. 350. Edge of ingot.

Chill cast from  $160^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours.

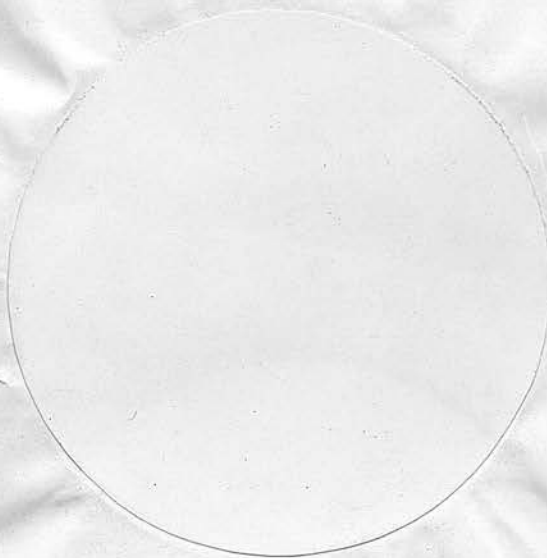


FIG. 351. Middle of ingot.

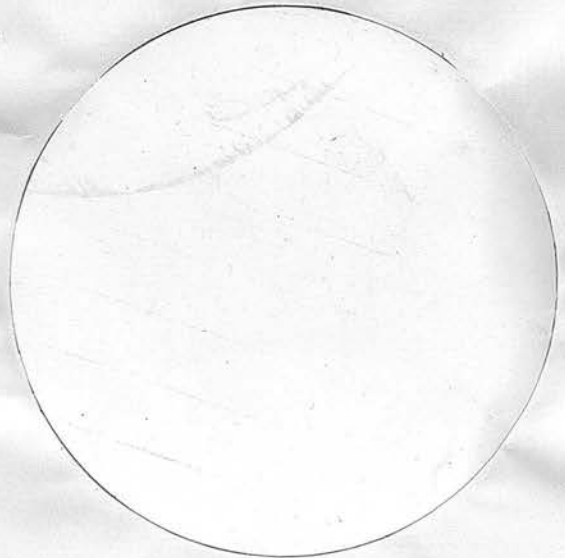


FIG. 352. Edge of ingot.

Chill cast from  $300^{\circ}$ , and annealed at  $100^{\circ}$  for 300 hours.

Diamuth 50, tin 50 per cent; etched with ferric chloride, and magnified 100 diameters.

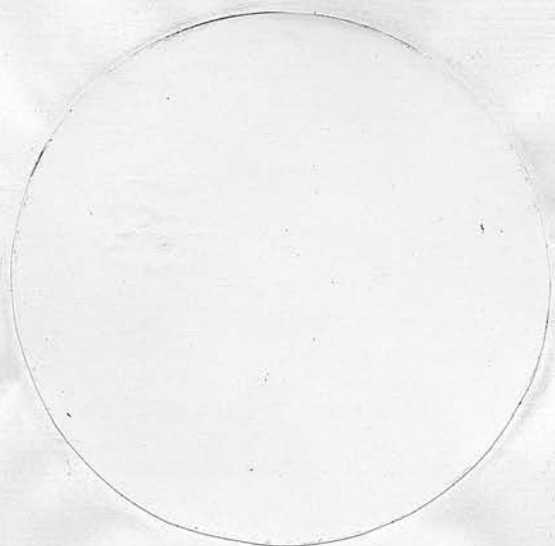


FIG. 353. Chill cast.

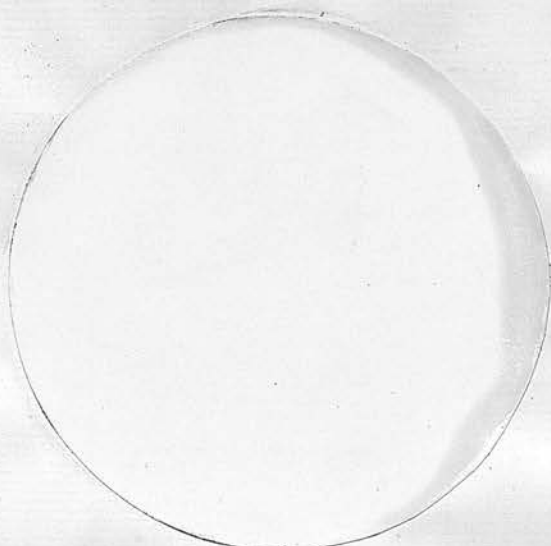


FIG. 354. Slowly cooled.

Copper 57, antimony 43 percent. ; etched with copper-ammonium chloride, and magnified 100 diameters.

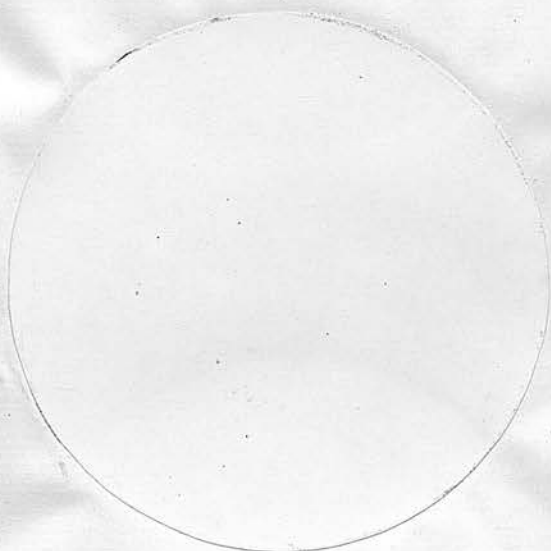


FIG. 355. Copper 46, zinc 54 percent. ; slowly cooled and reheated to  $750^{\circ}$ ; etched with chromic acid; magnified 50 diameters.

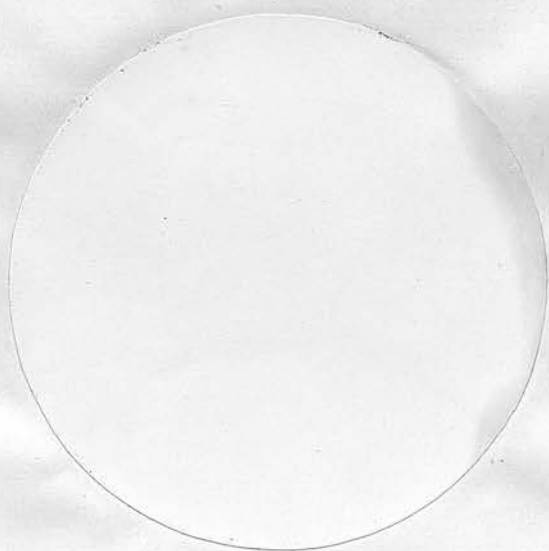


FIG. 356. Copper 32, zinc 68 percent. ; slowly cooled; etched with chromic acid; magnified 25 diameters.

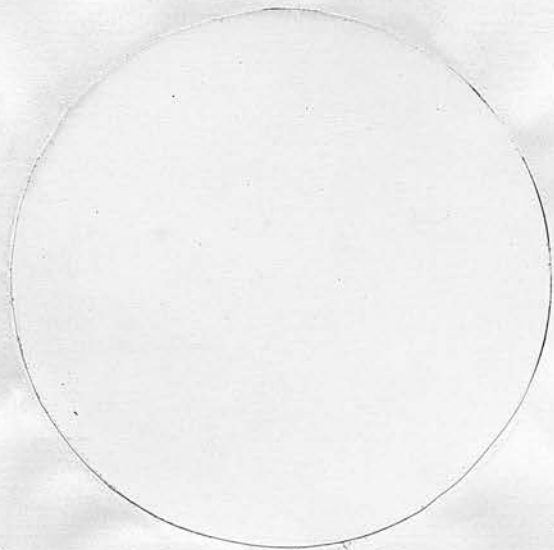


FIG. 357. Copper 88, aluminium 12 percent; chill cast; etched with ferric chloride; magnified 25 diameters.

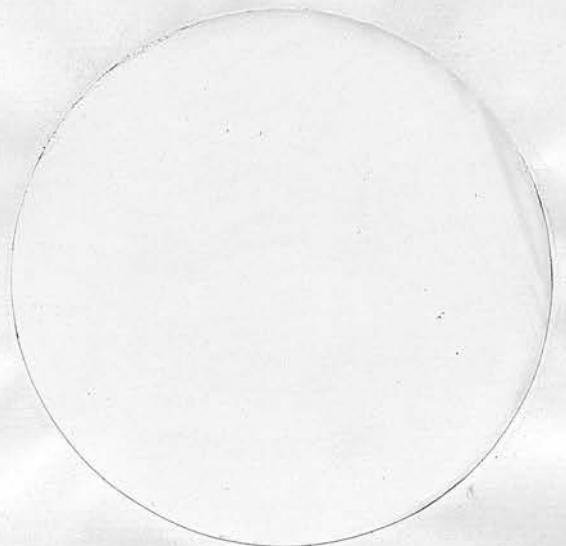


FIG. 358. Copper 65, tin 35 percent.; chill cast; etched with chromic acid; magnified 25 diameters.

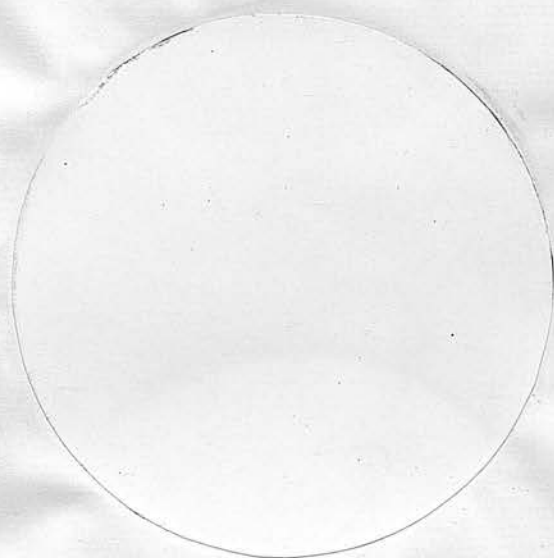


FIG. 359. Copper 77, tin 23 percent.; slowly cooled; etched with ferric chloride; magnified 50 diameters.

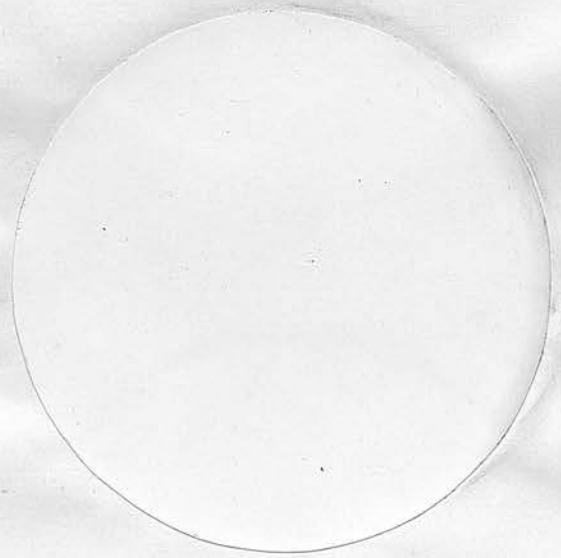


FIG. 360. Copper 90, aluminium 10 percent.; slowly cooled; etched with ferric chloride; magnified 25 diameters.