

V. *Gold-Aluminium Alloys.*By C. T. HEYCOCK, *F.R.S.*, and F. H. NEVILLE, *F.R.S.*

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[PLATES 4-5.]

THIS paper is a study of the binary alloys composed of gold and aluminium. The fact that metals in many cases form definite chemical compounds with each other, is becoming increasingly evident as attention is given to the subject. But there are many pairs of metals whose freezing point-curve affords no indication of chemical combination, and which probably do not combine with each other under the conditions of our experiments. It is therefore desirable, in seeking for such compounds, to select a pair of metals which are known to have a peculiar relation to each other. We chose gold and aluminium for several reasons. First, on account of the beautiful purple compound of Sir W. ROBERTS-AUSTEN, and on account of our own experiments ('Journal Chemical Society,' vol. 74, 1894), which showed it to be a very stable body in solution. There was also the important point that the alloys of gold and aluminium admit of fairly rapid analysis by the determination of the gold.

In the present paper the freezing point method is combined with a microscopic study of the alloys, and we hope that it will be found that the interpretation of the results is more conclusive than in previous papers of our own and of others in which only the one method or the other was employed.

Section I. describes the methods of experiment.

Section II. contains tables of freezing points, figures of the freezing point-curve, and an account of the curves.

Section III. is devoted to a description of the microscopic appearance of the alloys, and is illustrated by photomicrographs.

SECTION I.

In the experiments on which the freezing point-curve is based, the method of procedure was similar to that described in our paper ('Phil. Trans.,' A, vol. 189, p. 25) on the freezing point of copper tin, silver copper, and other alloys.* The freezing point of pure gold was first determined, and then successive roughly weighed amounts of aluminium were added, the freezing point being taken after each addition.

* For the method of determining temperatures, see also our paper ('Journ. Chem. Soc.,' 1895, p. 160).

Owing to the rapid oxidation of the aluminium, even when a current of coal gas was led into the crucible, the synthetical method of arriving at the composition of the alloys from the weights of metal added was impracticable. It was therefore necessary, between every two readings of the freezing point, to extract a sample of the alloy for analysis. This was done by sucking out a portion of the thoroughly molten and stirred metal in a pipette of Jena combustion glass. If rapidly performed, this process is practicable, even at the melting point of gold. The samples were thus obtained in the form of rods, or occasionally as tubes, about 4 millims. in diameter. After breaking off the glass these rods could easily be cut up for analysis and for microscopical study. The order of operation was as follows :—

- (1.) A dose of aluminium was added, and the alloy well stirred.
- (2.) The freezing point was determined roughly.
- (3.) The metal was re-melted, stirred, and a sample extracted.
- (4.) The alloy was again re-melted, if necessary, and the freezing point determined accurately.

The cycle was then repeated.

Except when we approached the composition AuAl_2 , each sample extracted was a rod of very uniform composition, so that analyses of the upper and lower portions gave identical results. But at the very high temperatures of extraction needed for alloys near AuAl_2 , the operation had to be conducted very rapidly on account of the softening of the Jena glass, and it was not always possible to obtain solid rods. In such cases the upper and lower portions of the same extract sometimes differed in their composition to the extent of almost 1 per cent. This and other causes, which will be referred to later, made the determination of the curve in the neighbourhood of AuAl_2 a difficult matter.

The analyses were conducted as follows :—A weighed quantity of the alloy, from 2 to 4 grammes, was digested with aqua regia in a covered porcelain dish, until all soluble matter had dissolved. It was then evaporated with excess of hydrochloric acid, diluted and filtered. The residue on the filter paper seldom weighed more than a few milligrams, except when portions of glass adhered to the alloy. This residue was ignited and weighed; it consisted, partly at all events, of graphite. The weight of the residue was subtracted from the weight of the alloy taken for analysis, and the difference regarded as pure alloy. The filtrate containing the chlorides of gold and aluminium was considerably diluted, and the gold precipitated by sulphurous acid gas. The gold was filtered off, ignited and weighed, and the percentage of gold in the pure alloy thence calculated. In the majority of cases we obtained the percentage of aluminium by difference, assuming that the pure alloy contained only gold and aluminium. This procedure was justified for all parts of the curve except those near AuAl_2 , by the test analyses given in square brackets in the tables, in which a complete determination, both of the gold and of the aluminium was made. In these test

cases the aluminium was determined by evaporating the filtrate from the gold in a porcelain dish to remove the sulphurous acid, adding a few drops of methyl-orange and precipitating the aluminium by a very slight excess of ammonia. The liquid was then heated just to boiling and the alumina filtered off on the pump, washed, dried and strongly ignited in a platinum crucible. The gold and aluminium add up to the weight of the pure alloy, except when we are dealing with alloys not far from AuAl_2 . But in the complete analyses of alloys in this region the gold and aluminium usually add up to only a little over 99 per cent. of what we call the pure alloy. It was noticed that in these alloys the residue was always larger than in alloys formed at lower temperatures. We do not feel absolutely certain as to the nature of the missing 1 per cent. It was certainly not due to errors in the estimation of the gold or aluminium, but we are inclined to attribute it to the presence of a considerable amount of carbon in the alloy weighed. In most of these cases the alloy had been exposed for several hours to a temperature of over 1000° in contact with the carbon of the crucible and of the stirrer. Under these circumstances the alloy certainly took up carbon mechanically, and a portion of this carbon, which would be in a very fine state of division, probably disappeared either during the solution of the alloy in aqua regia, or, more probably, during the subsequent ignition of the residue.

In those cases where both the gold and the aluminium were determined, it was easy to ascertain with certainty the atomic percentage.* Curve 4 gives a small number of points near AuAl_2 , which were determined in this way; they are free from any source of error known to us. In all the other points determined in this region the aluminium was arrived at by difference only, and it is not improbable that some of the alloys may have contained quite one atomic per cent. less aluminium than our tables indicate. We have not attempted to correct for this error on the main curve, but we feel quite sure that it is sufficient to account for the summit in Curve 3 lying a little to the right of the formula AuAl_2 .

Near the lower summit of the curve, corresponding to Au_2Al , it will be seen from the tables that it is immaterial whether the composition is arrived at from the percentage of gold alone, or from a complete analysis. We believe that this is true for all alloys containing less than 50 atomic per cents. of aluminium. The aluminium itself was, as analysis shows, very pure, and it, apparently, only takes up carbon and other impurities after a prolonged exposure to a very high temperature.

* For example, take the alloy in which the percentages directly determined were

Au 93.21 per cent., Al 6.86 per cent.

Dividing these numbers by 197.2 and 27.08, the atomic weights of gold and aluminium respectively, we get the formula

Au 0.4727, Al 0.2533.

Hence the atomic percentage of aluminium is

$$\frac{0.2533}{0.4727 + 0.2533} \times 100, \text{ that is, } 34.89.$$

2 D 2

The Curve.

The curves record the freezing points observed during the experiments. The mean composition of the alloy in the crucible is represented in atomic percentages by the figures above each curve, and temperatures are measured vertically in degrees Centigrade, and recorded by the figures below the curves. For the sake of conciseness we shall use the term *atoms* instead of atomic percentages. A statement of the number of atoms present completely determines the composition of the alloy, it being understood that the number of atoms of gold is obtained by subtracting the number of atoms of aluminium from 100.

Let us consider the case when the alloy in the crucible has, taken as a whole, the composition AuAl, that is to say, contains 50 atoms of aluminium. The observed points on a vertical line drawn through 50 give a record of the way in which the alloy cools and solidifies. Above 850° it is wholly liquid, but when the crucible has cooled to this temperature there is an evolution of heat causing the thermometer to remain stationary for a short time, and we observe the upper freezing point. The cooling soon recommences, but more slowly than before, and when the temperature has fallen to 625° there is another halt. After some time, however, the temperature again begins to fall, and soon falls rapidly until about 568° is reached, when an extremely steady temperature is indicated, and the alloy, if it has not done so before, sets to a solid mass. These three points are the freezing points of the alloy. They may, of course, be due to any exothermic changes going on in the crucible, such as the breaking up of the alloy into conjugate liquids or to allotropic changes; but the microscope has satisfied us that in the case of gold-aluminium we have only to do with the separation of solids, in fact, that at each of the three observed points a new substance begins to solidify.

It will be seen that multiple freezing points, although frequent, are not universal; for example, the alloys Au_2Al and AuAl_2 have only one freezing point.

It is important to bear in mind that the diagrams of Curves 2 and 5 give a record of all the freezing points observed, and contain more information than an ordinary equilibrium curve. The first, or upper, freezing points of each alloy do indeed constitute an equilibrium curve, but our lines of second and third freezing points do not, strictly speaking, belong to the equilibrium curve. For example, the second freezing point which we mentioned as occurring at 625° does not represent a state in which a liquid having the composition $\text{Au}_{50}\text{Al}_{50}$ is in equilibrium with solid. For in the solidification of this alloy the liquid part of the matter in our crucible has, ever since the first freezing point at 850° , been getting richer and richer in gold, until when the freezing point at 625° is reached the matter still liquid is of the composition $\text{Au}_{56}\text{Al}_{44}$ or thereabouts. In fact all the freezing points on the horizontal line through G are points of equilibrium between this same liquid and a certain solid. In an equilibrium curve as usually drawn all these freezing points would be represented by the point G. The other lines of second and third freezing points have a similar meaning.

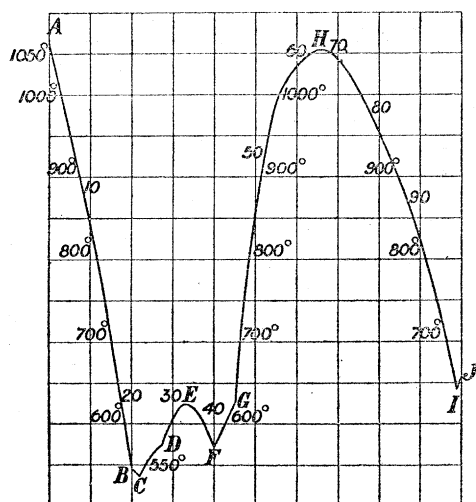
We will now briefly discuss the singularities in the curve.* From A, the freezing point of pure gold, to B, the curve is nearly a straight line. The freezing points of the very dilute solutions are, as usual, very steady temperatures, but as we approach B the upper freezing point is indicated by a slight pause only in the cooling, and lower second freezing points become well marked. These are all at about 545° , and are very steady temperatures. They evidently occur when, after the crystallisation of some gold, the residual liquid has reached a composition of 19 or 20 atoms of aluminium.

From B onwards a new branch of the curve starts which ends in a eutectic point at C, when the alloy contains about 21.5 atoms of aluminium. An alloy of this composition has the low melting point of 525° . This is lower than that of any other mixture of gold and aluminium. We have here the true eutectic of these two metals. The second freezing point at 21 atoms probably belongs to the horizontal line of eutectics through C, which is better marked by other points. There was surfusion at this second freezing point, and therefore it is certain that a new solid now began to form in the crucible. It was noticed that the alloy with 22.3 atoms of aluminium solidified at an extremely constant temperature. This is in harmony with the fact that we are now close to the eutectic angle.

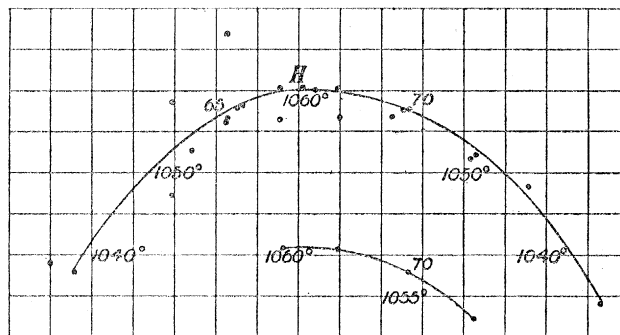
If we pass from C towards D by adding aluminium, the upper freezing point is at first very transient, while the lower one, belonging to the same alloy, is a very steady temperature. But as we approach D, near 28 atoms, the reverse is true. For example, above 26 atoms of aluminium the lower freezing point is lost, and the upper one becomes an extremely steady temperature. Surfusion was noticed at most of the freezing points, both upper and lower, between C and D.

At D there is a singularity in the curve; the freezing points have become very steady temperatures, and, as usual with very steady freezing points, the curve is flat. At a point close to 28 atoms of aluminium a new and rapidly rising branch of the curve begins, the earlier freezing points on it being fugitive. Moreover, through the point of bifurcation the original line of freezing points is continued in a line of second freezing points, which is horizontal for some distance and then descends a little. The points on this line are marked by very steady temperatures like a line of eutectics. From the experimental data for the curve it is difficult to decide whether the summit of the branch CD is to the left or right of the point of bifurcation, or whether there is a short flat to the left of D. But the microscope supplies some reason for thinking that the branch DE cuts the branch CD so that the summit of the latter is a very little to the right of the intersection D, and therefore corresponds to a body that could only be obtained quite pure by surfusion. If we assume that the summit has the formula Au_5Al_2 , it should be at 28.6 atoms of aluminium. The curve of second freezing points starting from D, at first horizontally and gradually sinking, simulates a continuation of the branch CD, but as they

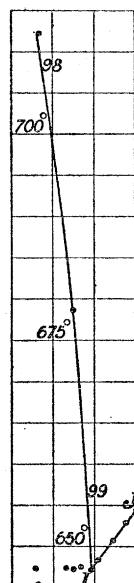
* The rapid depression in the freezing point of gold, due to the presence of small quantities of aluminium, and the great rise in the freezing point as the composition corresponding to the compound AuAl_2 is approached, have been already discovered by Sir William Roberts-Austen.



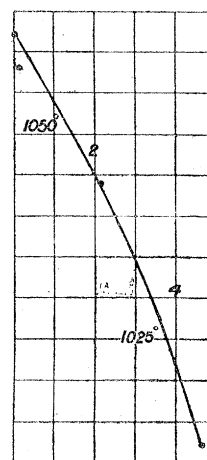
Curve 1.



Curve 3 (upper) and Curve 4 (lower).



Curve 5.



Curve 6.

DESCRIPTION OF THE CURVES.

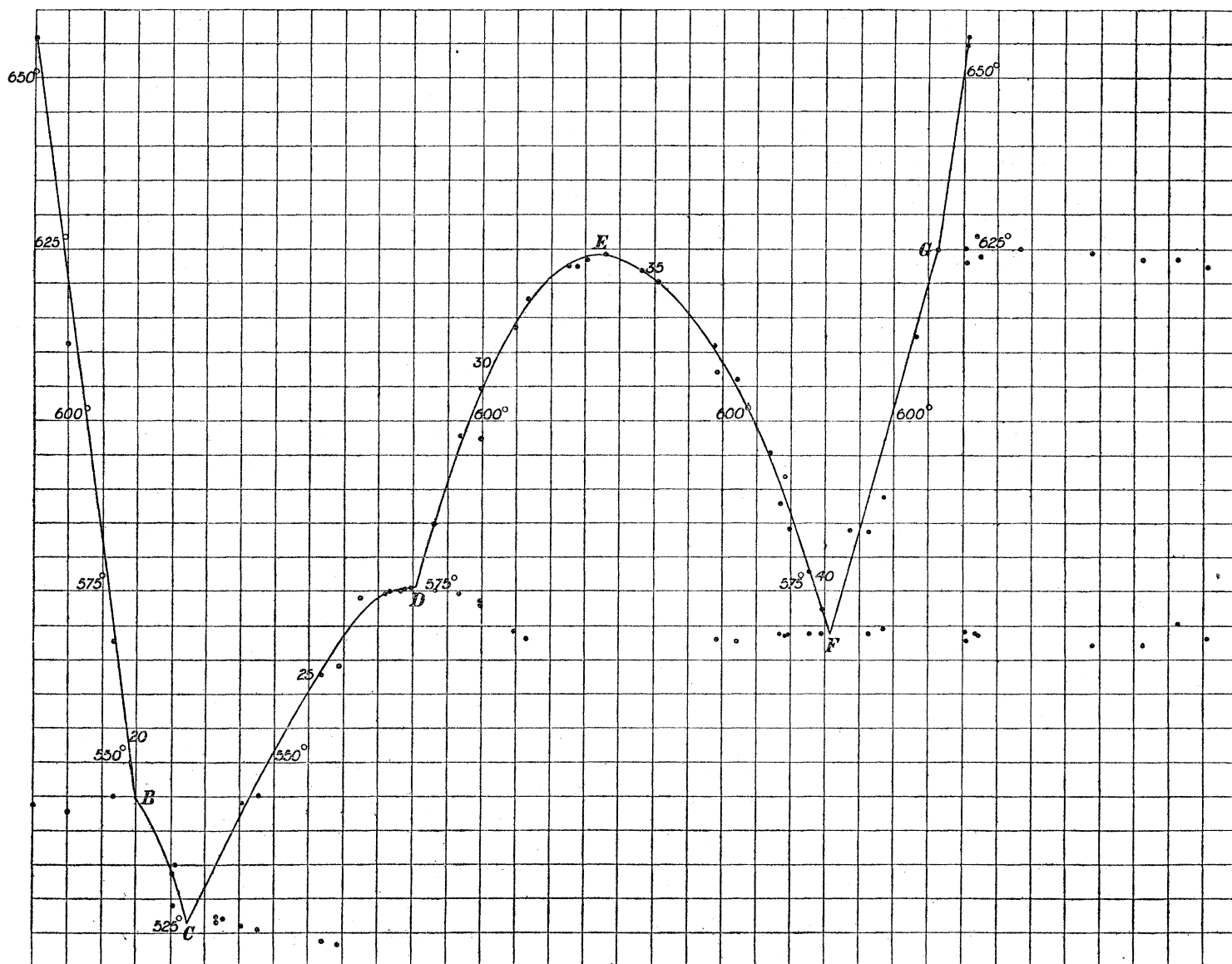
Curve 1 is a diagram on a small scale of the whole freezing point-curve. It is intended especially as a key to the larger figures which give special parts, but it also affords an idea of the relative magnitude of the various branches of the curve.

Curve 2 gives the part of the curve lying between 17 and 44 atoms of aluminium. Experimental points are marked on it by dots, and a continuous line is drawn through the first or upper freezing point of each alloy. This line is what we conceive to be the equilibrium curve.

Curves 3 and 4 give on the same scale the summit of the curve near AuAl_2 , Curve 4 being the most correct. For the points in Curve 4 both the gold and the aluminium were determined; the pyrometer was in good order.

Curve 5 gives the shape of the curve close to the aluminium end, and Curve 6 that close to the gold end.

The numbers placed above the line of the curve are atomic percentages of aluminium, those below the line of the curve are degrees Centigrade. In Curve 5 the numbers plotted are those of the table diminished by 0.7° , to reduce them to our standard value for the freezing point of aluminium, 654.5° .



Curve 2.

were second freezing points and not alternatives to those on the upper line, it is certain that they are not a continuation of CD. We think that, as usual, these second freezing points indicate the moment of solidification of the mother-substance of the alloys between D and E. The composition of this mother-substance would be given by the intersection D, and we should expect it to be an almost pure body. In the case of the alloys near E, the amount of this mother-substance must be very small, the heat produced by its freezing will be small, and therefore thermometer-lag may lower the observed freezing point. This appears a reasonable explanation of the downward curving of the line of second freezing points. The analyses of a number of alloys in this region were conducted with special care, both the gold and the aluminium being determined, and the atomic percentage calculated from their

ratio as well as from the gold alone by difference, the two methods agreeing to within a few tenths of an atomic per cent. It must be remembered that at 27 atoms of aluminium the alloy contains only 5 per cent. by weight of this metal, and that an error of 0.3 per cent. in our analyses would shift the point one atomic per cent. along the curve. It is evident that our analyses are consistent with each other to a higher degree of accuracy than this, but they leave the exact position of the intersection D a little uncertain. The microscope shows that the summit of the branch CD is not exactly at the intersection. On the branch rising from D the freezing points become steadier as we go up the curve, and near the summit E, which is reached with 33.5 atoms, the alloy solidifies wholly at one temperature, like a pure metal. Adding more aluminium after the point E, we have a descending branch ending in a eutectic point F, close to 40 atoms of aluminium.

The eutectic angle F is associated with a horizontal line of second freezing points as usual. Adding more aluminium after F, we follow a steeply rising branch of the curve to G, at which point the alloy contains about 44 atoms of aluminium. Here there is probably a slight angle, another branch rising very steeply from G, while a horizontal row of second freezing points for alloys with more than 44 atoms of aluminium begins. At the freezing points on this horizontal line the halt in cooling was well marked, but not very prolonged, that is to say, no great amount of metal crystallised at the temperature G. These freezing points are not eutectics like those at C and F, nor are they such steady temperatures as those at B, D, and E. We shall find this an important point when we attempt to interpret the curve.

The branch rising from G is steep and the first freezing points are very fugitive; but near the summit H at 66.6 atoms of aluminium they are again very steady temperatures. At H the alloy freezes homogeneously, it being the pure substance AuAl_2 . On adding more aluminium the curve descends rapidly to the eutectic point of gold dissolved in aluminium, the branch being, so far as we know, devoid of singularities. There is a short branch rising from this eutectic angle I to the freezing point of pure aluminium as shown in Curve 5.

The information given by the curves as to the compounds formed by the two metals may be summed up thus:—

Along the branch AB gold crystallises first.

Along the branch BC a compound crystallises first which is nearly pure at B, and is probably Au_4Al .

Along the curve CD a body crystallises first which is nearly pure at D, and is probably Au_5Al_2 , but may be Au_8Al_3 .

Along the curve DE the substance crystallising first is Au_2Al , a body of some stability which occurs pure at the summit E. The same body crystallises first along the branch EF.

Along the branch FG a new body crystallises first, but its formula is not given even approximately by the point G; it is perhaps AuAl .

Along the whole of the curve GHI the substance crystallising first is AuAl_2 , the remarkable and beautiful purple substance discovered and studied by Sir W. ROBERTS-AUSTEN.

So far as we have been able to see, the above are the only compounds indicated by the curve; but, owing to the rapidity with which the excess of red-hot aluminium attacks the porcelain cases of our pyrometers, we have not been able to determine the points on the curve HI with as great accuracy as the rest of the curve, and there might possibly be singularities in this branch, if it were not for the microscopical evidence against such a supposition.

We had much difficulty in determining the exact freezing point at the summit H, because the pyrometer tubes, after some hours' immersion in the alloy at 1000° , were very apt to become perforated, and hence to cause a change in the constants of the coils. But our best experiments, carried out with freshly made alloy, and with pyrometers in perfect order, which had immediately before been checked by the determination of the freezing point of gold, give the freezing point of the purple alloy at H, as identical with that of gold (see Curve 4). This coincidence is a remarkable feature in the relations of gold to aluminium, perhaps more remarkable than if the compound had frozen at a higher temperature than gold. It is impossible to misread the freezing points at H on account of the steady temperature.

SECTION II.

The Tables.

In column 1 of the table we give the number of the alloy in chronological order, in column 2 we state the percentage by weight of aluminium in the alloy as given by analysis, and in column 3 the atomic percentage. The numbers in square brackets are the percentages of aluminium based on a direct determination of both the gold and the aluminium. Column 4 contains the temperature of the freezing point on the platinum scale; this is CALLENDAR's *pt.* Column 5 contains the temperature of the freezing point on the Centigrade-air scale. In columns 4 and 5 the successive freezing points of the same alloy are placed under each other. In calculating the Centigrade temperature we strictly followed the method of calculation described in our paper "On the determination of high temperature" ('Journ. Chem. Soc.,' 1895, p. 160). Assuming, as we did, CALLENDAR and GRIFFITHS' value for the boiling point of sulphur, the δ of our platinum wire proved to be 1.50. If CHAPPUIS and HARKER's value for sulphur be taken, the δ will be slightly greater, and the melting point of gold will be raised a few degrees above 1062° , lower temperatures being raised by a corresponding amount. This correction can be made at any time, but as it does not affect the argument of the present paper, we have not thought it necessary to apply it. We give the platinum temperature *pt.*, that is, $100 \times \frac{R - R_0}{R_{100} - R_0}$ because this,

together with the fact that the ratio of R_{100} to R_0 is 1.385, enables the observed resistance to be re-calculated for an imaginary wire whose $R_0 = 1$. The symbols R , R_0 , R_{100} , are the resistances at the observed freezing point of the alloy, at 0°C . and at 100°C . respectively.

The number of the alloy referred to is placed before each note.

No. of alloy.	Percentage of aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [pt].	F.P., Centigrade. $\delta = 1.5$.	Notes.
0	0.00	0.00	909.0	1062.2	(0) Pyrometer 28. F.P. of 700 grammes Au.
1	0.30	2.14	896.2	1044.0	
2	0.66	4.62	873.7	1012.2	
3	1.04	7.11	843.9	970.7	
4	0.85	5.88	850.7	980.1	
5	1.27	8.56	806.0	918.9	
6	2.00	12.94	719.1	804.0	
7	2.74	17.02 [17.10]	601.2	655.9	(7) Upper F.P. very fugitive. Lower F.P. very steady, like eutectic.
			507.7	543.9	
8	3.85	22.57	493.1	526.9	
9	5.05	27.92	534.5	575.6	
10	6.20	32.50	573.7	622.5	
11	7.39	36.76	564.1	611.0	
12	7.88	38.39	551.2	595.5	
13	8.62	40.73	541.6	584.0	
14	9.91	44.48	574.8	623.9	
			528.7	568.7	
15	9.88	44.39	700.9	780.6	
			577.4	627.0	
			528.9	569.0	
16	12.19	50.27	761.9	860.0	
			574.6	623.6	
			530.1	570.4	
17	9.78	44.12	601.2	656.0	(17) Pyrometer 28. F.P. of 390 grammes Au + 43 grammes Al.
			574.1	623.0	
			528.0	567.8	
18	11.15	47.75	692.4	769.7	
			575.4	624.5	
			527.3	567.1	(21) Al. determined as sulphate.
19	11.76	49.25	736.3	826.3	
			574.6	623.6	
			527.4	567.1	
20	13.26	52.68	779.2	882.9	
			570.8	619.0	
			526.9	566.6	
21	14.76	55.77 [55.01]	823.8	943.1	
			571.1	619.4	
			526.6	566.3	
22	15.76	57.67	852.7	982.8	
			571.7	620.1	
			525.8	565.3	
23	16.75	59.43	874.7	1013.6	
			571.0	619.2	
			525.3	564.6	
24	17.68	61.00	892.7	1039.1	
			570.1	618.2	
			525.9	565.4	

No. of alloy.	Percentage of aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [pt].	F.P., Centigrade. $\delta = 1.5$.	Notes.
25	19.57	63.92	906.3	1058.6	(25) The abnormal values of 25 and 26 are neglected in plotting the curve; they are almost certainly due to injury to the pyrometer.
26	20.50	65.26	569.8 526.3 912.2	617.8 565.8 1067.0	
27	20.51	65.27	905.1	1056.7	(27) Pyrometer 27.
28	21.46	66.55	907.7	1060.5	
29	20.69	65.52	905.9	1057.9	
30	22.11	67.40	907.4	1060.1	
31	23.86	69.54	905.7 518.2	1057.7 556.3	
32	26.63	72.55	899.3	1048.5	
33	28.40	74.29	888.7	1034.2	
34	32.70	77.97	874.3	1013.1	
35	36.13	80.46	853.4	983.9	
36	41.92	84.02	837.2 585.6	961.5 636.9	
37	41.93	84.04	837.2	961.4	(37) Pyrometer 25.
38	42.80	84.50	815.0	931.1	
39	45.36	85.82	792.7 584.0	901.0 635.0	
40	59.06	91.31	768.7	868.9	
41	92.45	98.90	593.5	646.5	(41) Pyrometer 21 gave immediately before this experiment the freezing point of pure aluminium as 654° C.
42	89.83	98.48	619.8 593.7	678.8 646.8	
43	84.88	97.63	646.8 592.1	712.2 644.8	
44	79.21	96.54	682.4 592.9	757.1 645.7	
45	72.40	95.05	713.4	796.7	
46	65.39	93.22	754.3	849.9	
					(46) Pyrometer broke down whilst searching for eutectic.
47	63.49	92.70	746.8 583.7	840.1 634.6	(47) Pyrometer 23.
48	57.53	90.80	770.0	870.6	
49	50.14	88.00	799.3	909.8	
50	43.66	84.96	828.3	949.3	
51	2.72	16.92	603.4 507.7	658.6 543.9	
52	3.19	19.35	527.9 508.8	567.7 545.1	
53	3.54	21.09	500.2	535.1	
54	3.80	22.34	493.5	527.4	
55	3.95	23.05	507.9 492.4	544.1 526.0	
					(51) Pyrometer 23 in new tube. 584 grammes Au + 16.2 grammes Al.

No. of alloy.	Percentage aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [pt].	F.P., Centigrade. $\delta = 1.5$.	Notes.
56	4.57	25.86	525.0 490.1	564.2 523.4	(60) Pyrometer put in new tube and constants found unchanged.
57	4.91	27.33	534.1	575.0	
58	5.54	29.93	552.8 533.1	597.3 573.7	
59	5.80	30.96	566.4 529.4	613.7 569.4	
60	6.35	33.06	574.6	623.5	
61	6.92	35.13	571.9	620.4	
62	7.42	36.85	560.9 528.2	607.1 568.1	
63	7.98	38.71	544.8 528.9	587.8 568.9	
64	8.94	41.69	545.6 529.5	588.8 569.6	
65	9.76	44.06	600.2 575.9 529.0	654.7 625.1 569.1	(67) Nos. 66 and 67 were successive extracts of the same alloy.* (69) Pyrometer constants redetermined and found satisfactory after putting in new tube.
66	12.57	51.15	780.8 573.7	885.1 622.5	
67	12.52	51.04	528.3	568.2	
68	15.56	57.30	864.0	998.5	
69	18.05	61.60	891.9	1038.0	
69A	19.58	63.93	898.5	1047.3	
70	19.91	64.41	902.3	1052.7	
71	21.44	66.53	904.9	1056.5	
72	22.58	68.00	905.2	1056.9	
73	23.61	69.24	905.2	1056.9	
74	25.31	71.17	901.7	1051.9	
75	2.93	18.02	564.5 506.8	611.4 542.8	(75) Pyrometer 13A. 584 grammes Au gave a freezing point 1061.4
76	3.53	21.04	499.2 494.9	534.0 529.0	
77	3.80	22.33	492.8	526.5	
78	4.06	23.55	508.8 491.9	545.2 525.5	
79	4.46	25.37	523.8 490.4	562.8 523.7	
80	4.88	27.19	533.9	574.8	
81	4.98	27.62	534.1	575.0	
82	5.55	29.96 [30.02]	559.2 532.4	604.9 573.0	
83	7.59	37.42	560.1 528.1	606.1 567.8	
84	8.02	38.83	548.1 528.6	591.8 568.6	
85	8.04	38.91	541.7 529.0	584.1 568.8	(82) Pyrometer constants redetermined and found right.
86	8.25	39.57	536.6 529.0	578.0 568.9	

* In 66 the first and second freezing points only were determined, and in 67 the third or lowest freezing point.

No. of alloy.	Percentage of aluminium by weight.	Atomic percentage of aluminium.	F.P., platinum scale [pt].	F.P., Centigrade. $\delta = 1.5$.	Notes.
87	8.36	39.91	532.0	572.5	
88	8.80	41.27	529.0	568.9	
89	9.26	42.63	541.4	583.7	
90	9.50	43.30	529.0	568.9	
91	10.36	45.70	565.3	612.3	
			575.7	624.9	
			637.4	700.4	
			575.8	625.0	
92	20.50	65.25	904.7	1056.2	(92) Pyrometer 13A. F.P. Au 1062.5.
93	20.78	65.63	906.2	1058.3	
94	21.87	67.08 [66.65]	907.8	1060.6	
95	23.12	68.66 [67.95]	907.8	1060.6	
96	23.87	[69.70]	905.8	1057.8	
97	25.09	[71.30]	902.0	1052.3	
100	4.72	26.50 [26.59]	533.2	574.0	(100) Pyrometer 19. F.P. of Au 1062.6.
101	5.01	27.74 [27.91]	534.3	575.3	
102	5.22	28.63 [28.86]	542.4	584.9	
			534.2	575.2	
103	5.39	29.32 [29.13]	553.3	598.0	
			533.7	574.6	
104	5.89	31.31 [31.42]	569.7	617.7	
			528.4	568.2	
105	6.27	32.77	573.6	622.4	
106	6.50	33.61 [33.20]	575.2	624.3	
107	6.79	34.66 [34.89]	573.2	621.9	

TABLE showing the Freezing Points of Dilute Solutions of Gold in Aluminium.

Atomic percentage of gold.	F.P., platinum scale [pt].	F.P., Centigrade.
0.00	600.6	655.2
0.23	599.4	653.7
0.55	597.6	651.4
0.93	595.7	649.2
1.32	594.9	648.2
1.70	594.9	648.2
2.45	594.9	648.2

The higher freezing points of the last three alloys, that is to say, those lying on the branch HI, were not determined.

SECTION III.

The Microscopic Study of the Alloys.

Sections, usually transverse, were cut from the rods of alloy extracted for analysis, and from other alloys, some of which had been slowly cooled. These sections were polished on graded emery paper and when necessary finished with rouge. They were then examined under the microscope both before and after etching. We found bromine water or aqua regia the only satisfactory etching reagents, these being about equally effective in developing detail.

Most of the reproductions in Plates 4 and 5 are from photomicrographs taken with an arc light, but in two cases, in which the photograph did not satisfactorily reproduce the detail of the object, we give drawings by Mr. E. WILSON of Cambridge, who has had a large experience in this kind of work. Except in the case of some low power photographs, for which oblique light was used, the illumination of the alloy surface was normal, a Beck's axial illuminator being used. The photographs are arranged in order according to the number of atoms of aluminium in the alloy, so that they can be readily referred to while reading the text; but reproductions are not given of all the alloys described.

However perfect photomicrographs may be, they rarely give as much information as a direct examination with the microscope. The descriptions which follow are therefore based on what was visible under the microscope rather than on the photographs, although we hope that the latter will confirm our statements.

The different ingredients of the alloys have, in some cases, well marked colours, but with different illuminants the tint of the same patch of alloy varies a good deal. It was therefore desirable to select a standard method of illumination for the eye examination. We employed a Welsbach gas-burner, an image of the flame being thrown a little out of focus on to the surface of the alloy. The colours of the various substances found in an alloy were then fairly constant, and could be employed as an aid in identifying them in different sections.

As a rule Zeiss' apochromatic lenses were employed, the powers ranging from 50 diameters to over 1000.

It will be seen that the microscopic examination confirms in every respect the information given by the freezing point-curve. The microscope reveals seven substances in the series of alloys, although they are never all found in the same alloy. They are gold and aluminium, pure at A and J, the ends of the curve, and four bodies which are nearly or quite pure at the points B, D, E, and H respectively. The seventh substance is present in all alloys between E and H, but never in a pure state. We shall sometimes refer to these as the B, D, E, H, and X bodies respectively.

Nearly all the alloys, when polished long enough on dry emery and rouge, acquire

a more or less golden tinge, and under the microscope show smears of gold, or a pattern of gold, on white or purple; and in cases where the polishing leaves a pitted surface, the pits are full of gold. On the other hand, the unpolished alloys are white if they contain more than 3 per cent. by weight of aluminium, except in the neighbourhood of H, where they are purple. This constant appearance of free gold on the polished surfaces troubled us a good deal at first, but we finally satisfied ourselves that most of it had been set free by the superficial oxidation of the alloys during polishing, and that after the oxidation of the aluminium the gold was smeared over the harder surfaces and rubbed into the pits. This, whether it be due to oxidation or not, can be to a large extent avoided by finishing the polishing on emery kept wet with benzene. The alloys are then almost free from gold smears, and we believe that in the solid unpolished alloys containing more than 20 atoms of aluminium, that is, after the point B, there is no free gold. This is an important point, for if free gold occurs to the right of B, the steps in the process of solidification become difficult to understand. One of the uses of the etching is to remove these smears of gold.

The types of pattern visible on the etched surface depend on the position of the freezing point in the curve. It is hardly too much to say that, given the freezing point-curve of any pair of metals, one can predict the microscopical structure of the alloys they form.

For alloys whose freezing point is near a summit of the curve, that is, near A, E, H, and probably J, the whole surface of the section is filled with one substance, although it is sometimes possible to detect fine boundary lines marking out the separate crystals. These lines are most often seen at the angles where three crystals meet, in which case (figs. 18 and 21) the boundary line consists of three branches meeting in a point.

When, by the addition of either metal, we leave a summit of the curve, the lines between the polygonal sections of the crystals become distinct, so that the pattern is that of a tessellated pavement, the unit being an irregular polygon, generally without re-entrant angles, often approximating to a regular hexagon, and often with somewhat rounded angles, so that it may be called a blob. It does not seem necessary to attribute the hexagonal shapes to any peculiarity of crystalline structure, but rather to the limitations of space in which the closely packed crystals have formed.* As we go further down hill along the curve, the spaces between the polygons widen and are seen to be full of a substance different from that of the polygons themselves. As we still go down-hill the interpolygonal matter becomes a continuous network, and the isolated polygons or blobs arrange themselves into patterns. Sometimes, as with 16.9 atoms of aluminium, the pattern is mainly one of rectangular crosses, but more often the blobs are in rows with other rows branching from them, the individual

* Mr. J. E. STEAD draws attention to the non-crystalline character of the shape of these polygons in his valuable paper on "The Crystalline Structure of Iron and Steel," in the 'Journal of the Iron and Steel Institute,' 1898.

blobs being often oval or elongated into bars as with 28.6 (fig. 16) and 29.9 atoms (fig. 17).

As we approach a minimum freezing point the rows of blobs become smaller in area, and the mother-substance around them, when examined with a high power, is sometimes seen to consist of a much smaller pattern of two substances, one being the material of the blobs. The 38.9 atom alloy (fig. 22) shows this well. Finally, at a minimum freezing point, a eutectic angle, the large blobs disappear entirely, and the whole alloy consists of the small pattern; it is a eutectic alloy. The 40 atom alloy (fig. 23) corresponding to the point F is an almost perfect example of this. If we now, by the continued addition of the same metal, cause the freezing point to rise, we again get large blobs surrounded by a minute pattern, but, while the fine pattern is the same as before, the blobs are of a different material; they consist of the second substance of the network (fig. 24). Thus in crossing from one side of a eutectic point to the other the two proximate constituents of the alloy exchange places.

If we think only of the plane surface of such a section of alloy as that with 29.9 atoms (fig. 17), the rows of blobs, each blob isolated from the next, yet obviously connected with it by some law, are puzzling. But if we think of the solid alloy as consisting of a mass of crystals with other crystals branching from them, the whole system immersed in mother-substance which solidified after the formation of the crystals, we see at once that a section of the mass would present the observed appearance. To be more precise, we may picture the 29.9 atom alloy during the first stage of freezing as like a thicket of fir trees in which the branches are at right angles to the stems and in which the stems are not all vertical. If a section were made of this thicket by a plane inclined to the vertical we should get patterns very like those of the photograph. If a stem lay in the plane of section we should get lines at right angles to each other. If the stem were parallel to the plane, but not in it, we should get parallel rows of dots. With the stem oblique to the section we should get the elongated dots which are so numerous in the photographs. A comparison of the X-ray photograph of the quickly cooled 96.6 atom alloy with the ordinary surface photograph of the same alloy illustrates the above. These considerations, together with the straightness of the lines of dots, show that the large pattern of blobs, and the polygons with which they are related, are the pure substance, which crystallised first and without constraint, because it was surrounded by liquid, whereas the surrounding matter is a mother-substance that was liquid during the first stage of crystallisation. It would be convenient to call the polygons and blobs primary crystals, inasmuch as they formed first in order of time, while the mother-substance may be said to contain secondary and tertiary crystals. It is probable that the marked absence of crystal form observed in the blobs of primary crystallisation is due to these blobs being what LEHMANN calls "crystal skeletons"; a snow crystal is the most familiar type of crystal skeleton. If we imagine the interstices between the fern-like pattern of such a crystal to be filled up by sub-

ordinate crystallisation of the same body, the original outline will become lost, and the final outline will be rounded as we see it in the photographs. Prolonged etching of the 18·1 atom alloy breaks up the surface of the blobs and partially reveals a structure that may be that of an original skeleton, although this structure is not altogether what we should expect in such a case.

We will now consider the alloys taken in order, starting from the pure gold end of the curve.

The first alloy examined carefully was that containing 1·27 per cent. by weight of aluminium, that is, 8·56 atoms. It has to the eye the appearance of gold, is soft, and does not polish well, and the unetched surface shows no detail. Etching with bromine water produces a very brilliant surface, and a 2 millims. immersion objective, with a power of 500 diameters, now shows it to be made up of approximately hexagonal polygons, apparently of gold, with an incomplete network of fine brown lines between them. We do not give a figure of this as it is identical with types that occur later in the curve, for example at E and H. BEHRENS, ARNOLD, ANDREWS, and all who have studied dilute solutions of one metal in another, have observed the same type of structure.

The alloy with 12·5 atoms similarly treated shows the polygons of gold somewhat rounded at the angles, and surrounded by much more of the brown mother-substance. This brown substance has a minute sparkle in it when examined with a power of 500. A power of 1500 and careful focussing showed this sparkle to be due to numerous spots, which sometimes appeared white; this is presumably the detail of the eutectic. In the photograph (fig. 1) the darker parts are the spaces full of eutectic, but the scale is too small to show the smaller detail.

The next alloy contained 16·9 atoms of aluminium. It was very white when polished by the wet method, and the microscope showed, before etching, golden crosses dimly visible on a white ground. When lightly etched, a power of 50 diameters brought out a beautifully regular pattern of rectangular crosses and bars on a dark ground that was finely mottled with gold. The ground was brown and the pattern generally golden, but under some conditions of etching the pattern seemed to be white, and many of the minute specks in the brown mother-substance seemed to be white also. A power of 1000 brought out very clearly the fact that the ground was a eutectic mixture. A slowly-cooled alloy, containing 18·1 atoms, of which we give a photograph (fig. 2), presented a very similar pattern, but on so large a scale that it was visible to the naked eye; the pattern in the slowly-cooled alloy was, however, always golden. Although we have mentioned the occasional whiteness of the pattern in the 16·9 atom alloy, we do not feel able to attach any importance to it, as it was probably due to some electrolytic action occurring during the process of etching.

Light etching with bromine water shows very clearly that the ground of the 18·1 atom slowly-cooled alloy is a eutectic mixture, as the gold is left standing up in bent rods and crinkles while the other substance of the eutectic is eaten away. We

give a photograph (fig. 3) of a patch of this etched eutectic taken between the bars of pattern so that no primary crystals are in the field. The somewhat cellular character of the eutectic strongly suggests three stages in the freezing, first, the formation of the large primary crystals of gold, then, probably after surfusion, the solidification of most of the second substance, and, finally, that of the residual gold in the interstitial spaces to form what becomes the minute raised pattern of the eutectic. Various other sections have suggested the same three stages. In the case of the slowly-cooled alloy with 18.1 atoms, the primary crystals or blobs, which are presumably gold, show a marked pattern after etching. Each blob, instead of being uniformly attacked by the etching agent, is eaten away into deep grooves running in various directions, and having no relation to the lines of polishing.* This, as we have said, may mean that the blob is not a crystal, but a mass of crystals; a longer etching reduces a blob to a cellular appearance very much like the drawing of the 19.8 alloy.†

With 19.4 and 19.8 atoms of aluminium we see a complete change in the pattern of the sections. Instead of the isolated primary crystals of gold, fairly uniformly scattered through a finely grained eutectic that constitute the pattern at 16.9 and 18.1 atoms, we now have, after bromine etching and with normal light, a dark brown or black surface finely reticulated by a system of slender golden lines that divide it up into cells (fig. 5). Thus the appearance is that of a nearly pure body, the material inside the cells presumably being that of the primary crystallisation, and the slender golden boundaries being the mother-substance that solidified last in order of time. The two alloys are very similar in appearance, but there is more of the golden network in the 19.4 atom alloy. The curve gives for this alloy two freezing points, at the upper of which primary crystals of gold should have formed, but the section polished was cut from a portion of the extract that had run out of the Jena pipette after removal from the crucible, hence it was the most fusible part, and probably had a composition nearer to B than the point recorded on the curve. Oblique illumination brings out the golden boundaries of the polygons much better than normal light, and

* In this and other cases where there seemed a danger of the scratches causing a false pattern, care was taken to polish by motion parallel to one direction, so that scratches might be easily recognised by their parallelism to this direction.

† *January 30, 1900.*—As the transition from the alloy with 18.1 atoms of figs. 2 and 3 to the 19.8 atom alloy of figs. 5 and 6 was a considerable one, we have lately made an intermediate alloy (fig. 4) containing 19 atoms of aluminium. This alloy was made by melting together in a sealed and vacuum tube of Jena glass appropriate amounts of the 18.1 atom alloy and of aluminium. This alloy, when slightly etched, showed a small number of very slender rows of dots of gold on a brown ground; it was evident that the primary crystallisation was much less in amount than that of the 18.1 atom alloy of fig. 2. The surface of the 19 atom alloy was then deeply etched by immersion for twenty-four hours in bromine water. The resulting surface, photographed by oblique illumination (fig. 4), shows very well the slender but very regular crystal skeletons of gold that exist in the alloy. Owing to the small amount of the primary crystallisation (due to nearness to the eutectic point) these skeletons have not filled up with gold, and so lost their crystalline form. Fig. 4 gives us much the same insight into the structure of the solid alloy as that afforded by fig. 30, the Röntgen ray photograph.

shows also another feature of both sections. This feature, of which we cannot at present see the explanation, consists in a much coarser polygonal structure, the whole area being divided by dark bands into spaces, each of which contains from ten to fifty of the smaller gold-edged cells. The width of the dark bands is about that of an average sized gold-edged cell, and the material of the bands seems to be that of the inside of the cells. Photographs of the 19·8 alloy, taken with oblique illumination, show the larger polygonal structure, but only very imperfectly that of the gold-edged cells; we, therefore, give a drawing of this alloy (fig. 5). These sections, when magnified 200 diameters, very much resemble the figures given by Professor ARNOLD ('Engineering,' February 7, 1896) for gold containing 0·2 per cent. of bismuth or silicon, that is, for a nearly pure substance.

Whatever the meaning of the larger polygonal structure may be, our immediate point is that the cells of dark material, for the most part isolated from one another, are primary crystals, probably of a body pure near B. Both of these sections are far more intelligible under the microscope than in the photographs. With careful focussing and a power of 1000 one sees that the golden network of the 19·8 alloy is, where it widens at the angles, a eutectic mixture of gold and dark not unlike the drawing, only far more minute.

The 19·8 atom alloy of fig. 5 was not one of the extracts made during the determination of the freezing point-curve, but was specially prepared for microscopic examination, it was, however, extracted from the crucible by sucking up in the usual way. We have since polished a section of the ingot left in the crucible after extracting this alloy. The ingot, of course, cooled much more slowly than the rod extracted. The polished section of the ingot shows before etching a cellular pattern, the cells being full of a uniform material, while the intercellular matter, or mother-substance, of which there is a good deal, broadening at the angles, is plainly a fine eutectic (fig. 6). A power of 400 diameters shows this well. This section, even when lightly etched with bromine, shows no trace of the larger polygonal structure. Both these alloys polished to very white surfaces. The rod of alloy from which the latter section was cut was white and brittle with a conchoidal fracture.

At 21·1 atoms we have, after bromine etching, the same brown polygons forming the mass of the alloy, but now the interstices are filled with a new white body, with which we shall become familiar later on. We give a drawing, under oblique illumination, of this alloy (fig. 7). The drawing accurately represents a portion of the surface, but is rather misleading as to the amount of interpolygonal matter, for if one takes a general survey of the surface one sees that there is very little of this. We give a photograph (fig. 8) to make this fact clear. Hence the alloy is extremely near to being a pure substance, nearer, for example, than the previous alloy. After the drawing was made, the section was subjected to a prolonged etching with strong bromine water. This brought out very clearly the white interpolygonal substance standing in relief above the level of the brown. This alloy before polishing was brassy-white with a

conchoidal fracture. Thus near B, on both sides of it, we find the structure characteristic of an almost pure substance.

The next alloy with 21·6 atoms shows a pattern that varies a good deal in different parts, but the most usual is that of armies of very minute dots and short lines of white in a ground which, after etching, is a golden brown. There are a few larger spots of white, so that we may have now just passed the eutectic angle C. In the middle of some of the brown spaces, between the bars and dots of white, a power of 1200 shows patches of a network of white lines, similar to that on the golden mother-substance of the 26·1 atom alloy to be referred to later; this is probably the real eutectic structure (fig. 9).

These features in the alloys, taken together with the shape of the curve between A and C, and especially the horizontal line of second freezing points at the temperature B, make it extremely probable that the solid alloy containing 20 atoms of aluminium is a homogeneous chemical compound with the formula Au_4Al . With rather more gold the solid alloy must consist of primary crystals of Au_4Al in a eutectic of this body and gold, the eutectic angle being probably near 19 atoms. With more gold we have, as at 18·1 atoms, primary crystals of gold immersed in a eutectic mixture of gold and Au_4Al .

With more than 20 atoms of aluminium we are on the new equilibrium curve BC, along which Au_4Al should crystallise first, and be found in the solid alloy embedded in a eutectic containing also the new white body D. Unfortunately we have not enough alloys on this branch, but the 21·1 atom alloy (figs. 7 and 8) unmistakably shows this white substance. As the rod of extract at 19·8 atoms shows, both before and after polishing, the body Au_4Al is itself a white substance, but it is very readily attacked by etching reagents, and therefore under the microscope it appears brown or purple from a film of gold.

As the alloy Au_4Al would contain only a little more than 3 per cent. by weight of aluminium, it is obvious that our analyses, though very consistent with each other, leave the exact atomic percentage at B a little indefinite; the method of plotting in atomic percentages may be said to magnify the scale of the curve here, on account of the disproportion between the atomic weights of the two metals. But we think it justifiable to use the law of multiple proportions in selecting the formula Au_4Al as that of the compound which is pure near B.

We have three sections of alloy containing 22·3 atoms of aluminium; they are all similar, and have a curious pattern. With a low power of 50 or 100 one sees dark polygons outlined not by lines but by small somewhat oval spots of white, which punctuate, as it were, the margin of the polygons. This is best shown in a section of a part of the alloy which ran out of the pipette after removal from the crucible. This must have been the most fusible part of the extract, and was therefore probably very near the composition of the eutectic C. With a higher power and the 2 millims. immersion one sees that these white spots have all the character of the D body, they

are a rough brilliant silvery white. Moreover they are rounded, and have no appearance of having been squeezed into the interstices of crystals already formed. So that it is hard to say which of the two ingredients crystallised first ; but the higher the power one uses the more disposed one is to say that the white spots were the primary crystals. With a power of 1000 or 1500 the ground shows a detail in it of small spots like minute grains of wheat, some of which are white. Probably this alloy represents the eutectic as fairly as that with 21.6 atoms.

With 23.1 atoms (fig. 10) the blobs of white are very uniformly distributed in a dark field, filling about one-third of it. They are a brilliant silvery pitted white. At 23.6 atoms the white blobs have increased in area, and form a beautiful object when examined with a low power. At 25.9 they fill two-thirds of the field (fig. 11), and are a remarkable example of rectangular crystallisation. At 26.5 atoms the white blobs have grown into elongated polygons, only separated by a broken network of dark lines ; in other words, the D body is nearly pure, the slowly-cooled 26.1 atom alloy (fig. 12) gives a good idea of these.*

This slowly-cooled alloy shows between the masses of white a network of golden-brown, which broadens at the angles. These broader patches of mother-substance under a power of 700 diameters prove to be full of minute polygons, bounded by bright, and often white, lines. This we presume is the structure of the eutectic corresponding to the state C. This mother-substance was formed after surfusion. The pattern is found on every patch of the mother-substance, although the boundary lines of the polygons are often incomplete (fig. 13). The section at 27.2 atoms (fig. 14) is very remarkable ; it consists, like the preceding one, of polygons separated by lines which are now fine and broken ; but the polygons are in groups, some of the groups being of a greyish-white rough substance, while other groups are a very smooth brilliant ivory-white. With oblique illumination the rough polygons show the effect of changing from bright to dark, as the stage is rotated through a right angle. Examination with a high power, however, forces one to the conclusion that the rough and smooth patches are of essentially the same material. The photograph of this section, with a magnification of 50 diameters and normal illumination (fig. 15), shows how very misleading a photographic reproduction may be. It does not give the impression of being the homogeneous substance that it really is. Even with a high power one cannot say to a certainty whether the interstices between the polygons are filled with the same eutectic as that found in the 26.1 atom alloy or with a new one : this point, if settled, would determine the formula of the D body.

At 28.3 atoms we have a complete change ; with oblique illumination, as in figure (fig. 16), one sees scanty groups of primary crystals of a new substance on a uniform ground. Some of the new crystals, examined with a power of 1000, show traces of

* This photograph was taken with oblique illumination, and the white and dark patches are of the same material differently orientated.

the door-panel moulding described later as characteristic of the E body. This alloy polishes to a fine white surface. We must have passed the intersection D of the branches CD and DE of the curve. The curve and the microscope here, as usual, agree very well, the upper fugitive freezing point being due to the small amount of the new primary crystals, and the lower very steady freezing point to the solidification of the large mass of mother-substance. As by adding aluminium we now pass up the curve towards E, the successive alloys show the primary crystals increasing at the expense of the ground, the 29.9 atom alloy being a good example (fig. 17), until at 32.5 atoms we have the new body in polygons separated from each other only by a fine ribbon network of a different material (fig. 18); and at the point E, close to 33.3 atoms, we have a practically pure substance.

The D and E bodies are white, both before and after etching, and each appears in two forms, according to the orientation of the crystals to the plane of section; one form is smooth, like milky ice or ivory; the other is uniformly pitted, or in some cases ruled with lines. It would seem that the crystals are made up of minute rods closely packed together,* and that section by a plane parallel to the rods gives a smooth surface, perhaps a cleavage plane of the crystal. On the other hand, a section making an angle with the rods breaks off each rod along another cleavage plane, which will not generally be that of the section, in which case the surface will be serrated or pitted. This way of accounting for the markings on a section of a mass of crystals has no doubt occurred to many persons;† but it was suggested to us by Professor EWING's slip-lines. He has shown that the minute elements of a crystal, even of metal, are rigid, and that they can only slip along certain planes. In the same way it is almost certain that they can only break along certain planes.

The remarkable effects that one often sees on rotating a section under oblique light are due to these serrations.‡ The fact that the pitted crystals give this *rotation* effect, shows that the sides of the pits have a definite orientation. The variation in the appearance of different crystals of the same substance, dependent on their orientation to the plane of polishing, is liable to mislead anyone who trusts to microscopic study only. For example, the alloy with 27.2 atoms photographed with normal light (fig. 15) appears to consist of at least two materials, while in reality all the patches in it are of the same substance; oblique light would be even more deceptive as the slowly-cooled alloy with 26.1 atoms (fig. 12) proves.

* An examination of the door-panel moulding of the alloy with 33.6 atoms almost forces one to the conclusion that these minute rods or laminae came into existence *during* the crystallisation, and are not a later product due to strain or other cause; that they are, in fact, the *crystals* of which the blob or polyhedron is built up. This is the view insisted on by Mr. STEAD (*loc. cit.*).

† Since writing the above we see that this is the view of the phenomenon given by Professor ARNOLD ('Engineering,' February 7, 1896).

‡ The nature and cause of this change of appearance when a section is rotated under oblique light is very clearly explained by Mr. STEAD (*loc. cit.*). He attributes the first mention of it to Professor ARNOLD. We shall call it the *rotation* effect, as no name appears to have been given to it hitherto.

The bodies D and E are so similar under a high power, that we found it difficult to believe them to be chemically unlike each other, but the form of the curve, and the relative positions of the two bodies in the sections examined, are both best explained by the hypothesis of their not being the same substance. The E body, which is most certainly Au_2Al , is in equilibrium with the liquid along the curve ED, while at D there is a triple point. This point corresponds to a temperature and concentration at which both solid bodies can exist in equilibrium with the liquid. At points between E and D we therefore have primary crystals of E immersed in white mother-substance. The door-panel moulding, distinctive of the E body, and described later, is found on the primary crystals as far back as 28.3 atoms. The mother-substance along DE is very white and uniform, and does not resolve into a eutectic mixture, but under the 2 millims. immersion it shows a tendency to break up into polygons, with thin lines between them. This can with care be detected in all sections, from 27 to 31 atoms of aluminium, and is just what we should expect to see if D, the intersection of the two branches CD and DE, lay a very little on one side of the summit of the branch CD.

While we are confident that the E body is Au_2Al , we cannot feel the same confidence as to the formula of the body which would be pure at the summit of the branch CD. The formula Au_8Al_3 would put the summit at 27.3 atoms of aluminium. This would fit in very well with the curve; and our alloy (fig. 14), which professes to contain 27.2 atoms, has, as the photograph shows, very little mother-substance between the polygons; that is, it is nearly a pure body. On the other hand, the formula Au_5Al_2 puts the summit of CD at 28.6 atoms. Alloys of this composition can be seen in the photograph (fig. 16) to have in them a small quantity of primary crystals of E, so that if Au_5Al_2 is the formula, the summit must lie a little underneath the branch DE, and be therefore unrealisable.

Before leaving the branch DE, the very rounded shape of the blobs of the primary crystals of E should be noticed. Their shape is just what one would expect to see if an emulsion of two conjugate liquids were suddenly solidified. We have been sometimes strongly tempted to think that E did separate in liquid drops along this branch. The same effect is seen, but not so strongly, along EF, and indeed in almost all the primary crystals, but such a supposition would leave unexplained the larger regular patterns in which the blobs arrange themselves, and we are disposed to think that, as we have already stated, the blobs are filled out crystal skeletons.

The alloy Au_2Al , which is pure at E, shows when examined with a high power, a great deal of detail. Many of the polygons are ruled with fine lines (fig. 19), the direction of ruling being often different in different polygons. These patches of course present the *rotation* effect. In many places it shows a beautiful crystalline structure with a pattern resembling the moulding of the panels of a door, and not unlike the well-known appearance of crystalline bismuth. We give a photograph of this (fig. 20) taken with a magnification of 450 diameters. Practically no eutectic is

visible between the crystal aggregates, but in some parts of the section the polygons are marked out by very fine lines; one polished section showed this before etching. The alloy itself is a somewhat brittle white substance. Etching with bromine or aqua regia develops large patches of various shades of grey, some very silvery: these are well seen with a hand lens. Oblique illumination, with a power of 50 diameters, shows groups of silvery spots on a dark ground. These spots disappear on rotation of the stage, and others become visible. The large patches also change from light to dark in the same way. As far as one can see, the whole surface shows this *rotation* effect, and consists of groups of polygons of the same substance in different orientations.

The alloys between E and G are a mixture in varying proportions of the above described Au_2Al and of the body named X. This latter, when unetched, is of a fine ivory white, but etching attacks it more rapidly than is the case with the E body, and turns it grey or brown. All the alloys between E and G are, when unetched, a mixture of pure white X and of E, which is often covered with gold. The effect of etching is to remove this gold and to show the pure white of Au_2Al , while the X body is darkened and rapidly eaten away. The alloy with 35.1 atoms (fig. 21) shows the smooth and the rough kinds of E and the door-panel moulding, and there is only a little mother-substance, the structure being that of a nearly pure body. The alloy with 36.6 atoms of aluminium, after etching with aqua regia, is shown, by a power of 50 diameters, to consist of silvery blobs almost isolated from one another. With a power of 500 this is a magnificent section. The white silvery spots of Au_2Al , each uniformly pitted, are surrounded by a eutectic consisting of a minute pattern of the same white, intimately mixed with the X body, which is grey or brown. With 38 atoms etched in the same way there are about equal amounts of the pitted form of E, and of the eutectic made up of E and X. The alloy with 38.9 atoms (fig. 22) shows a very good eutectic between the larger crystals of E. That with 39.9 atoms shows lines of silver dots of E, very slender, but beautifully rectangular in arrangement. The eutectic, which fills nine-tenths of the whole area, is resolved by a power of 500 into its two components. We are now very close to the eutectic point F, but still have a slight excess of gold. A slowly-cooled alloy, containing 40 atoms of aluminium, is the large scale but very uniform eutectic given in fig. 23. But one point of this alloy showed a primary crystal of Au_2Al that, magnified to the scale of the photograph, would be 2 inches across; this was the only primary crystal in the section. We mention its size to emphasise the relatively fine grain of the eutectic.

With 40.7 atoms the positions of the two ingredients are reversed; instead of the scanty rows of white spots of the alloy at 39.9 atoms, we now have a few very straight rows of spots of grey X immersed in the same eutectic. We have thus crossed over to the other side of the eutectic point F, and the X body is crystallising first. The alloy with 42.7 atoms, like all those between F and G, polishes well,

showing the X body in pure ivory white, and the network of eutectic somewhat in relief and golden from rubbed gold. When lightly etched, the X body shows in the form of grey blobs in a white and golden network; it is possible to entirely remove the gold, although at the risk of etching the X body somewhat deeply. The eutectic is somewhat coarse. With 43.3 atoms of aluminium the unetched surface shows only the usual pure white patches of X in a golden network. When lightly etched with aqua regia a power of 50 shows grey or brown blobs in a white network (fig. 24). With a still higher power the striated appearance of the dark blobs of X is seen. There are no traces of purple. A photograph of this is given in order that the relative amounts of X and the eutectic may be noted. We are practically on the horizontal line of freezing points running through G, yet the X body is very far from being the only substance present.*

Close to 44 atoms of aluminium we pass the point G, and an upper freezing point appears on the branch GH, so that the alloy has three freezing points. The microscope now begins to show crystals of purple in the alloy; at first very little, but as the percentage of aluminium increases, so does the amount of purple, until at H the alloy is pure purple. The photograph of the alloy with 51.2 atoms of aluminium (fig. 26) shows the isolated rows of crystals of the purple AuAl_2 . But in all the alloys between G and H there are three substances. This is well seen in the slowly-cooled alloy containing 45 atoms of aluminium, in which the detail is naturally large. A vertical section of this ingot of alloy contains a small amount of purple in large crystals near the top and on one side of the ingot, but most of the section consists of long-shaped isolated crystals of the X body in a network which is shown by a power of 20 diameters to be an exquisite eutectic of the E and X bodies. The photograph, before etching, of a horizontal section of this alloy (fig. 27) shows several dark crystals of the purple AuAl_2 , bordered by white X, and surrounding the large patches of white, the eutectic is seen. It is evident that the uppermost fugitive freezing point is due to the solidification of the purple AuAl_2 , that the well-marked freezing point at the G temperature marks the moment when purple ceases to form and the crystallisation of X begins. At this moment the still liquid part of the alloy has reached the composition given by G. As the alloy continues to cool, the liquid part traverses all the stages of temperature and composition corresponding to the points on the branch GF, crystals of pure X crystallising during this period. Finally, the residual liquid attains the composition of F, and the eutectic network forms at a constant temperature. The facts that the alloys between H and G are the only ones which plainly show three solid constituents, and that the solid alloy at G is a

* *January 30, 1900.*—An alloy whose analysis gave 44.1 atoms of aluminium, which therefore must be close to the transition point G, shows after prolonged etching with bromine water a very fine eutectic surrounding isolated spots of the primary crystallisation of X. A photograph of this is given in fig. 25. Figs. 22 and 25 are complementary; both contain the same eutectic, but the large primary crystals are in fig. 22 of Au_2Al and in fig. 25 of the X body, dark through etching.

mixture, not an almost pure substance like the alloys at B and D, somewhat differentiate the transition at G from those at B and D. The most probable explanation of what happens at G is that the curve FG, along which the X body is in equilibrium with the liquid, would, but for the formation of the purple alloy, be continued to a summit, X, on the right of G, and then no doubt downwards towards the aluminium end of the system. In the same way we must suppose that the equilibrium curve HG between the purple crystals and the liquid would, but for the existence of the X body, be continued below GF. Our experiments give, as is usually the case, only those parts of the two equilibrium curves which have no other branch above them. Our method of stirring the liquid vigorously until solid begins to form prevents very great surfusion and destroys any chance of finding freezing points on the hypothetical branch GX. But a cooling curve, conducted without stirring, might show such points. We have no conclusive evidence as to the formula of the X body, but as at G it forms considerably more than half of the alloy, the summit cannot be very much to the right of G; the formula AuAl seems to us an extremely probable one. The microscopical study of alloys near the point G shows how rash it would be to assume that an angle in a freezing point-curve, together with a horizontal line of second freezing points, necessarily gives the formula of a compound.

Alloys with more than 44 atoms of aluminium contain increasing quantities of purple the nearer we get to the summit H, at which point the whole area of the section is full of purple separated into large patches by slender lines of white that do not form a complete network. The alloy with 65.3 atoms of aluminium (fig. 28) shows the structure well. It is necessary to examine these alloys without etching them, as all etching reagents destroy the purple and cause an electrolytic deposit of gold on the other bodies present. Most of the alloys between G and H had been polished by the dry method, and hence the polished surface shows three things: the beautifully uniform crystals of purple AuAl_2 surrounded by the white X body, and, generally in the middle of the patches of white, some golden spots of eutectic. This eutectic is the matter solidifying under the conditions of the point F. As we have explained, the gold can be removed by wet polishing, in which case the eutectic is white, but distinguishable from the pure X. It appears to be the harder Au_2Al that retains the gold. Even at H the thin bands of X contain thinner lines and spots of eutectic. The purple is so generally surrounded by a border of pure white X, that the purple and the F eutectic are rarely in contact (fig. 27).

The alloys at 66.6 and 67.4 atoms have about the same amount of thread-like mother-substance, not more than 1 per cent. of the area, and at the latter percentage one does not see any marked change in the material of the threads. At 69.2 atoms the area of the bands of mother-substance has trebled at least, and it is greyer than at the same distance from the summit on the other side. At 72.6 atoms the mother-substance has of course increased, and it is now a soft greyish body full of scratches and quite unlike the substance X. Moreover these bands of grey have no threads of gold

running through them. This soft grey easily-scratched body increases in amount as we add more aluminium up to the end of the curve. The purple body seems to retain its character unchanged, although decreasing in area. With 99.3 atoms of aluminium one still sees small occasional spots of the unchanged purple, on the dirty grey ground, which is no doubt aluminium. Hence there is probably no new compound between H and the aluminium end of the curve. The alloys with more than 66.6 atoms of aluminium that were extracted for analysis polished so badly that we have not attempted to take photographs of them. But a specially made ingot of alloy, containing about 20 per cent. by weight of gold, that is 96.7 atoms of aluminium, was successfully polished (fig. 29). On the curve this alloy would be a little to the left of the eutectic angle I, and the pattern of the polished section naturally resembles that at a corresponding position on the other branches. It consists of rather scanty rows of small spots of the purple body arranged in straight lines at right angles to one another.

We give also a Röntgen ray photograph of a thin section of this alloy cut parallel to the surface of the previous section. This has been enlarged 5 diameters. In this shadow-photograph the opaque AuAl_2 is dark, while the eutectic ground, which is almost wholly composed of the transparent metal aluminium, is light. The resemblance between the pattern of the two is complete, but the Röntgen photograph naturally shows the numerous crystals in the body of the alloy as well as those on the surface.

Slowly-Cooled Alloys.

It might be thought that the rapidly-cooled samples of alloy extracted by the Jena pipettes would not give a fair picture of the character of the crystallisation of a more slowly-cooled mass. For this reason, and also to obtain larger detail, we prepared a number of slowly-cooled ingots of alloy by the method described in our paper on X-ray photography ('Journ. Chem. Soc.,' 1898, p. 721). Each ingot weighed about 100 grammes. We found, however, that these ingots when cut and polished gave results identical with, though on a larger scale than, the quickly-cooled alloys. The slowly-cooled alloy containing 26.1 atoms of aluminium (fig. 12) shows by its marked *rotation* effect that the slow-cooling facilitates the grouping of the crystals into aggregates having the same orientations, and other slowly-cooled alloys confirm this. But as we have not found the slowly-cooled alloys contradict the evidence from the quickly-cooled ones, we do not give a detailed description of the former. There is, however, one exception to this due to the great difference in specific gravity of aluminium and the body AuAl_2 . A slowly-cooled alloy of these two substances, that is, one on the branch HI, will show a settlement of the heavy crystals of AuAl_2 to the lower part of the crucible. The Röntgen ray photographs (figs. 30 and 31) of the slowly- and quickly-cooled alloy, with about 96.6 atoms of aluminium, show this difference. We see in the photograph of the slowly-cooled alloy

that the very opaque AuAl_2 which crystallised first has settled to the bottom of the crucible, leaving a mother liquid which afterwards crystallised with the usual fine grain of a eutectic. The shape of the AuAl_2 crystals is distinctly visible in the negative, and is very similar to that of crystals of the same body in alloys between G and H.

The slowly-cooled alloy (figs. 32 and 33), containing 0.7 atomic per cent. of gold, is near the bottom of the branch JI, the quantity of AuAl_2 present is insufficient to saturate the aluminium, and, therefore, during the process of solidifying, the aluminium has crystallised first on the walls of the crucible, perceptibly concentrating the opaque AuAl_2 in the central portion of the ingot.

The Bodies B, D, E, X, and H.

The body B, pure at 20 atoms of aluminium, to which we attribute the formula Au_4Al , was obtained in the form of a brittle rod of white with a faint yellow tinge. It has a silky conchoidal fracture. Although containing little more than 3 per cent. by weight of the white aluminium, the colour of the gold is gone, in fact there is no free gold in it. This alloy is more easily attacked by etching reagents than pure gold, or than the D and E bodies, hence, after etching, we never see it as a white body but as yellow or brownish purple from a film of finely divided gold. D and E are pure white bodies, both before and after etching with bromine or aqua regia. Fused caustic potash dissolves out the aluminium from them and leaves them with a golden surface. They also break with a conchoidal fracture, and are hard and brittle.

The X body, which we think may be AuAl , has not been obtained pure in large masses, but a slowly-cooled alloy with 45 atoms of aluminium contains pure white patches of X; these are soft. The X body when in contact with Au_2Al is very rapidly attacked and eaten away by bromine or aqua regia, leaving a grey finely lined surface with the more resistant Au_2Al in relief.

The purple AuAl_2 is attacked by hydrochloric acid, a reagent which has little or no effect on the other bodies, the colour being destroyed and an electrolytic deposit of bright gold forming on the surrounding X body. It is curious that the compounds containing only a little aluminium should be white, while AuAl_2 with nearly 22 per cent. by weight of the white metal should have the splendid purple of finely divided gold. The identity in the melting point of AuAl_2 and of gold also marks out this compound as worthy of further study.

Eutectic Alloys.

As the photograph of the alloy with 40 atoms of aluminium shows, there is a typical eutectic at F. This alloy contains practically no primary crystals, but consists of two interlacing networks of E and of X, which must have crystallised almost simultaneously. It is an alloy of minimum and constant freezing point. This is probably the only section exactly at a eutectic point that we have polished, but there must be a eutectic corresponding to the point C, and also at a point a little to the left of B. But one can study eutectics in many other sections; an examination of the mother-substance between the blobs of primary crystallisation enables us to do this. For example, alloys between 36 and 40 atoms show the F eutectic very well, and it is also well seen here and there on the branch FG, and in the slowly-cooled 45 atom alloy a little above G. Again, although we have not absolutely located the eutectic point between A and B, yet the mother-substance of the 18.1 alloy shows the structure of this eutectic; the 19.8 atom alloy, which must be on the other side of the eutectic point, also shows a minute network in its golden mother-substance. The mother-substance of the branch CD, for example, at 21.6 atoms shows a eutectic mixture; but this was one of numerous cases in which surfusion preceded the solidification of the eutectic. One would expect surfusion to modify the pattern of the eutectic considerably, and, perhaps, to give three stages of solidification altogether, so that the eutectic structure would have that polygonal form characteristic of a nearly pure substance. The alloys on the branch DE show us that a *mother-substance* can be a pure body. This will occur whenever a branch of the curve cuts the next lower branch at the summit of the latter. The question whether a *eutectic* can be a pure body is really one of nomenclature. If we use the term eutectic for the mother-substance of the branch DE, the answer is, Yes; this mother-substance solidifies at a constant temperature, but is not an alloy of minimum freezing point.

The mother-substance along GH is a mixture, but not a eutectic. It, however, contains the F eutectic as one of its constituents; this is very well shown in the horizontal section of the 45 atom slowly-cooled alloy (fig. 27), the gold-smeared E of the eutectic having a minute pattern of pure white, X, scattered through it; this is, of course, in the unetched alloy. The quickly-cooled alloys of the branch GH do not always show the detail of the eutectic very well, but the row of very steady third freezing points makes the matter certain. The fact that these freezing points occur after marked surfusion may explain the scantiness of the F eutectic along the branch GH, and the fact that many of the blobs of E are large.

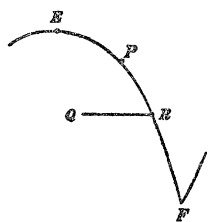
Summary.

The results obtained as to the equilibrium between gold and aluminium may be stated briefly.

Each point on the diagram of Curve 1 corresponds to a mixture of a certain composition at a given temperature.

All points above the curve correspond to homogeneous liquids. A point P on any branch of the curve corresponds to a state of possible equilibrium between a solid whose composition is given by the summit, real or imaginary, of the branch and a liquid whose composition is given by P itself.

A point Q below the branch of the curve, but above its lower end, corresponds to a mixture of a solid and a liquid. The composition of the solid is given by the summit of the branch, and that of the liquid by the point R, in which a horizontal through Q cuts the branch. An intersection of two branches, such as C, D, F, or G, corresponds to a state in which the two solids given by the summits of the two branches can both exist in equilibrium in the presence of the liquid given by the intersection point.



The phase rule for the case of two components in a system where the pressure is constant and the vapour pressure *nil* forbids the existence of more than three phases in true equilibrium. But the microscope shows that if an alloy containing 45 atoms of aluminium be cooled to the temperature of F, it must have contained the three solids AuAl_2 , X, and Au_2Al in contact with a liquid. This is true even in the case of slowly-cooled alloys; in other words, the purple AuAl_2 appears able to exist in the presence of a liquid that is not saturated with it. But the sections which present this paradox also give its explanation. In the slowly-cooled sections at 45 atoms the crystals of purple are always surrounded by a coat of the white X, which forms on them as soon as, by partial solidification, the state G is reached. Hence the crystals of purple take no part in the later equilibrium corresponding to points on GF.

The binary metallic system treated of in this paper has many points of resemblance with the system iodine-chlorine that has been already worked out. It illustrates general principles already accepted and adds nothing to them. But we hope it may have some value as a contribution towards the slowly accumulating proof that metals combine with each other according to the same laws that hold good for compounds not wholly metallic.

The metallurgist, moreover, who applies, as has already been partly done, the double method of this paper to pairs of metals likely to be of use in the arts would probably arrive at results of value to him.

We have to thank Dr. J. C. PHILIP for his untiring and most valuable assistance in

the experiments ; Professor EWING and Mr. ROSENHAIN for their kindness in advising us concerning the photomicrography, and for the loan of apparatus ; and Messrs. JOHNSON and MATTHEY for twice lending us considerable amounts of gold.

Much of the apparatus had been purchased at various times out of grants made by the Royal Society, and some by means of a grant made to us at the Dover meeting of the British Association.

GOLD-ALUMINIUM ALLOYS.

INDEX TO PLATE 4.

Fig.	Atomic percentage of aluminium.	Magnification.	Remarks.
1	12.5	100	Medium rate of cooling.
2	18.1	18	Very slow-cooling. Oblique light.
3	18.1	500	" " " Eutectic of 2.
4	19.0	45	Medium rate of cooling. Prolonged etching Oblique light.
5	19.8	250 (?)	Quick-cooling. A drawing under oblique light.
6	19.8	450	Medium rate of cooling. Vertical light.
7	21.1	(?)	Quick-cooling. Drawing under oblique light.
8	21.1	200	" " Vertical light.
9	21.6	1200	Medium rate of cooling.
10	23.1	60	Quick-cooling.
11	25.9	18	" " Oblique light.
12	26.1	4	Very slow-cooling. Oblique light.
13	26.1	1000	" " " Eutectic of 12.
14	27.2	120	Quick-cooling. Vertical light.
15	27.2	45	" " " "
16	28.6	45	" " Oblique light.
17	29.9	45	" " " "
18	32.5	120	" " Vertical light.
19	33.6 [33.2]	150	" " " "
20	33.6 [33.2]	550	" " " "

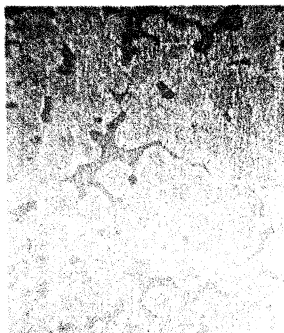


Fig. 1.

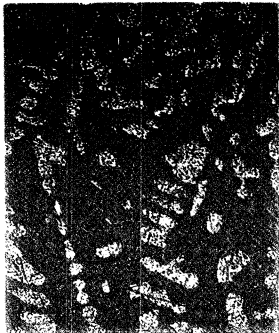


Fig. 2.

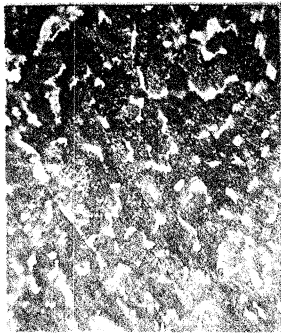


Fig. 3.

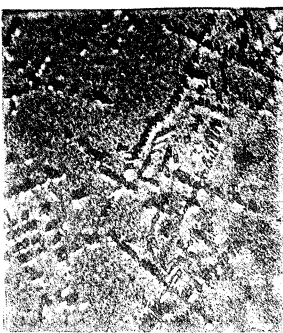


Fig. 4.

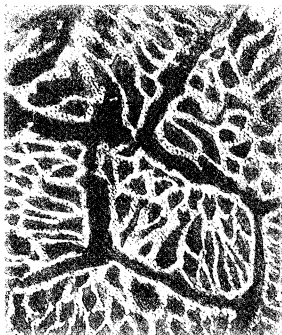


Fig. 5.

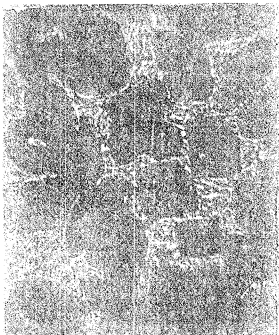


Fig. 6.

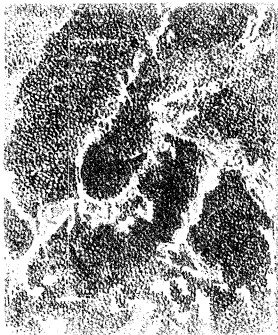


Fig. 7.

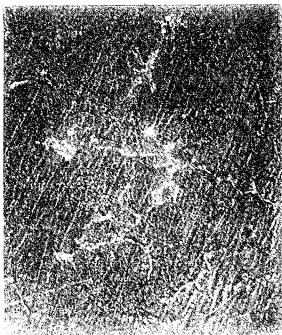


Fig. 8.



Fig. 9.

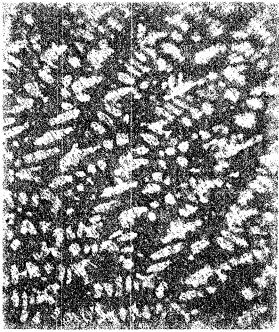


Fig. 10.

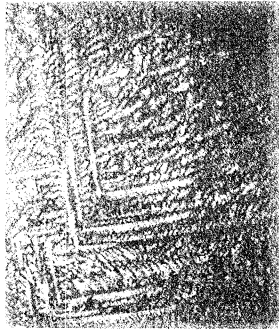


Fig. 11.



Fig. 12.



Fig. 13.



Fig. 14.



Fig. 15.

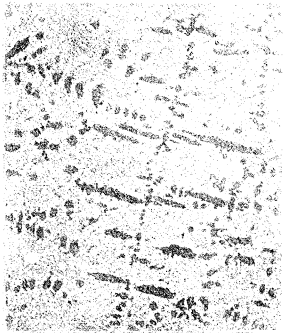


Fig. 16.



Fig. 17.

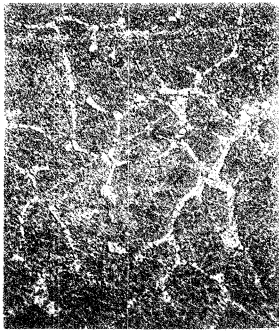


Fig. 18.

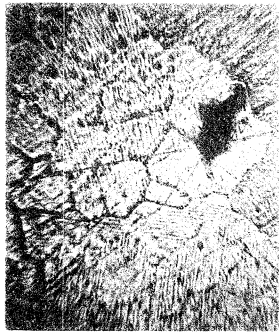


Fig. 19.



Fig. 20.

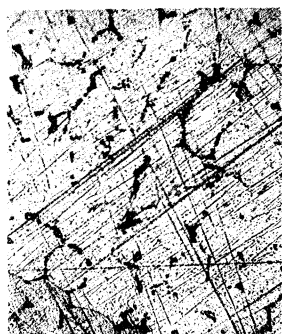


Fig. 21.

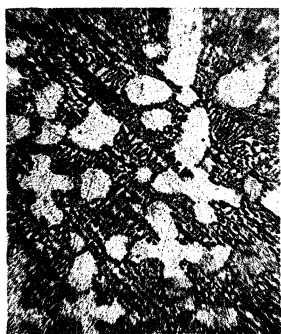


Fig. 22.

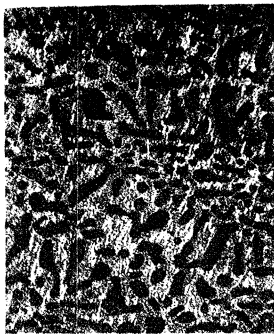


Fig. 23.

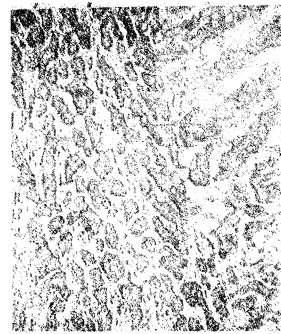


Fig. 24.



Fig. 25

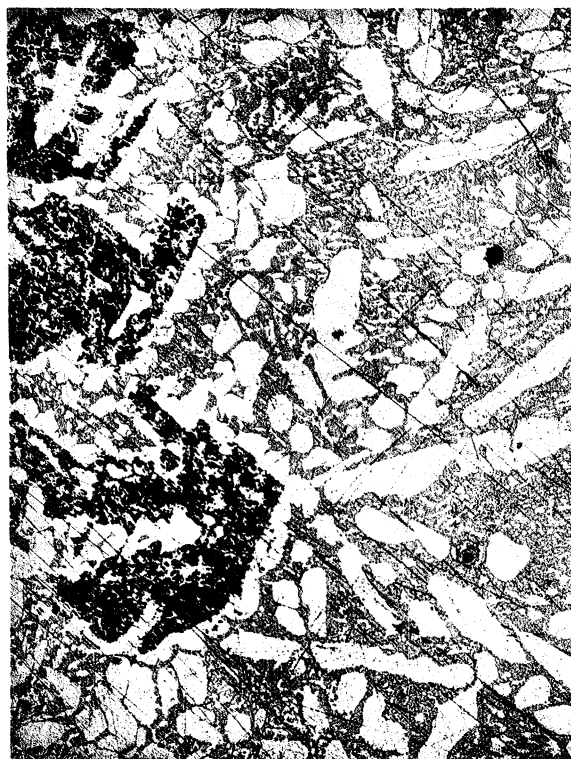


Fig. 27.

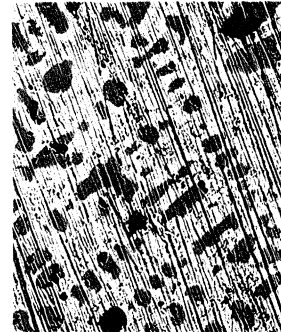


Fig. 26.

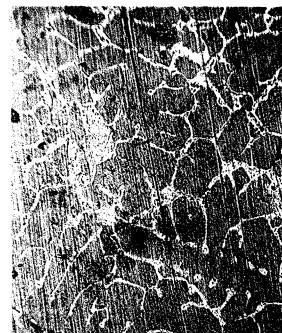


Fig. 28.



Fig. 29.

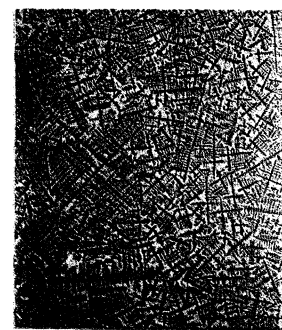


Fig. 30.



Fig. 31.



Fig. 32



Fig. 33.

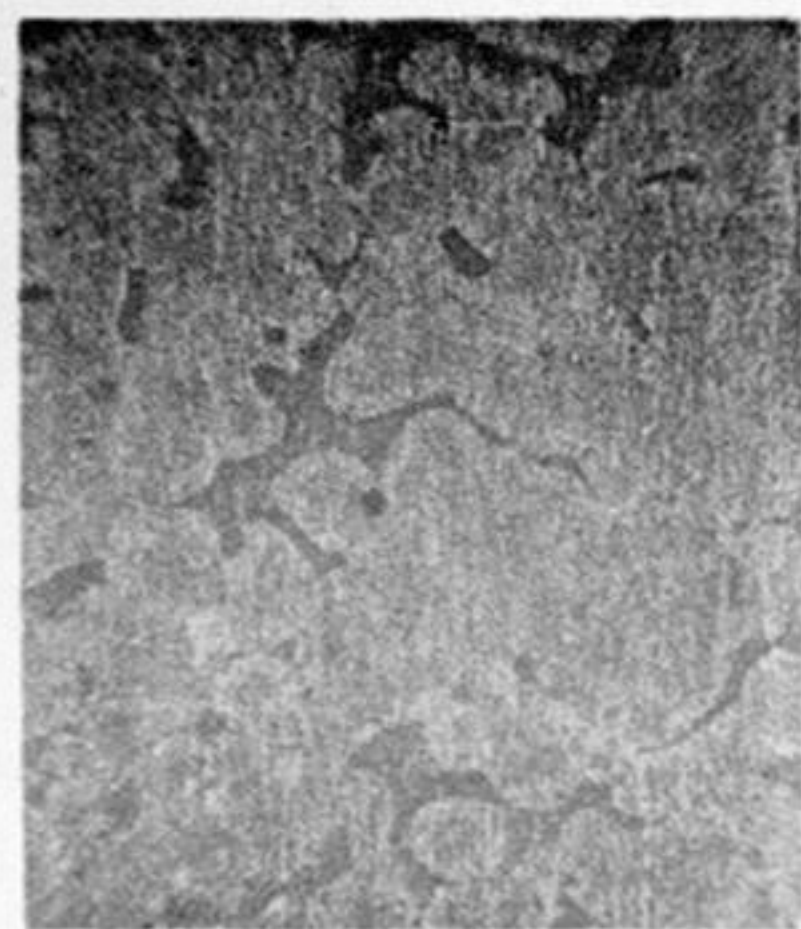


Fig. 1.



Fig. 2.

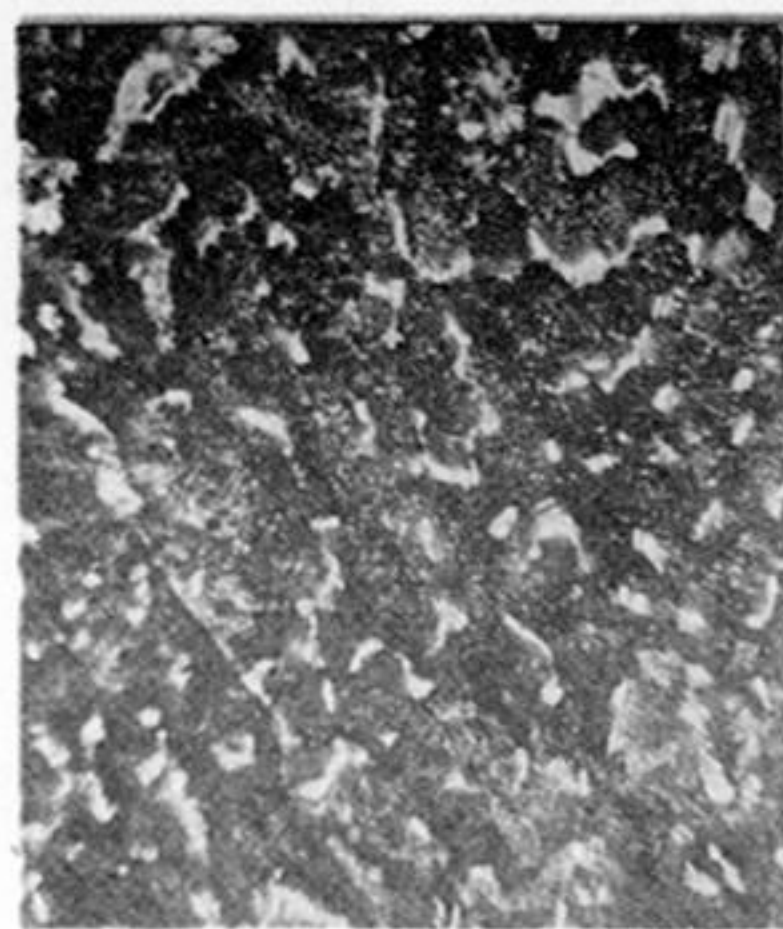


Fig. 3.



Fig. 4.



Fig. 5.



Fig. 6.

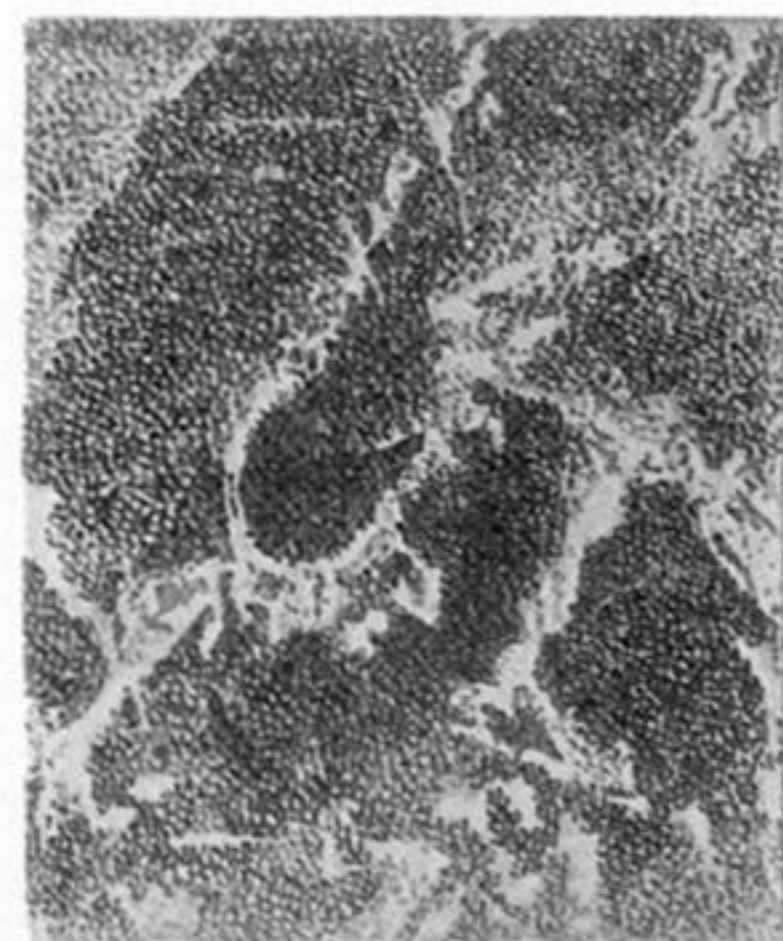


Fig. 7.



Fig. 8.



Fig. 9.

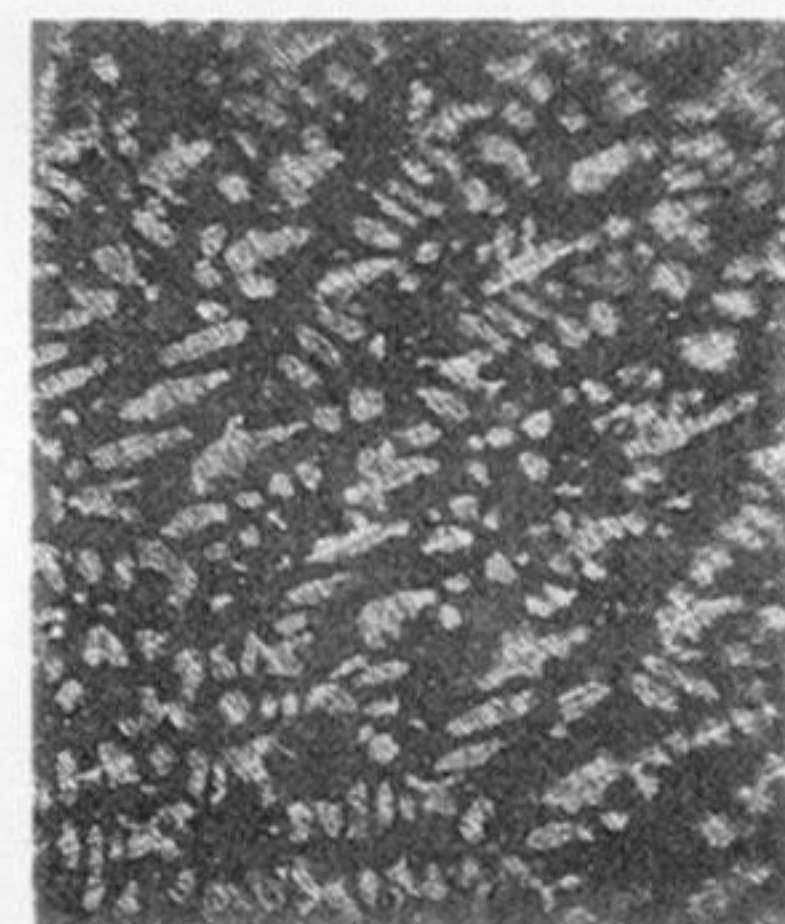


Fig. 10.

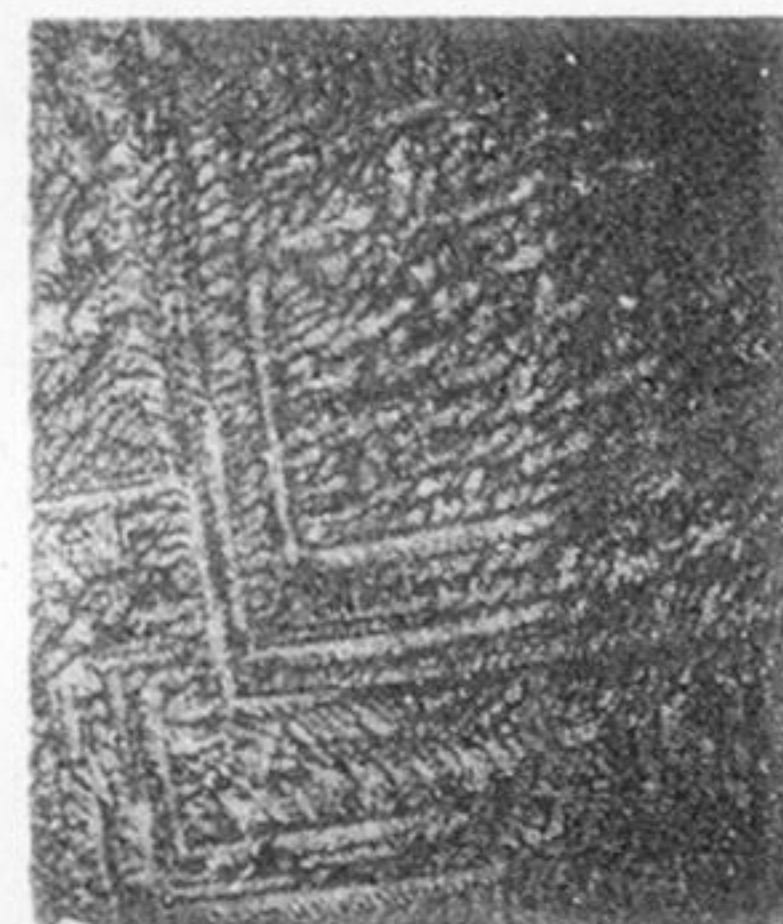


Fig. 11.



Fig. 12.



Fig. 13.

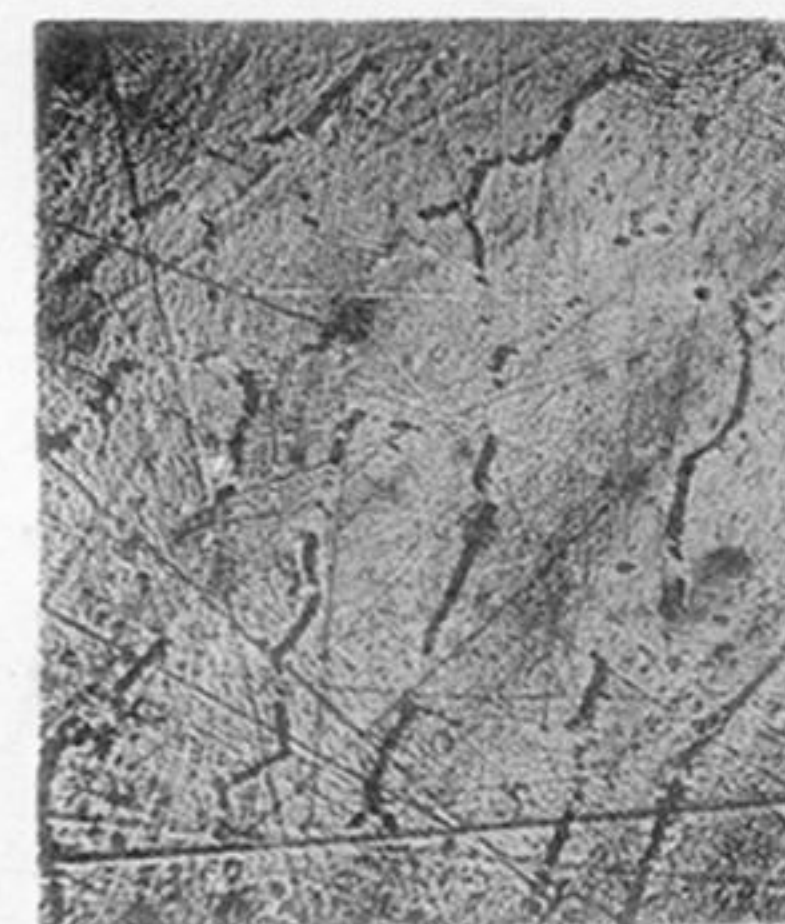


Fig. 14.

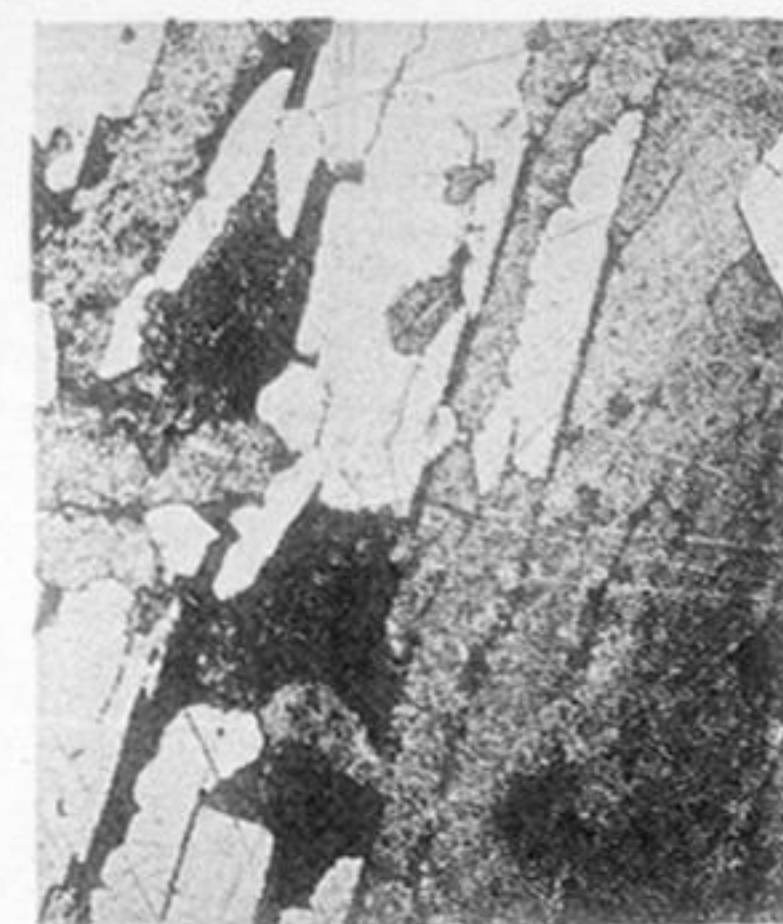


Fig. 15.

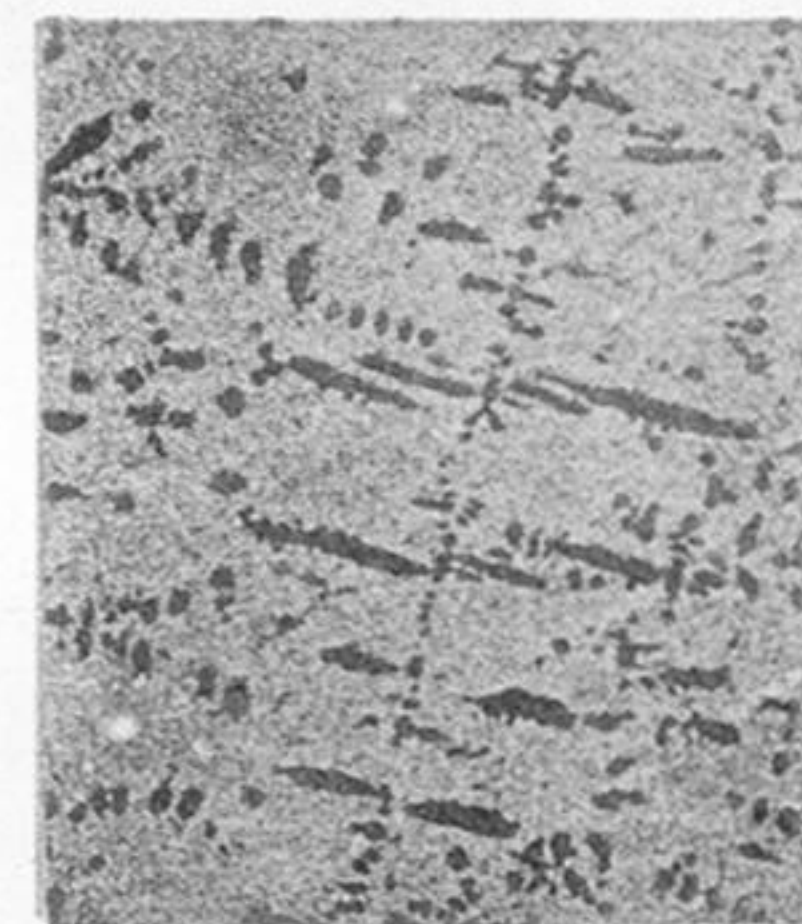


Fig. 16.

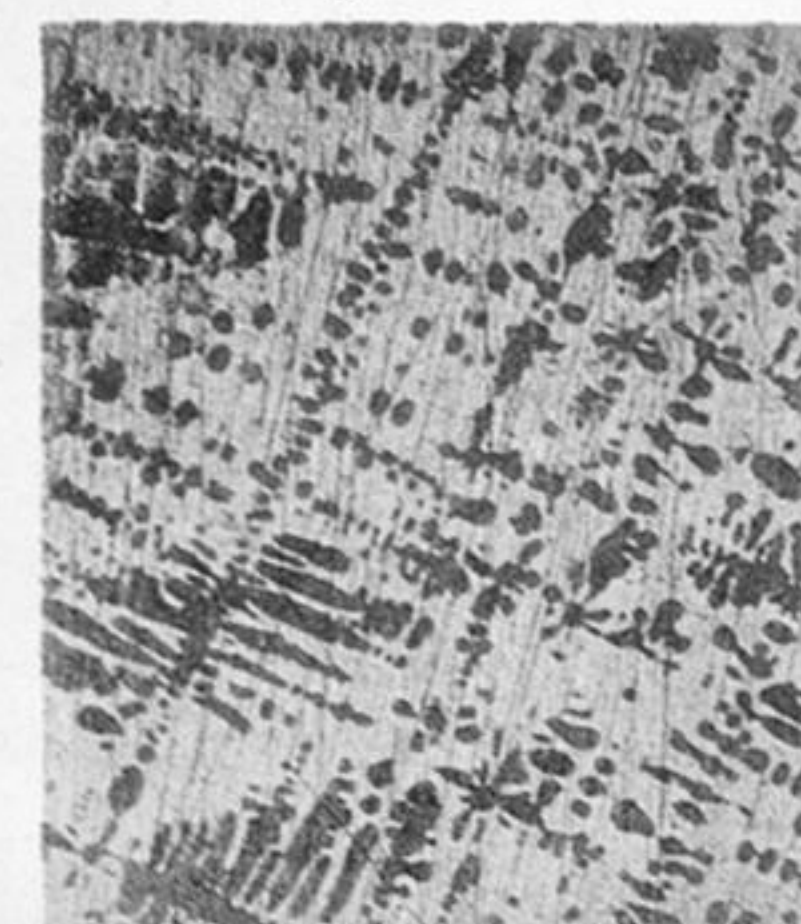


Fig. 17.

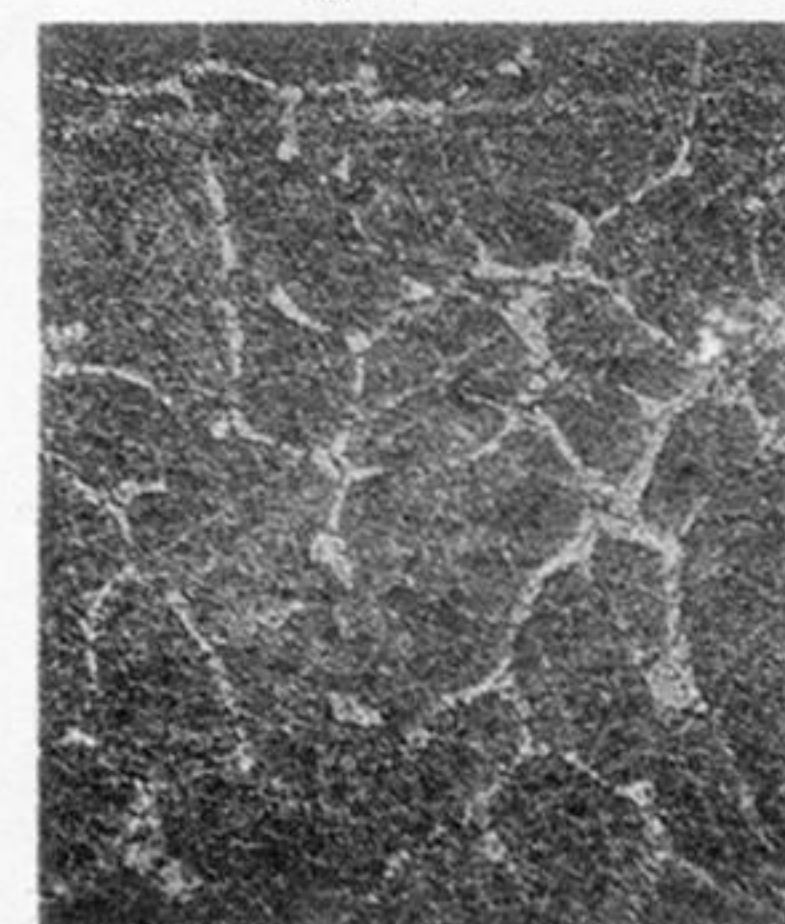


Fig. 18.

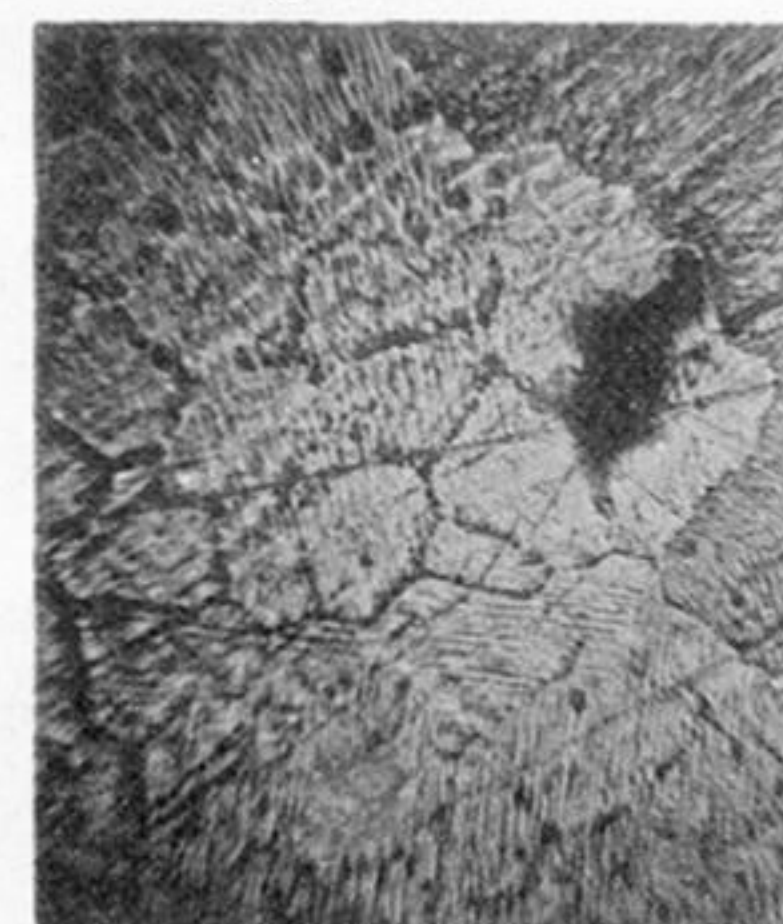


Fig. 19.

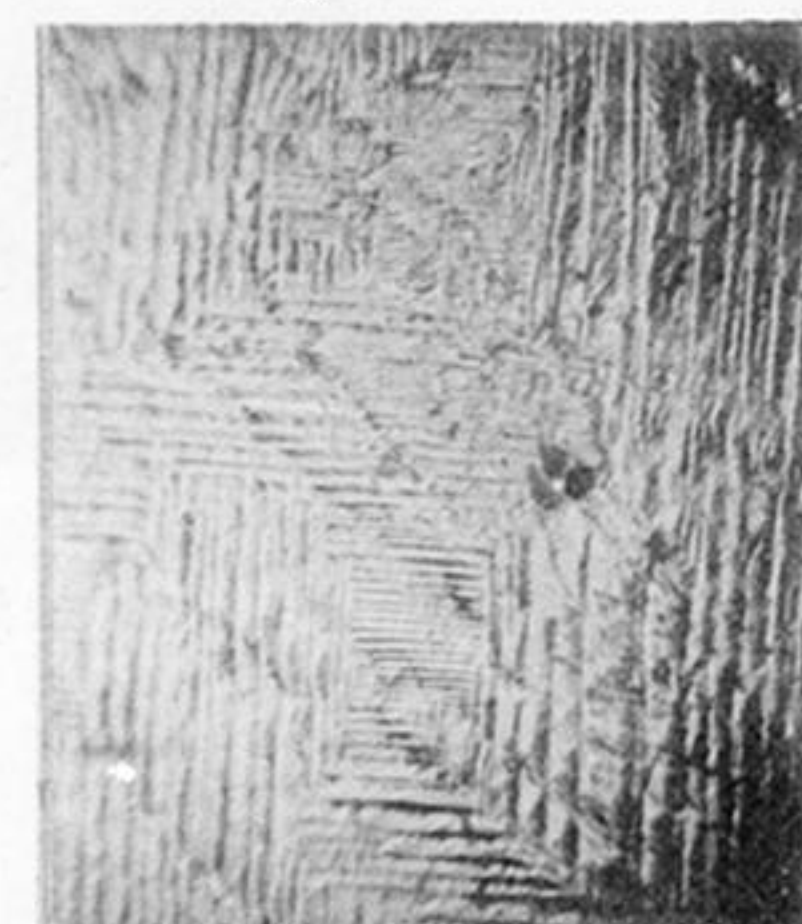


Fig. 20.

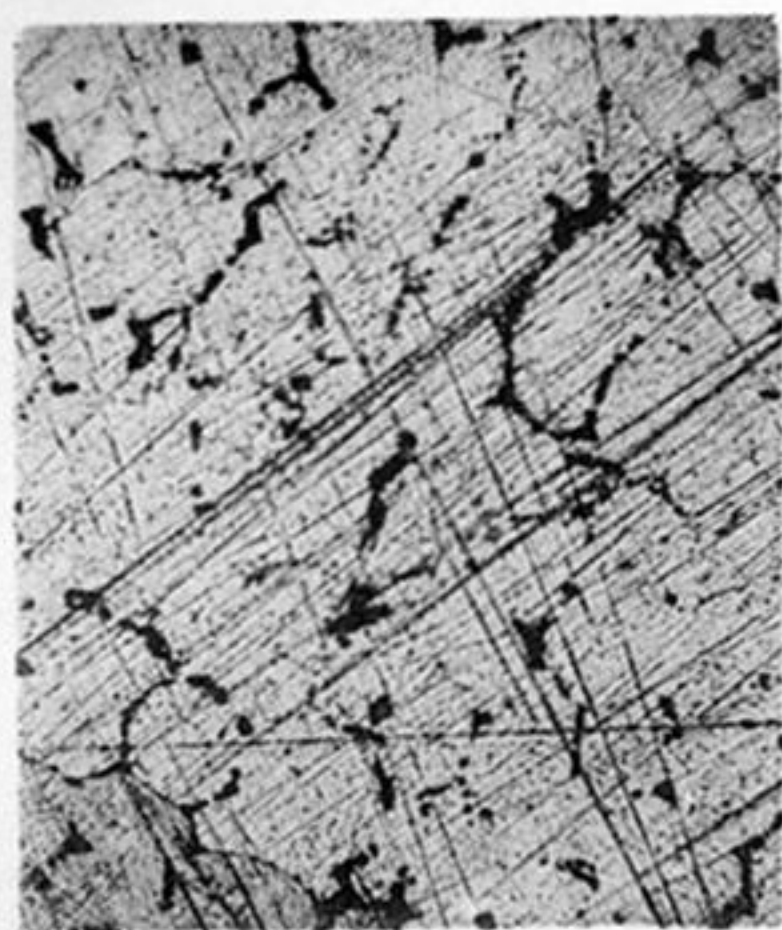


Fig. 21.

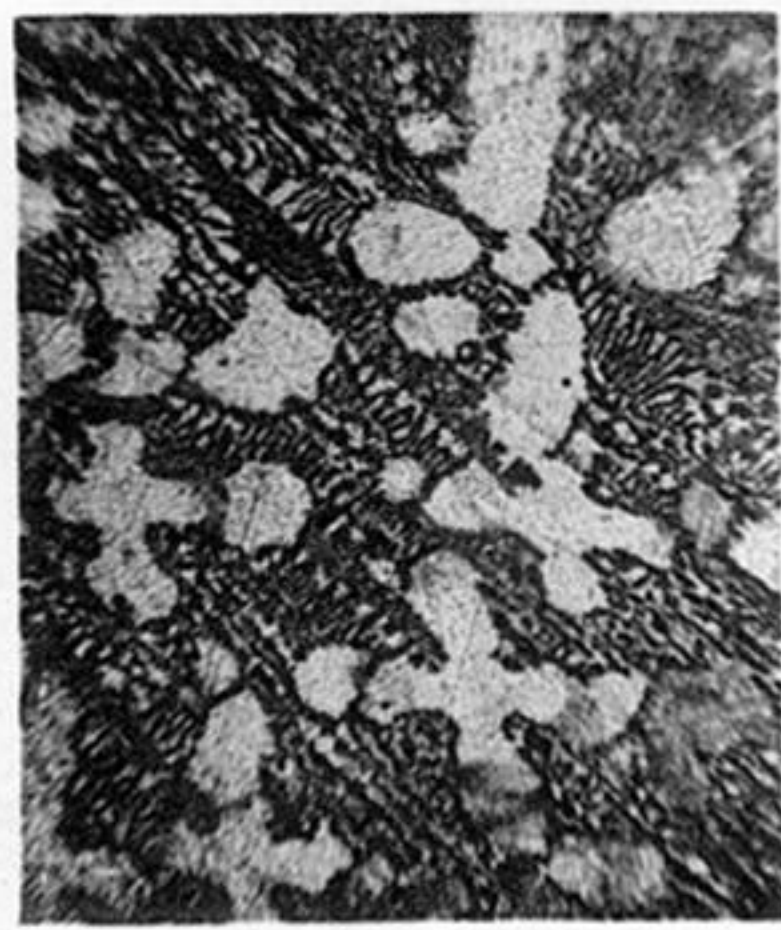


Fig. 22.

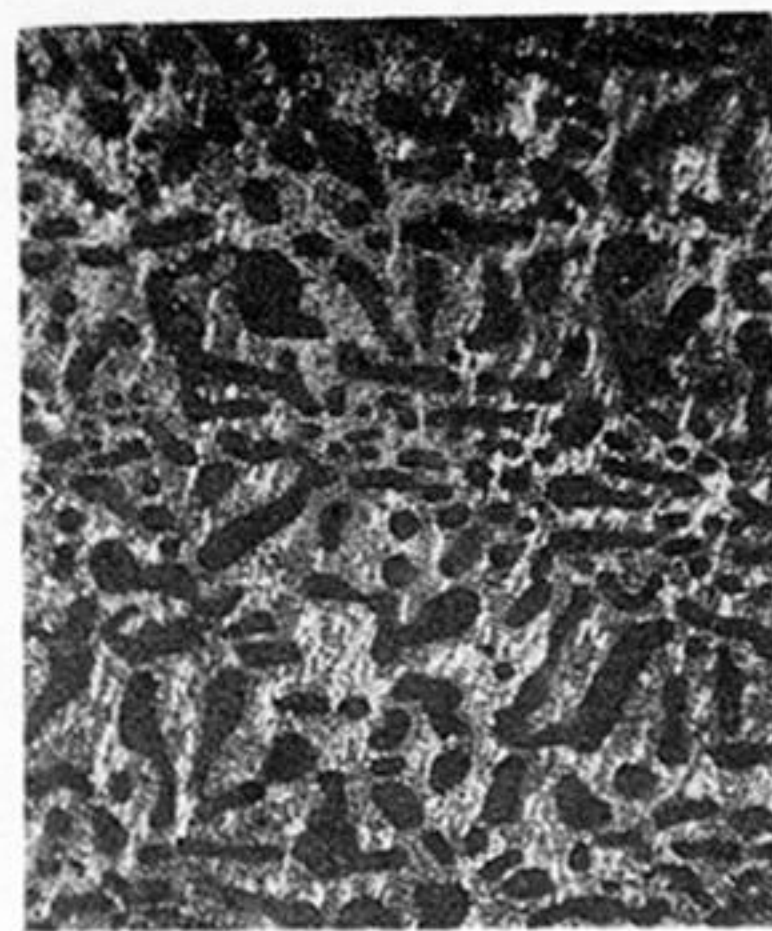


Fig. 23.

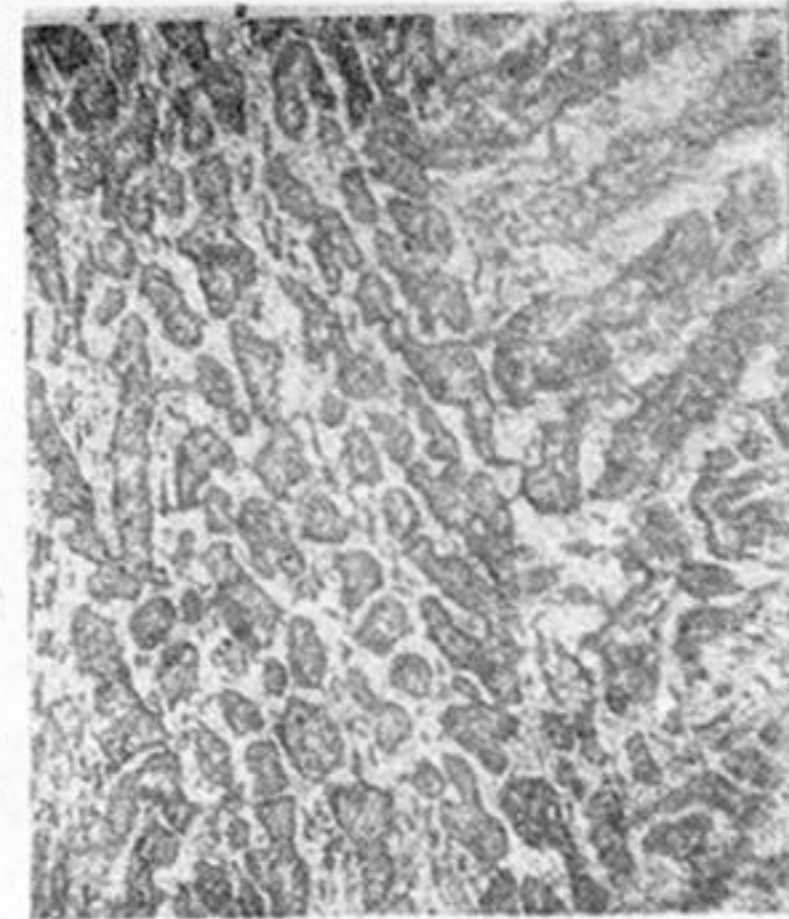


Fig. 24.



Fig. 25.

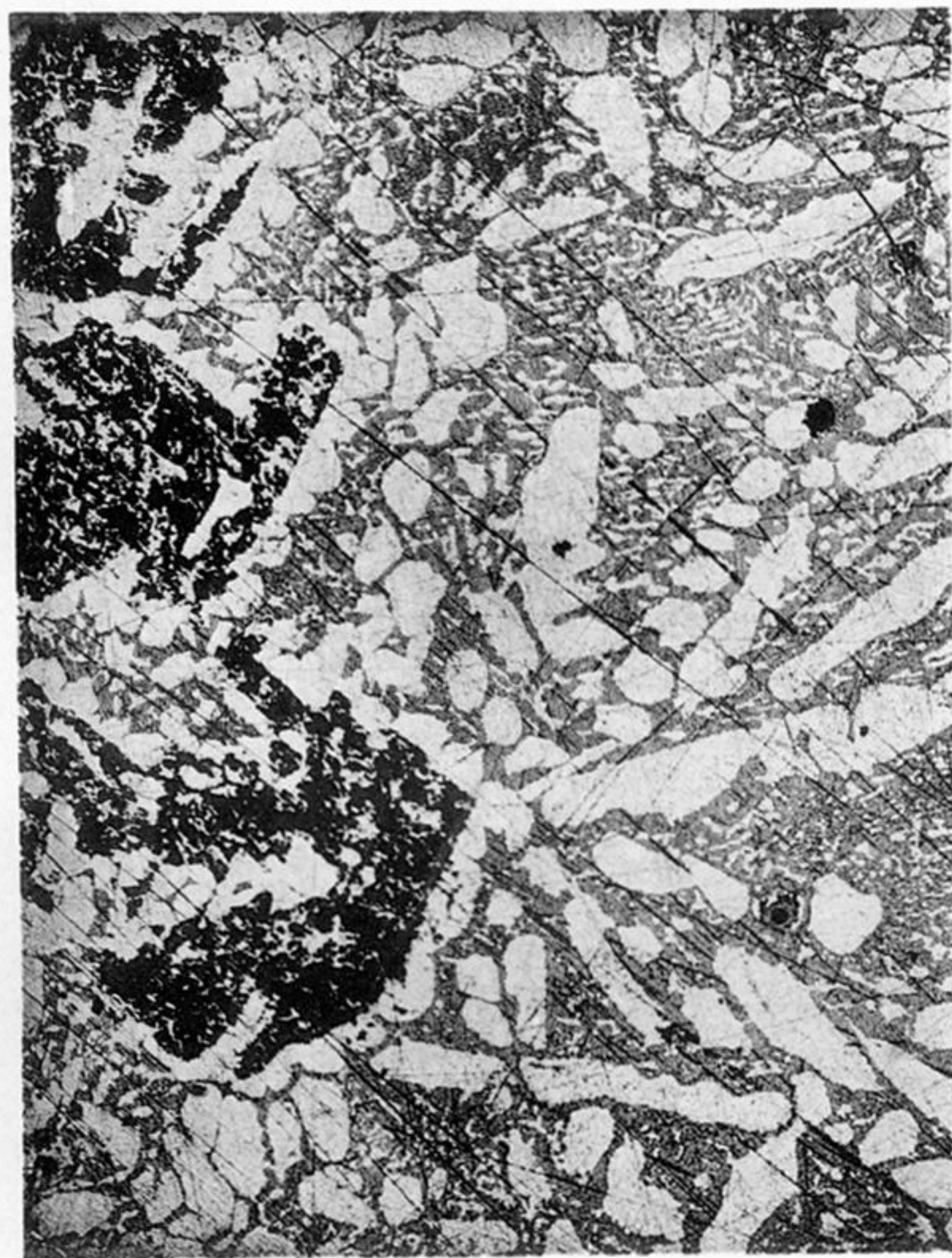


Fig. 27.

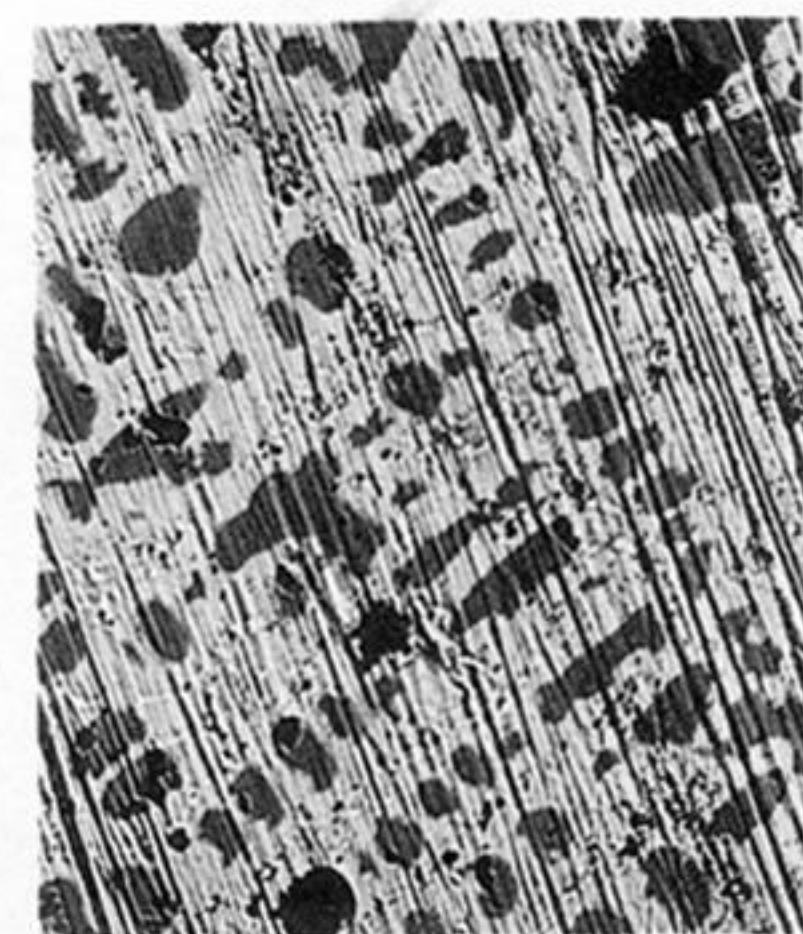


Fig. 26.

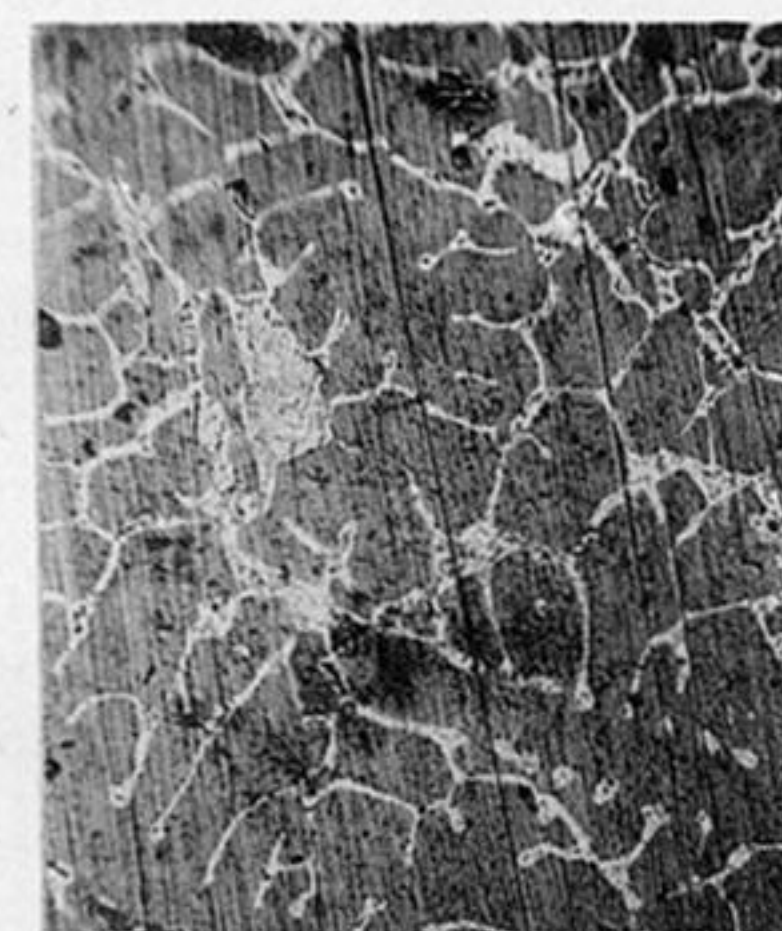


Fig. 28.

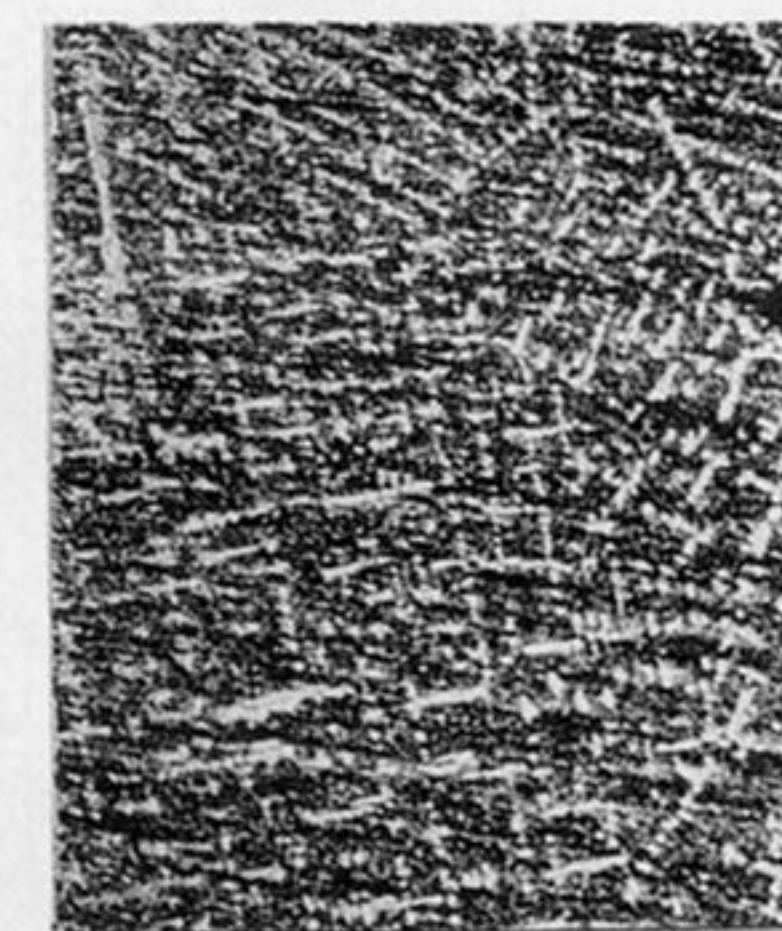


Fig. 29.



Fig. 30.

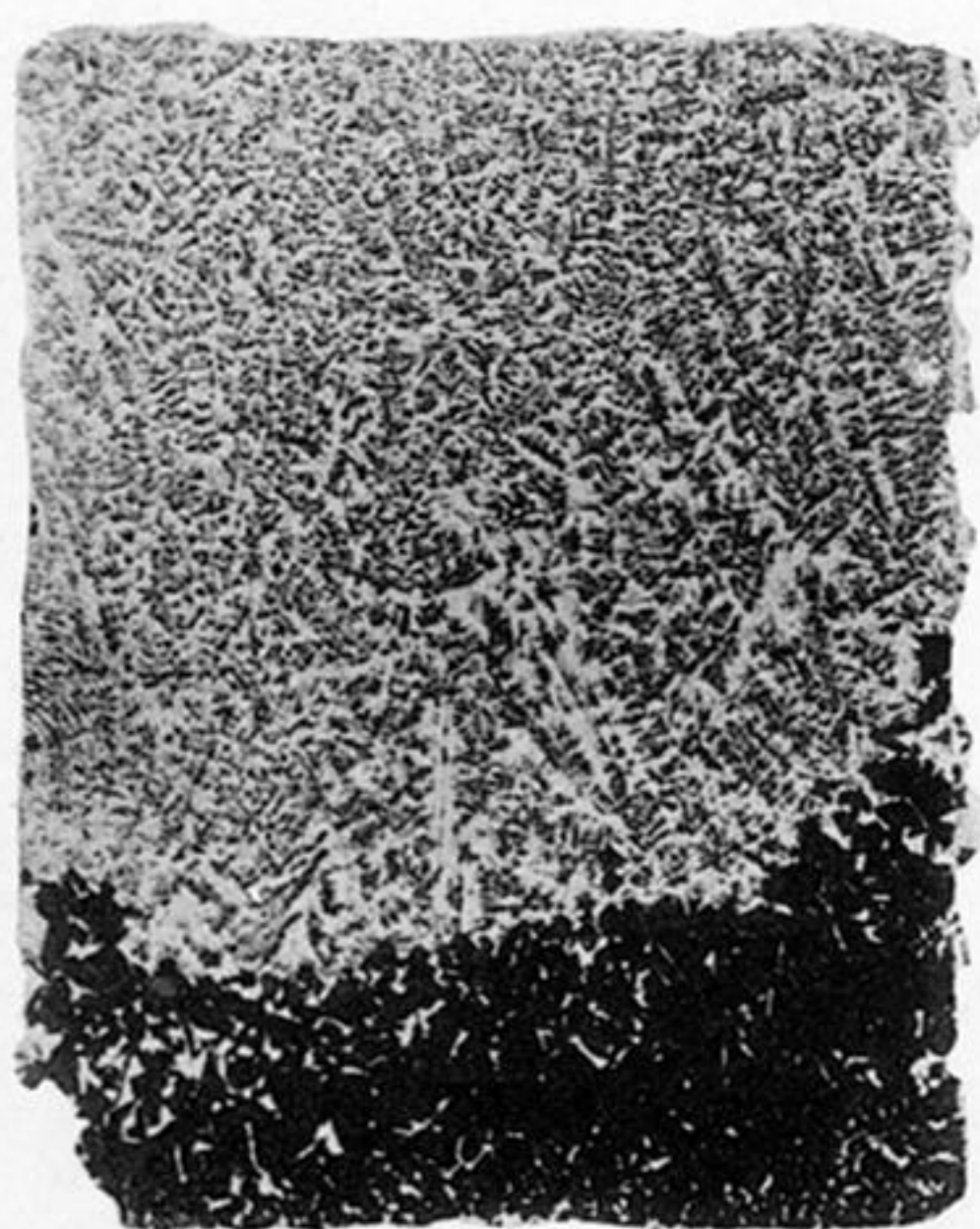


Fig. 31.

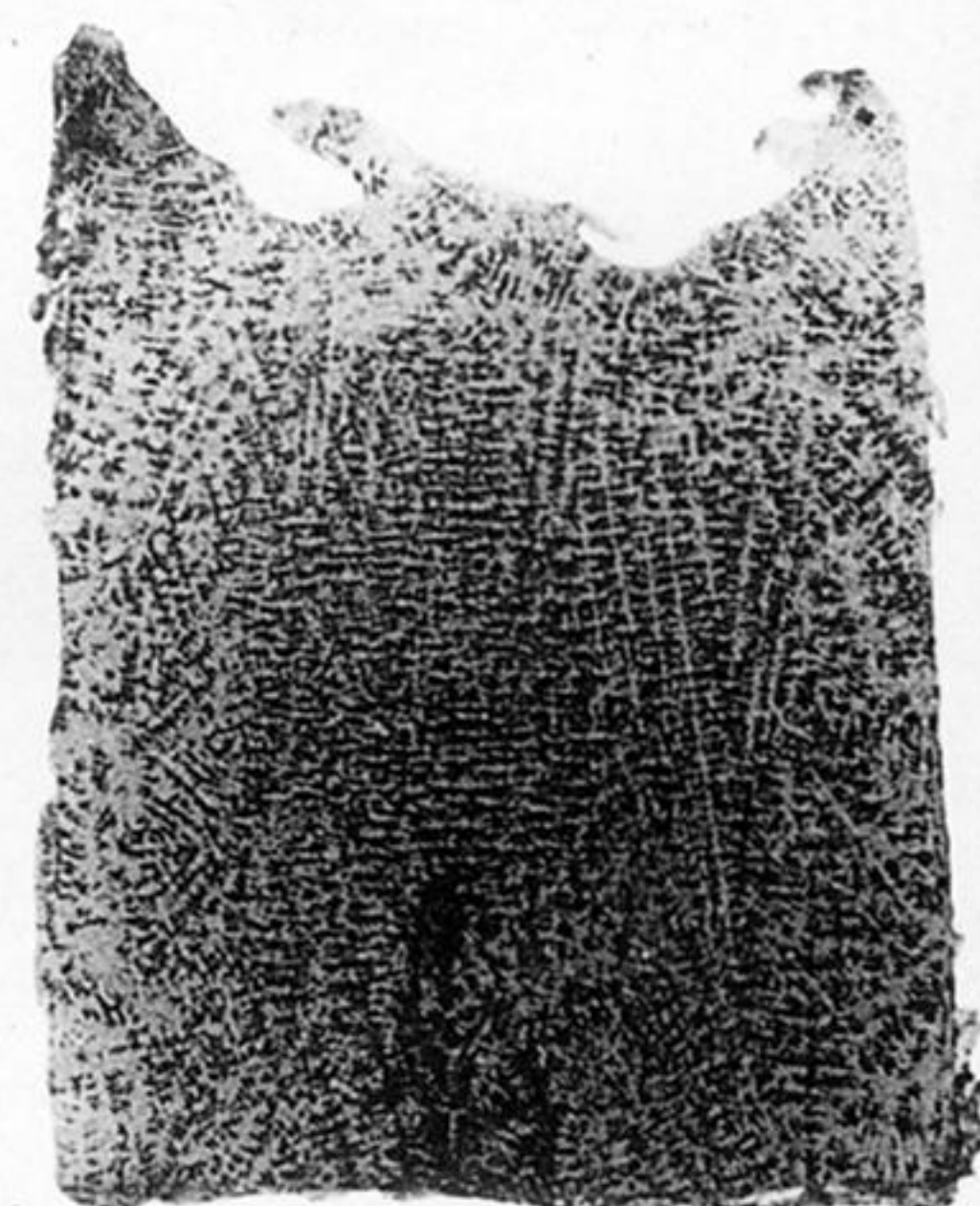


Fig. 32.

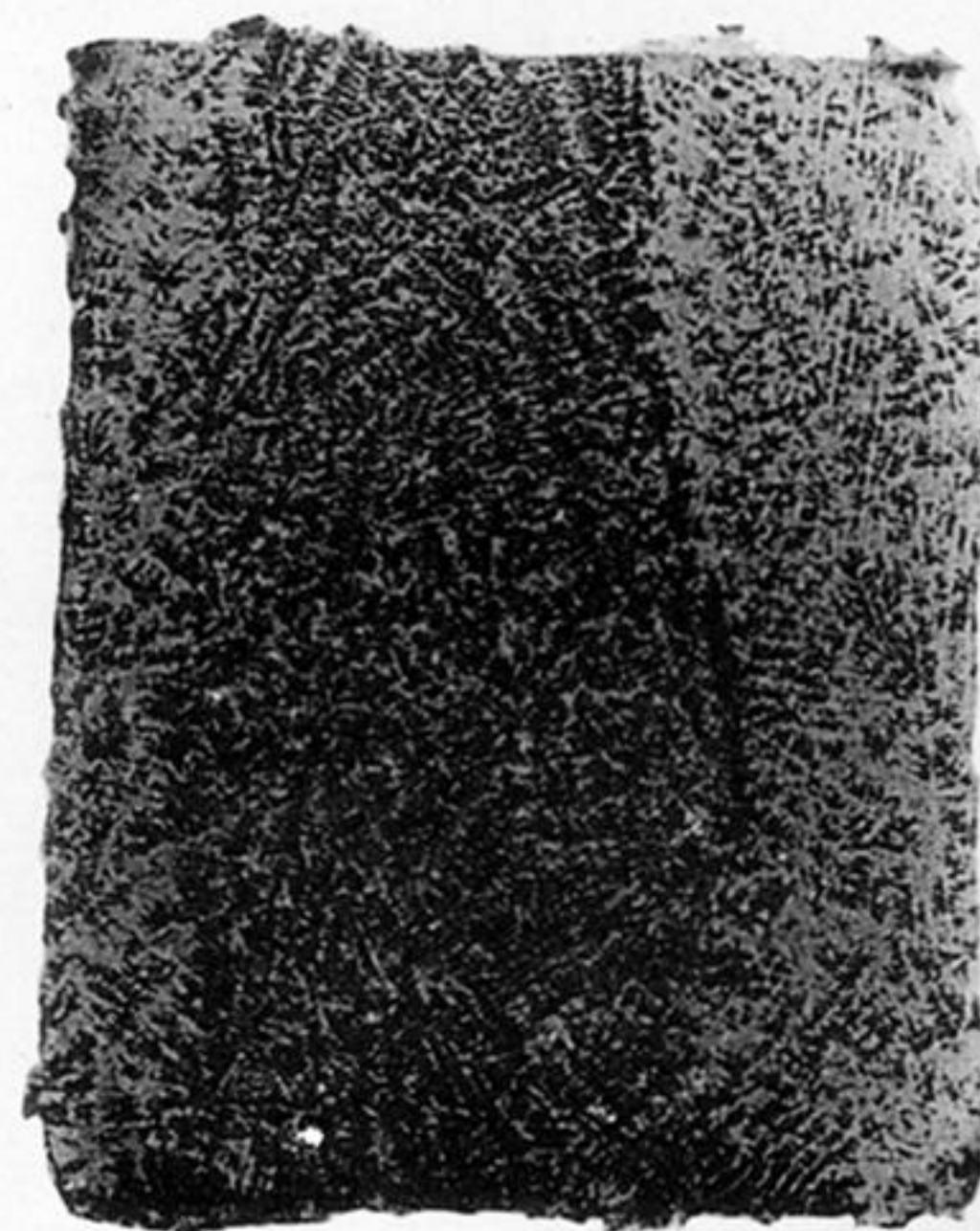


Fig. 33.