Further Investigation of the Crystalline Structure of Electrolytic White Tin

AUTHOR(S):

Hirata, Hideki; Tanaka, Yoshio

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By

Hideki Hirata and **Yoshio Tanaka**

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Abstract

The arrangements of the micro-crystals in electrolytic specimens of white tin, deposited from sulphuric acid solutions were examined with X-rays by the same procedure as in the foregoing investigation,[1] which dealt mainly with those deposited from hydrochloric acid solutions. From the diffraction patterns obtained, it was found that the micro-crystals of white tin have a tendency to be electrolytically deposited with the normals to their (111) faces arranged parallel to a definite common direction, as was the case in our previous research. But in some other respects, especially with regard to the direction of the growth of the deposited white tin, a few dissimilarities were observed from the results of the former experiments. The cause of such dissimilarities was supposed probably to be due to the difference in the chemical valencies of the ions in the electrolyte.

Introduction

In the previous investigation carried by Dr. Komatsubara and the present writers,[2] the crystalline structures of electrolytic specimens of white tin, deposited mainly from hydrochloric acid solutions, were examined with X-rays, by the so-called "transmission method." As a continuation of this investigation, similar experiments have been made with specimens deposited from sulphuric acid solutions. To take the Laue figures, the photographic plates were always placed perpendicularly to the incident X-ray beam emitted from the molybde-

1. H. Hirata, H. Komatsubara and Y. Tanaka; The Anniversary Volume dedicated to Prof. Masumi Chikashige, 261 (1930).

2. Loc. cit.

num anticathode, 3 cms. behind the specimen. The experimental results thus obtained are briefly described below.

Specimens

In the present experiment, specimens of electro-deposited white tin prepared at the Watanabe Laboratory of the Institute for Chemical Research of Kyoto Imperial University, were examined. The procedure employed for obtaining these specimens having already been published[1] in Japanese, a brief summary confined to the parts necessary for the present consideration, will suffice here.

To prepare the electolyte, white tin powder was first added in excess to a sulphuric acid solution of a mixture of copper sulphate and Glauber's salt [1 litre of H_2O, 125 gms. of $CuSO_4 \cdot 5H_2O$, 240 gms. of $Na_2SO_4 \cdot 10H_2O$ and 10 c.c. of conc. H_2SO_4 (sp. gr., 1.84)], so that the copper ions in the solution might be replaced by tin.

After this replacement had taken place, sulphuric acid was added again until the concentration of free acid amounted to 5–10 gms./100 c.c. in the solution. It was reported that in the electrolyte thus obtained, there was 5.5 gms./100 c.c. of tin, mostly (over 90%) in the stannous form. The conditions under which the specimens were deposited from this electrolyte, are given below :—

Composition of electrolyte : 5.5 gms./100 c.c. of Sn, 5–10 gms./100 c.c. of free acid.
Electrolytic bath : a glass vat measuring 1.5 cms. (height) × 6.5 cms. × 6.5 cms.
Cathode : tin plate 5 cms. × 6 cms. in area.
Anode : lead plate 2.5 cms. × 6 cms. in area.
Distance between the electrodes : 6 cms.
Current density : 0.008 amp./cm.^{2} (in front of the cathode)
Potential difference : 2.35–2.65 volts.
Temperature 22°–25° C.

As a result of the electrolysis above mentioned, the specimens of white tin appeared after some 30 hours, in a needle shape (0.4–1.3 mm. in diameter) with several longitudinal edges. The macrostructures of the typical forms of various specimens thus deposited, are reproduced in Figs. 1, 2 and 3, Plate I.

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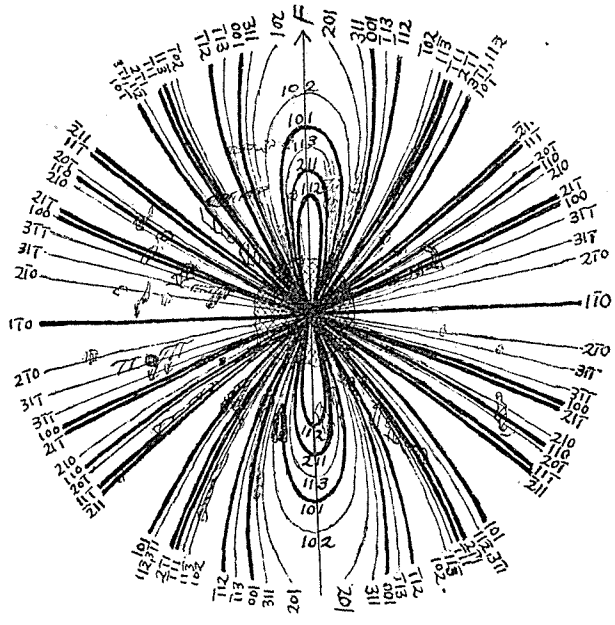
1. T. Nomitsu ; Mining and Metallurgical Monthly (Saiko-Yakin Geppo) **11**, No. 7, 1. (1933).

Experimental Results

With a fragment of the needle-shaped specimens above stated, the diffraction figure was taken, by setting its longitudinal axis perpendicular to the incident beam. The diffraction figure thus obtained, as can be seen in Fig. 4, Plate I, usually consists of a number of long radiating bands. This shows without doubt, that most of the specimens examined, are of nearly perfect fibrous structure.

Having confirmed this, the writers tried to determine the direction of the fibrous axis in some of the specimens under consideration. This determination could be done as in the case of electrolytic copper,[1] by the aid of an improved Yoshida's crystallographic globe.[2]

Fig. 9



In the annexed figure, Fig. 9, the theoretical positions of the prominent radiating bands expected to be produced, were compared with those appearing in the original photograph. This comparison was made by taking the direction of the fibrous axis (represented by

1. H. Hirata and Y. Tanaka; These Memoirs, A, **15**, 9 (1932).
2. T. Yoshida; Japanese J. Phys., 133 (1927), and S. Takeyama; These Memoirs, A, **11**, 467 (1928).

an arrow F in Fig. 4, Plate I) on the photographic plate perpendicularly to the direction of the maximum growth of deposited tin (represented by an arrow G in the same figure). The curves represented by the full lines in Fig. 9, are the theoretical positions above stated. To draw these curves, we assumed that the incident X-ray beam was made to strike a fibrous aggregation ef micro-crystals perpendicularly to the direction of their common axis, which coincided with the normal to one of the (111) planes.[1] The shaded parts in the same figure are a copy of the diffraction pattern in Fig. 4, Plate I.[3] As may be seen from this figure, the agreement between the theoretical curves and the observed ones is satisfactory. Moreover, this agreement was found to hold good, not only in Fig. 4, Plate I, but in all the figures belonging to the same category, except those consisting of a complex assemblage of long radiating bands (not reproduced), which were considered to be produced by a number of fibrous structures gathering irregularly.

Thus, it seems to be legitimate to presume that the micro-crystals of white tin in the specimens under consideration, generally arrange themselves in a fibrous way, having the normal to one of their (111) planes parallel to the axis of the fibre. This is in no way different from the experimental results we previously obtained with electrolytic white tin deposited from hydrochloric acid solutions. But, with regard to the relation between the direction of the axis of the fibre and that of the maximum growth of the deposited tin, a marked difference was observed in the results of the present experiment: i. e., the direction of the fibrous axis was found, as can be seen in Fig. 4, Plate I, to be perpendicular, instead of parallel, to the longitudinal axis of the needle-shaped specimen.

Moreover, it was found by calculation that the above presumptions, made on the basis of the diffraction phenomena due to the normal incidence of X-rays to the axis of the fibre, also hold good in the case of oblique incidence. Fig. 5, Plate I shows the diffraction pattern taken with the same specimen as was used in the case of Fig. 4, Plate I, when the axis of the fibre was tilted 45° from its

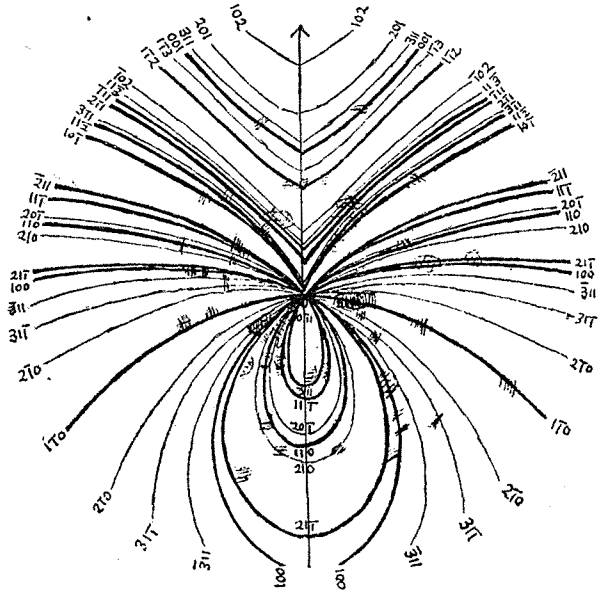
1. The designation of the indices of atomic planes is the same in the present investigation as in the previous one. This is in accordance with the results obtained by Arkel.[2]

2. A. E. van Arkel; Proc. Roy. Acad., Amsterdam, **27**, 97, (1924).

3. It is to be noticed that the diffraction patterns reproduced in Plate I, are interchanged from right to left as compared with those of the original plate.

vertical position towards the incident beam. In the annexed figure, Fig. 10, this diffraction pattern is represented by the shaded part, while the full lines in the same figure are the theoretical positions of the prominent radiating bands, expected to appear in the present configuration. As may be seen from Fig. 10, the agreement between

Fig. 10



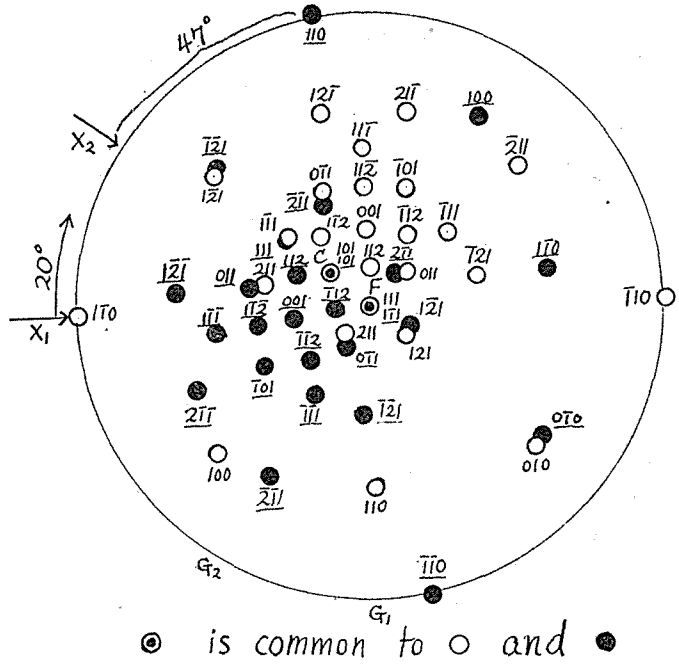
the calculated curves and the observed ones is satisfactory. Accordingly, our foregoing presumptions are confirmed, and we may conclude that the normal to one of the (111) planes is arranged in a direction parallel to the axis of the fibre making an angle of 90° with the direction of the maximum growth of the specimen.

Here, it must be remarked that the above statement is rather a general, or so to speak, a statistical one, obtained from several specimens. Here and there, occasionally a few exceptions were detected. Besides the figures consisting of an irregular assemblage of the radiating bands before mentioned, a number of short radiating bands, as can be seen in Fig. 6, Plate I, were found to be given by one of the specimens. Furthermore, with another specimen we obtained a diffraction pattern, reproduced in Fig. 8, Plate I, consisting of a set of Laue's spots. It goes without saying that the specimen giving rise to Fig. 6, Plate I, was of a fibrous-like structure, in which

the micro-crystals are rotated within a certain angle around their common axis, while, Fig. 8, Plate I shows that the latter specimen was composed of crystals of considerable dimensions.

Having thus assertained these facts, the writers tried to determine the crystalline structure corresponding to Fig. 6, Plate I more precisely. This could be done by making use of the crystallographic scale as in the foregoing calculations. From the results thus determined, it was confirmed that the crystalline structure giving rise to Fig. 6, Plate I, as will be described below, was represented by the annexed figure, Fig. 11.

Fig. 11



In Fig. 11, various atomic planes belonging to two crystals of white tin are projected by the stereographic method. To distinguish the atomic planes of these crystals from those of the other, their points of projection are expressed in Fig. 11 by the white circles, and those corresponding to the other by the black ones. It can be noticed from Fig. 11, that these two crystals of white tin are so situated in relation to each other as to have the atomic plane 101 in common: Moreover, the 111 plane of the crystal represented by the white circles is seen

Fig. 12a

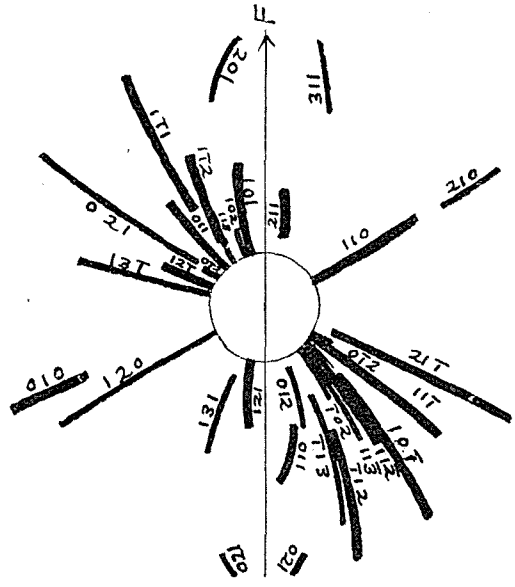
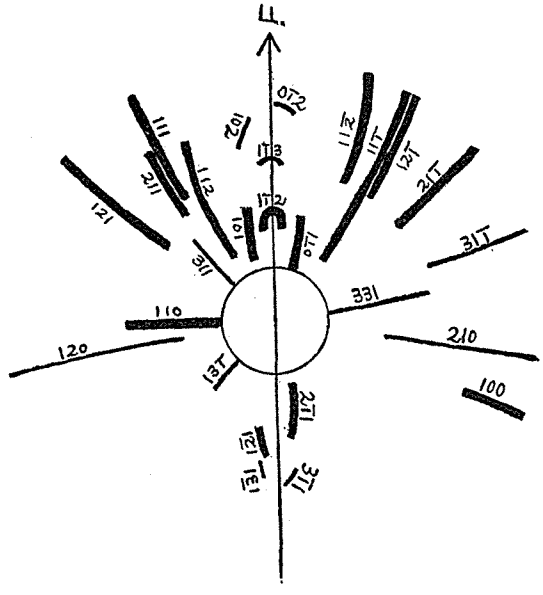


Fig. 12b

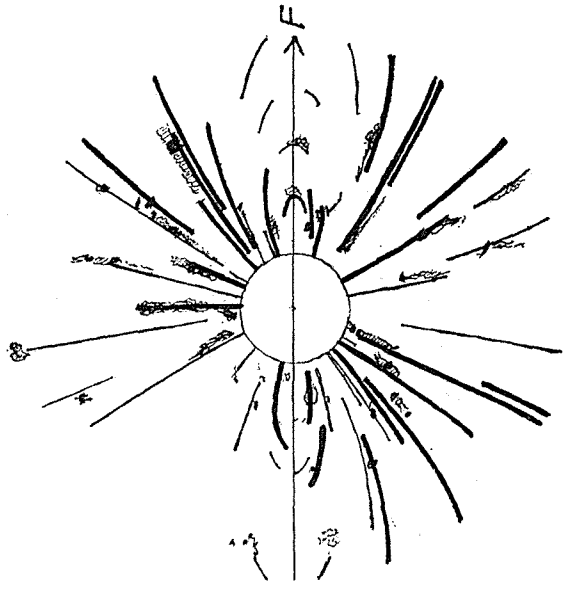


to coincide with the $1\bar{1}1$ plane of the other corresponding to the black ones. The normal directions to these common atomic planes belonging to the families (101) and (111), which make an angle of 19° 45′ to each other, are marked respectively by the letters C and F in Fig. 11.

Now, let us provisionally assume that these two crystals of white tin were rotated by an angle of 20°, around the axis represented by F. Then, if the incident X-ray beam were made to strike the crystals perpendicularly to this axis of rotation F, taking the direction represented by the arrow X_1, the radiating bands as shown by the full lines in Fig. 9, would be expected to appear partly on the photographic plate. From the results of a calculation, it was found in the present case, that these theoretical positions of the radiating bands are represented by a superposition of two figures, Figs. 12a and 12b; each of these two figures,

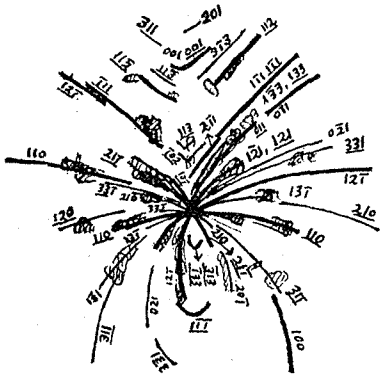
Figs. 12a and 12b is given rise to by the rotation of a set of atomic planes corresponding to the white and black circles in Fig. 11 respectively. To draw these figures, Figs. 12a and 12b, the direction of rotation of the crystals was taken in the clockwise sense.

Fig. 13



In Fig. 13, the theoretical positions of the radiating bands obtained by combining Figs. 12a and 12b are compared, similarly as in Fig. 9, with the observed ones reproduced from the original plate of Fig. 6, Plate I. To compare these two positions, the direction of the fibre F was taken in Fig. 6, Plate I perpendicularly to the longitudinal direction of the specimen G. As may be seen from Fig. 13, the agreement between the calculated and the observed positions of the radiating bands is satisfactory. This shows that the orientation of each microcrystal in the specimen giving rise to Fig. 6, Plate I can be realized by the above stated rotation of two crystals of white tin, situated in relation to each other as is suggested in Fig. 11. Moreover, the above considerations arrived at from the diffraction phenomena due to the normal incidence of the X-ray beam to the axis of the fibre, were also found to be in good accordance with those corresponding to the oblique incidence. In Fig. 14, the shaded part is a copy of the original plate

Fig. 14



of Fig. 7, Plate I, which was taken when the axis of the fibre was inclined at an angle of 45° to the incident beam; while the full lines in the same figure represent the theoretical positions of the prominent radiating bands expected to appear in the present case. As can be seen from Fig. 14, this agreement is also satisfactory.

Accordingly, our foregoing consideration is again confirmed, and we may conclude that the diffraction figures reproduced in Figs. 6 and 7, Plate I, are given rise to by incomplete rotations of the micro-crystals around the normal to one of the atomic planes (111), in the vicinities of two standard orientations, as were suggested by Fig. 11. Furthermore, the direction of the common axis above stated was found to be perpendicular to the direction of the longitudinal axis of the specimen, similarly as in the case of Fig. 4, Plate I. In short, the crystalline structure of the specimen giving rise to Figs. 6 and 7, Plate I, was found to be essentially the same as that corresponding to Figs. 4 and 5, Plate I, except that the micro-crystals rotate around their common axis by an angle of 20° in the former specimen, instead of nearly 360° in the latter one.

Here, it may be advisable to add that not only the common axis of the micro-crystal above stated, but the normal to the largest face of the specimen, which coincided with the direction of the incident beam in the case of Fig. 6, Plate I, (represented by the arrow X_1) also takes the direction perpendicular to the longitudinal axis. Consequently, the direction of the maximum growth of the specimen under consideration may be deemed to take the direction represented by G_1 in Fig. 11. This direction G_1 is remarked to coincide roughly with the [110] axis, in the mean position of the micro-crystals so situated as to be realized by the above stated rotation of a white tin crystal corresponding to the set of black circles.

The orthogonality between the direction of the normal to one of the atomic planes (111) and that of the maximum growth of deposited white tin, can be observed more clearly in the specimen which gave rise to the diffraction figure, Fig. 8, Plate I. As is seen in Fig. 8, the diffraction pattern consists of a set of Laue's spots, which were assertained with the crystallographic scale to be also due to two crystals of white tin, situated in relation to each other as was suggested by Fig. 11; i. e., it was found that it is only when the incident beam strikes these two crystals, taking the direction represented by the arrow X_2 in Fig. 11, that the distribution of Laue's spots agrees well with that of the pattern reproduced in Fig. 8, Plate I. In the present

case, the normal to one of the (111) planes (represented by F in Fig. 11), which had previously been found to coincide with the common axis of the fibrous specimens giving rise to Fig. 4 or Fig. 6, plate I, was again confirmed to be situated perpendicularly to the longitudinal axis of the specimen (represented by G_2 in Fig. 11). It is to be noted that this direction of the maximum growth of deposited tin G_2 roughly coincides with the $[10\bar{1}]$ axis of the crystal corresponding to the set of black circles in Fig. 11.

Accordingly, three kinds of diffraction figures, Figs. 4, 6 and 8, Plate I, obtained in the present experiments, may be said to be produced by a crystalline structure essentially the same, except for the difference in connection with the amount of rotation of the micro-crystals corresponding to these three figures.

Summary

From the results of the present investigation with regard to the crystalline structure of white tin deposited electrolytically from its sulphuric acid solutions, it was confirmed on the one hand, that the micro-crystals of white tin have a tendency to arrange themselves with the normals to their (111) planes parallel to a definite common direction, as in the experimental results previously obtained mainly with specimens deposited from hydrochloric acid solutions of tin. But, on the other hand, this direction of the common axis was observed in the present experiments to be perpendicular, instead of parallel, to the direction of the maximum growth of deposited tin. Moreover, instead of the set of Laue's spots given by a single crystal of white tin in the previous case, spots corresponding to two crystals, with one of the (101) planes in common, were detected in the present researches. Such dissimilarities are probably due to the difference in the chemical valency of the tin ions in the electrolyte.

In conclusion, the writers wish to express their best thanks to Professor D. Uno and Professor U. Yoshida for the interests they have taken in the experiments. Their thanks are also due to Professor T. Watanabe and Mr. T. Nomitsu, who kindly supplied many samples required, and to the Imperial Academy of Japan for the fund granted to the present investigations.

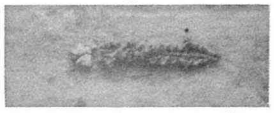
Institute of Metallography.
Kyoto Imperial University.

Plate I.

Fig. 1.

Specimen A. (1 : 8)

Fig. 2.

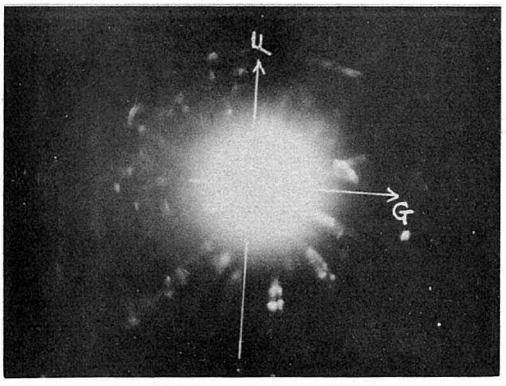


Specimen B. (1 : 8)

Fig. 3.

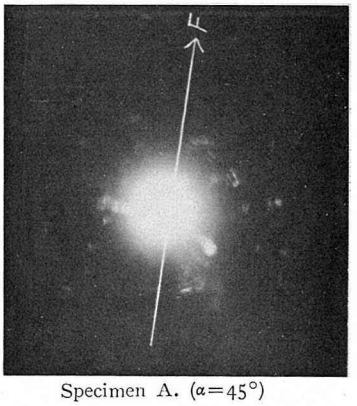
Specimen C. (1 : 8)

Fig. 4.



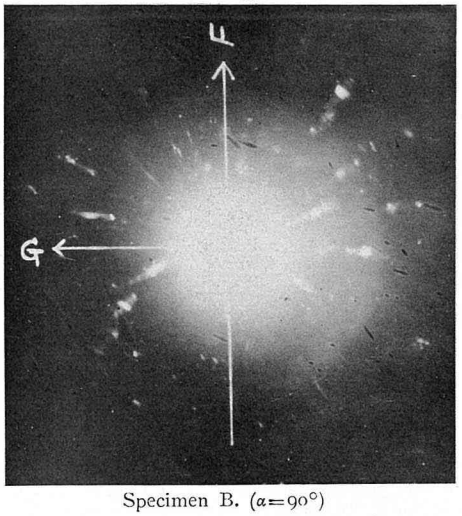
Specimen A. ($\alpha=90°$)

Fig. 5.



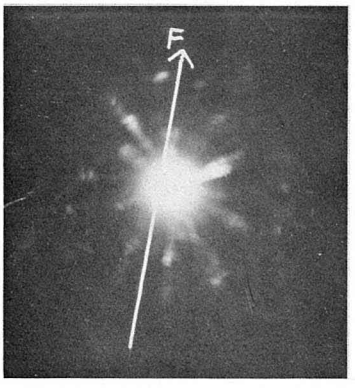
Specimen A. ($\alpha=45°$)

Fig. 6.



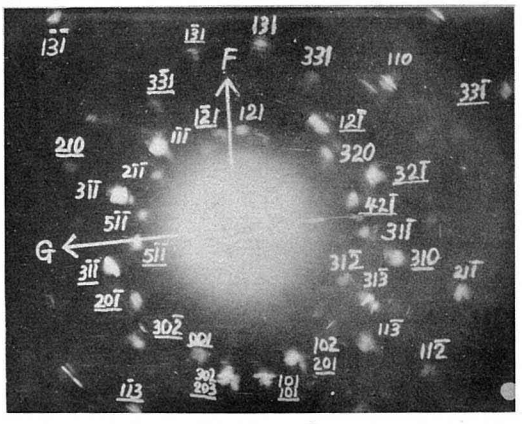
Specimen B. ($\alpha=90°$)

Fig. 7.



Specimen B. ($\alpha=45°$)

Fig. 8.



Specimen C.