On the Fibrous Structure in Metals Deposited by the Difference of Electrolytic Solutional Pressures

By

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Abstract

Metallic silver deposited by a solution of silver nitrate by putting a small piece of copper into it, has a fibrous structure, the common axis of which is 110 and makes an angle of 30° with the direction of the deposited siver. The micro-crystals show a rotation about this axis with an angle of some ±11°. As the (111) planes of the silver-crystal lie roughly parallel to the flat surfaces of the deposited metal, the direction of the growth of the deposited silver lies nearly parallel to the [112] axis.

Though the arrangement of the micro-crystals in electro-deposited metals have already been studied by many investigators, none of the metals deposited from their salt solutions by the difference of electrolytic solutional pressures have yet been examined. The writer has investigated, in the present experiment, the metallic silver which was deposited by a solution of silver nitrate owing to the presence of a piece of copper in it.

Specimen.

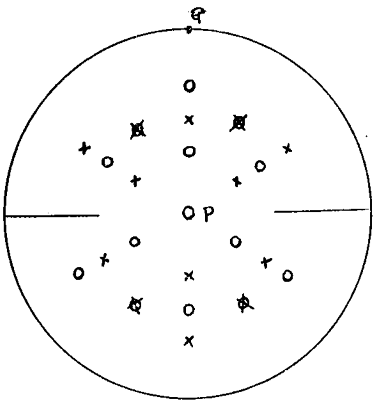
When we put a polished copper wire into a solution of silver nitrate the copper is covered, at the beginning, with black-coloured silver, which changes into grey with a further deposit, and after a few hours we can detect many long flat and acicular pieces of silver of the length of several mms. which are covered with smaller pieces branching off at an angle of about 60°.

The writer prepared many pieces of such deposited silver from the solution of the following three different concentrations: 0.3%, 0.6% and 2–4% in weight. We shall call the specimens obtained from these different solutions, Ag A_1, Ag A_2 and Ag A_3 respectively.

Experimental Results.

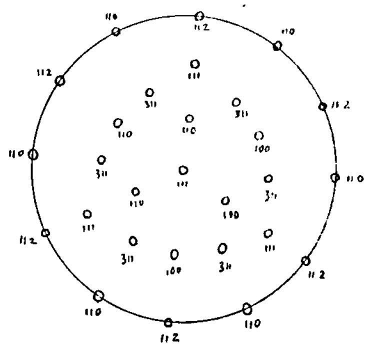
Ag A_1.—A specimen of the maximum breadth of 0 7 mms. and of a length of 38 mms. was obtained in this case. This specimen reflects light in many different directions as regularly as a single crystal of metal. If we project the directions of the normals of those reflecting planes in the stereographic projection, we get Fig. 1a. Where the pole P is the projection of the direction of the normal of the flat surface of the specimen, and the direction PG is parallel to the direction of the growth of the specimen (acicular axis).

Fig. 1a



☒ is common to o and ×

Fig. 1b



On the other hand, the stereographic projection of the normals of various atomic planes of the cubic crystals, when one of its [111] axes is taken as the pole, is shown in Fig. 1b. Comparing these two figures, we know that Fig. 1a consists of two sets of points: the one represented by the small circles is identical with the same set in Fig. 1b, and the other. represented by the crosses, is the same as that obtained by rotating Fig. 1b through an angle of 180° about P. This fact seems to suggest that the surface normal of the flat surface of the specimen corresponds roughly to one of the [111] axes of the crystal, and the direction of the growth roughly to one of the [112] axes.

Under a microscopic examination, the specimen shows an aggregation of micro-crystals, with about 0.01 mms. in diameter. Every one has several faces which reflect light regularly in different directions.

Now the Laue-photographs were taken by using a molybdenum target. In doing so the direction of the growth of the specimen was set vertically, and the horizontal beam of the x-rays was made to strike the specimen in the direction perpendicular to the flat surface. Fig. 2, Plate I is the reproduction of the photograph thus obtained, and it consists of six principal radiating bands which make an angle of 60° with one other, and which are provided with the K spectra of molybdenum. The writer could easily find from this photograph that the common axis of the fibrous arrangement of the micro-crystals is the [110] axis of the crystal. The observed angles between the directions of the common axis (denoted by an arrow in Fig. 2 Plate I) and the lines drawn to the position of the K spectra on various radiating bands from the central spot are compared with the calculated values in Table I, and we see that the observed values agree fairly well with those calculated. The absence of several bands on the photograph seems to show that the fibrous structure corresponds to that of incomplete rotation. In order to estimate the angle of rotation of the micro-crystals, let us consider band IV in Fig. 2, Plate I ((111) plane, $\alpha=90°$). If we consider the ideal arrangement of the micro-crystals without any rotation, as is suggested in the case of Fig. 1a, one of the (111) planes of the crystal is parallel to the surface of the specimen, and the other one of the (111) planes which is responsible to the band IV in Fig. 2, Plate I, makes an angle 19°30′ with the incident beam of the x-rays. On the other hand, for the same atomic plane of the crystal, the glancing angles for Mo $K\alpha$ are 8°40′ and 17°30′, respectively, for the first, and for the second order

Table I

Indices of the plane	$\alpha_{calc.}$	α_{obs} +	α_{obs} −	Band
311	27°	30°	30°	I
111	31°	30°	30°	I
111	34° 20′			
100	44° 10			
331	45° 20′	50°	48°	II
110	58° 50′			
311	63° 30′			
331	69° 30′	70°	70°	III
111	90°	90°	90°	IV
100	90°			
311	90°	90°	90°	IV
331	90°			
331	110° 30′	110°	110°	V
311	116° 30′			
110	121° 10′			
331	134° 40′	130°	132°	VI
100	135° 50′			
111	145° 40′			
111	149°	146°	152°	VII
311	153°	152°	149°	VII

spectra. So the reflection of the first order spectrum of Kα of Mo will occur when the micro-crystals are rotated by the angle $19°30'-8°40'=10°50'$, from the ideal arrangement above mentioned. In all the photographs obtained by the writer, the first order spectrum of the Kα line was just detected; and therefore it seems to be natural to estimate the angle of rotation of the micro-crystals about the axis of the fibre as $\pm 11°$.

If we draw the curves under the above considerations we get Fig. 2a. From the fact previously mentioned, in the case of Fig. 1a about the reflection of light, at last we reach Fig. 2b, in which are combined Fig. 2a, and the same one rotated through 180° in the plane of the paper. The general features of Fig. 2b are in fine accordance with Fig. 2, Plate I.

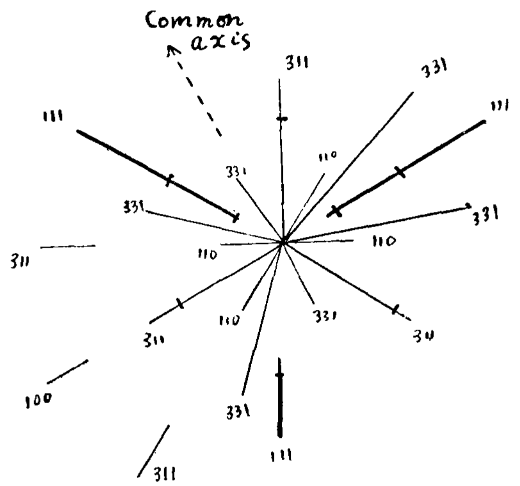


Fig. 2a

The above results may be stated in short, thus, that the micro-crystals have two ideal orientations as shown in Fig. 3, each one being obtained from the other by rotaing it through 180° in the plane of the paper. In these two ideal orientations, each one has one of the [111] axes in the direction parallel to the normal of the flat surface of the specimen, and one of the [112] axes in the direction of the growth; and the micro-crystals are arranged in a fibrous structure rotated through $\pm 11°$ about the common axis [110] from the two ideal orientations above mentioned.

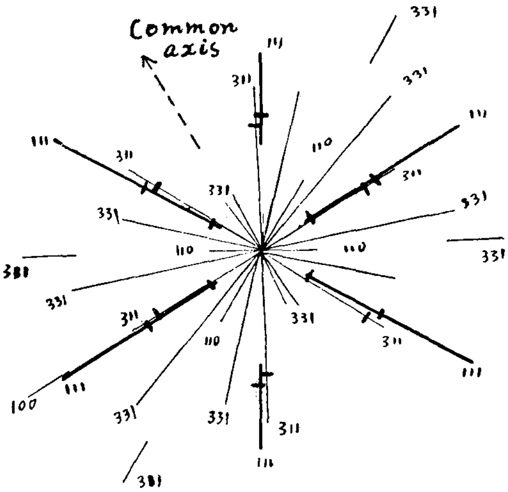


Fig. 2b

Ag A_2.—These speci-

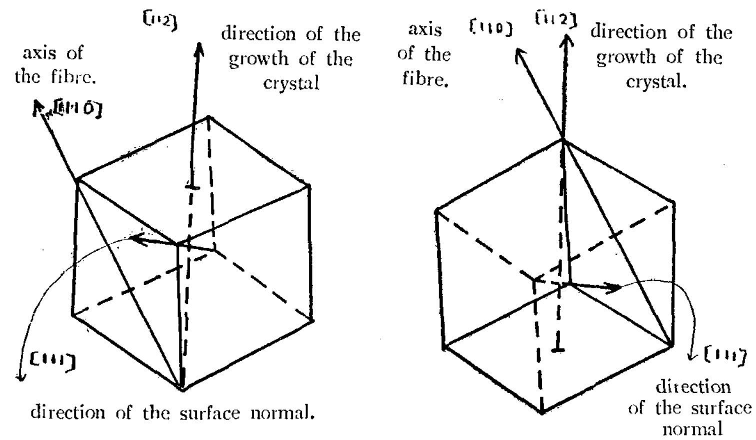


Fig. 3

mens were the same as Ag A_1 in light-reflection and in the Laue-photographs (Fig. 3, Plate I). In this case, however, having got good specimens branching off at 60°, Laue-photographs were taken of each branch; and it was seen that they were the same as Fig. 3 Plate I.

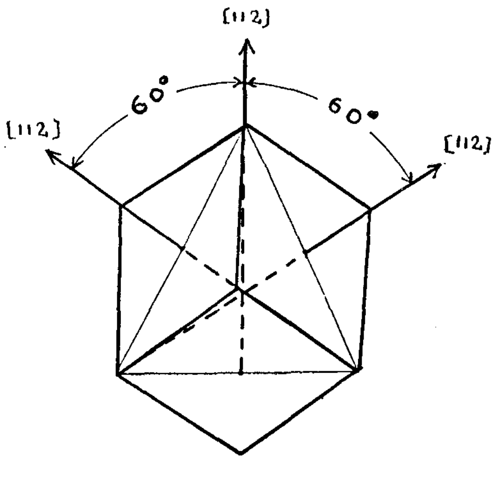


Fig. 4

From the fact that the direction of the growth is nearly parallel to the [112] axes, it seems to be understood why they branch out at 60°. Because these [112] axes lying in the same plane intersect at 60° to one other, and any one of these three axes may become the direction of the growth of the specimen.

*Ag A*3. —These were deposited from comparatively concentrated solutions after several days' standing, and they barely reflect light in many directions, as in the case of Ag A_1 and Ag A_2. A typical micro-photograph of the appearance of the specimen is shown in Fig. 4, Plate I. Taking the direction represented by the arrow in Fig. 5, Plate II, and one of the [110] axes of the crystal as the common axis of the fibrous arrangement, the position of the bands

Table II

Plane	α calc.	α + obs.	α obs. −	Band
311	27°	27°	——	I
111	31°	——	30°	I
111	34° 30′	——	——	
100	44° 10′	——	——	
331	45° 20′	46°	——	II
110	58° 50′	——	——	
311	63° 30′	——	——	
331	69° 30′	70°	——	III
111	90°	——	90°	IV
100	90°	——	——	
311	90°	90°	——	IV
331	90°	——	——	
331	110°	109°	——	V
311	116° 30′	——	——	
110	121° 10′	——	——	
331	131° 40′	132°	——	VI
100	135° 50′	——	——	
111	145° 40′	——	——	
111	149°	——	149°	VII
311	153°	151°	——	VII

is calculated under the consideration that there is only one of the two orientations shown in Fig. 3. The values calculated and observed are compared in Table II, and we can see a fair agreement. Sometimes we can obtain a very interesting specimen in this case, in which the rotation of the micro-crystals about the common axis becomes so small that we can treat it nearly as a piece of single crystal. One of the Laue-photographs taken of such a specimen is shown in Fig.6, Plate II; and from the distribution of the Laue-spots the writer was able to ascertain that the direction of the growth was in one of the [112] axes and the flat surface of the specimen was nearly parallel to one of the (111) planes of the crystal. This is in excellent accordance with the ideal orientation of the micro-crystals mentioned before.

The orientation of the micro-crystals thus determined with the aid of x-rays is in fine accordance with that suggested previously by examining the specimen from the side of the reflection of light. This result seems to indicate that the various atomic planes of the silver crystal the orientations of which are represented in Fig. 1b by the positions representing the direction of their surface-normals in stereographic projection, are developed actually as exterior surfaces of the silver-crystal.

Lastly, it must be noted that, for the testing of the fibrous structure and for the determination of the orientation of a crystal from the Laue-spots, the globe and the spherical scale constructed by Professor U. Yoshida[1] were mainly used.

1 U. Yoshida: Japanese J. Phys. **4**, 133(1927)

Summary.

(1) Metallic silver deposited by a solution of silver nitrate due to the presence of a piece of copper, consists of micro-crystals arranged fibrous-like in such a way that the common axis is the [110] axis of the silver crystal, and the micro-crystals are rotated about this axis by some $\pm 11°$.

(2) The (111) plane of the crystal is situated nearly parallel to the flat surface of the specimen for the majority of micro-crystals.

(3) The axis of the fibre makes an angle of 30° with the direction of the growth of the specimen; therefore the direction of the growth is nearly parallel to the [112] axis.

The results of the present experiment agree well with that of H. Hirata and H. Komatsubara's experiments[1] on electrolytic silver, excepting the point that the [112] axis, instead of the [110] axis in the case of electrolytic silver, is parallel to the acicular axis in the present case.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida of Kyoto Imperial University for his kind guidance, and also to Mr. K. Yajima, the principal of Shiga Normal School, by whose kind permission the writer was able to obtain the necessary apparatus for this experiment.

Shiga Normal School

April 15, 1928.

1 These Memoirs, **10**, 95 (1926)

Shogo Tsuboi.

Plate I.

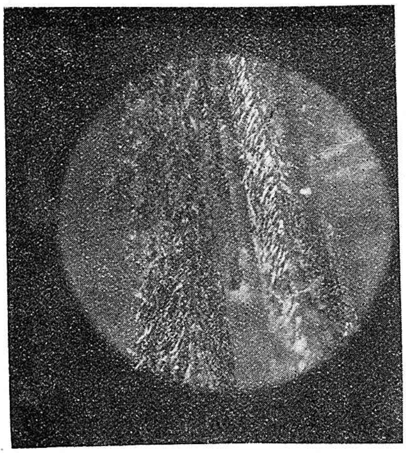


Fig. 1, Ag A_1
(magnification 100)

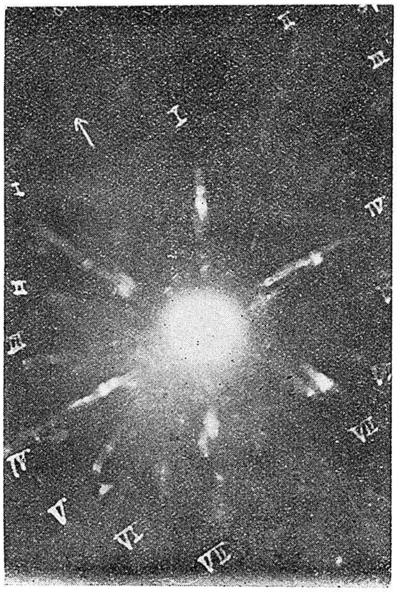


Fig. 2, Ag A_1

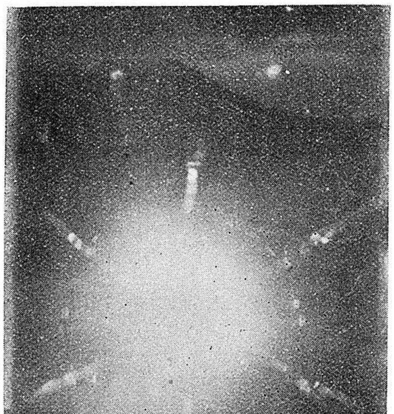


Fig. 3, Ag A_2

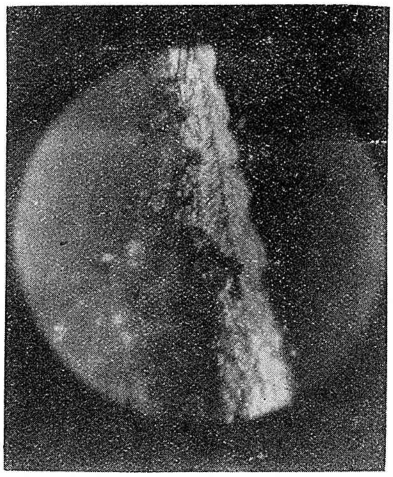


Fig. 4, Ag A_3
(magnification 100)

Plate II.

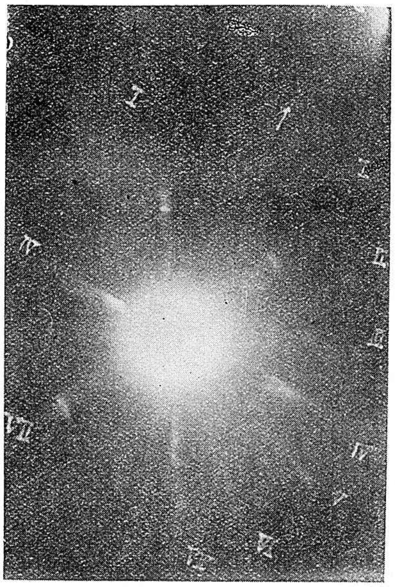


Fig. 5, Ag A_3

Fig. 6, Ag A_3