On the Fibrous Structure in Metals deposited through Difference in Electrolytic Solutional Pressures,

Part II

By

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Abstract

The arrangement of micro-crystals in the thin plates of metallic lead and cadmium, which were deposited out in some salt solutions by a piece of zinc being put into the solutions, was examined. The majority of the micro-crystals in the lead deposits have one of the (111) planes of the cubic crystal nearly parallel to the flat surfaces of the deposits. In the case of cadmium deposits, the (0001) plane of the hexagonal crystal is situated nearly parallel to the flat surfaces of the specimens.

The arrangement of micro-crystals in metallic silver, which was deposited out in a solution of silver nitrate due to the presence of a piece of copper in it, has already been examined by the writer.[1] In the present experiment, the crystalline structure of lead and cadmium deposits, which were separated out in solutions of lead acetate and cadmium sulphate respectively due to the presence of a small piece of zinc, was examined as in the previous experiment.

Lead

Small zinc plates were suspended in a 2% and in a 5% solution of lead acetate, in order to obtain the well known deposits named "lead tree." These deposits, which are of a spongy structure, consist of several very thin plates with metallic lustre. The experiment were carried on these thin plates. In a micro-photograph taken with one of

1 These Memoirs, **11**, 271 (1928)

these thin plates, we can see the dendritic structure of the deposits, as in Fig. 1, Plate I.

The direction of growth of a specimen in a dendritic form, which was obtained in a 5% solution, was set vertically, and a horizontal beam of the X-rays from a molybdenum target was projected normally to the flat surface of the specimen. Although most of the Laue-photographs thus obtained show a fibrous structure in the deposits, as is seen in Fig. 3, Plate I, there are some specimens which give X-ray diffraction patterns of ordinary Laue-spots, as is seen in Fig. 2, Plate I. The analysis of the distribution of the Laue-spots in that figure, by the aid of the globe and the spherical scale devised by Prof. U. Yoshida[1], proves that the distribution of the Laue-spots is due to two crystals at different orientations. The Laue-spots in Fig. 2, Plate I are represented by dots and small circles in Fig. 1, where all the dots correspond to one lead crystal at a certain orientation, and all the small circles correspond to the other lead crystal at a different orientation. It is also found, by the analysis stated above, that one of the [111] axes of the cubic crystal of lead is common to the two crystals under consideration, and that this common axis [111] is perpendicular to the flat surface of the specimen. The crystallographic direction [211], which is at right angles to the common [111] axis under consideration, is shown in Fig. 1 by the straight lines AA′ or BB′ according as the crystal belongs to that corresponding to the dots or the small circles respectively. Consequently the orientation of one crystal can be obtained from the other by rotating it through an angle of about 27° around the common axis [111]. In

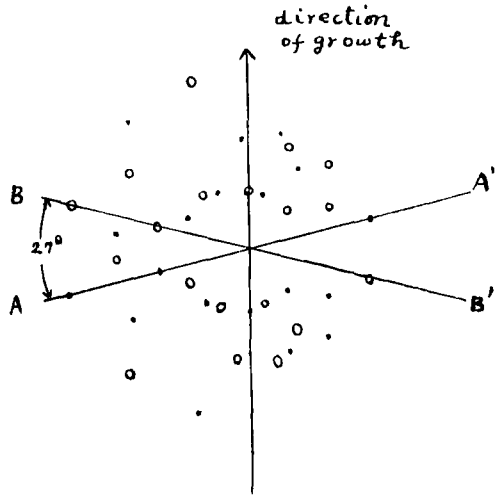

Fig. 1

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

Fig. 2 the direction of growth and the surface normal of the specimen are represented in stereographic projection, by taking the [100], [110] and [111] axes of the cubic crystal as the reference axes. The dot and the small circle in this figure correspond respectively to those in Fig. 1.

By comparing the two photographs in Figs. 2 and 3 in Plate I we can detect a close similarity between the distribution of the Laue-spots in Fig. 2 and that of the radiating bands in Fig. 3. This leads us to the supposition that the fibrous structure corresponding to Fig. 3, Plate I, may be due to the rotation of the micro-crystals within a certain small angle from their ideal orientation which corresponds to the distribution of the Laue-spots in Fig. 1. In this way the writer assumed with success that the radiating bands in Fig. 3, Plate I were due to two fibrous arrangements, the one consisting of the micro-crystals rotated around the direction parallel to AA′ in Fig. 1, within a certain small angle from the ideal orientation which corresponds to the dots in the same figure, and the other consisting of the micro-crystals rotated around the direction parallel to BB′ in Fig. 1, within a certain small angle from the ideal orientation which corresponds to the small circles in that figure. As to the amount of rotation of the micro-crystals from their respective ideal orientations, it was found, by tracing the radiating bands in Figs. 3 of Plate I on the globe and the spherical scale mentioned before, that the rotation within an angular interval of $\pm 5^\circ$ was enough for both fibrous arrangements. The radiating bands represented in Fig. 3, which are provided with the K_α spectra of molybdenum, are obtained under the above consideration. A fair agreement of its general aspect with Fig. 3, Plate I seems to show reversely the correctness of the previous supposition. Thus, if we disregard the small rotation of the micro-crystals around the ideal orientation, we may conclude that one of the atomic planes (111) of the micro-crystals in the lead deposits lies parallel to the flat surface of the specimen, and that the direction of growth

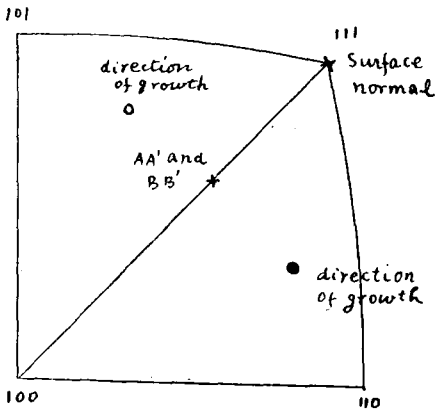

Fig. 2

in the same atomic plane is different for every specimen.

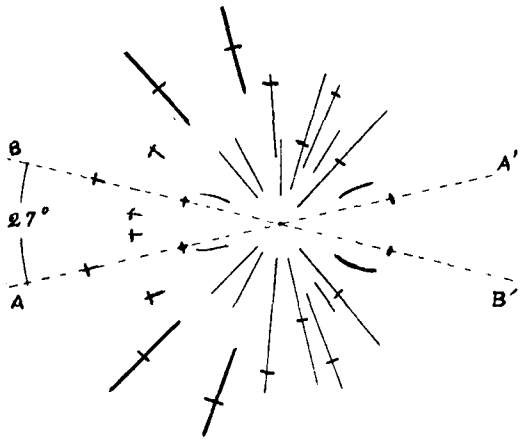

Fig. 3

On the other hand, a piece of the lead deposits reflects light in many different directions. Although the reflected light is a little diffused, due to a small scattering of the orientation of the micro-crystals as stated before, the direction of the light reflected with maximum intensity, due to the light incident on the surface of the specimen at definite direction could be determined easily with a simple goniometer. In Fig. 4 the direction of the normals to the reflecting planes, thus determined on the same specimen as that of Fig. 3, Plate I, is represented in a stereographic projection, where the dots and the small circles correspond respectively to the light reflecting surfaces on the incident and the emergent sides of the X-rays in photographing Fig. 3, Plate I. The pole in Fig. 4 coincides with the direction of the normal to the flat surface of the specimen, that is with one of the crystallographic axes [111]. The broken lines AA′ and BB′ in the same figure have the same meaning as in the case of Figs. 1 and 3. The distribution of the dots in that figure thus represents the angular relation between the crystal faces of the cubic crystal of lead at the side of the specimen on which the X-rays were incident, and the distribu-

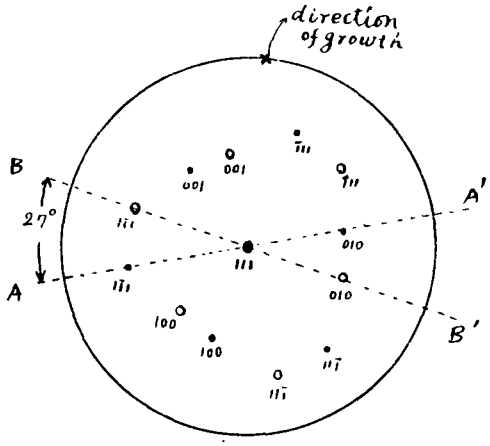

Fig. 4

tion of the small circles shows the angular relation between the crystal faces of the lead crystal at the side of the specimen on which the X-rays were emergent. The angular separation between the two orientations of the crystals on both sides of the flat specimen is equal to the angle between AA′ and BB′ and is about 27°. Consequently the orientations of the lead crystals in the specimen, which are obtained by the method of light reflection are in fine accordance with those found by means of X-rays in the case of Fig. 2, Plate I, that is with the ideal orientation of the micro-crystals of lead in the specimen.

This coincidence indicates that the (111) and the (100) planes of the lead crystals represented in Fig. 4 are really developed as the exterior surfaces of the micro-crystals. This point was also confirmed by microscopic observation, and the outward form of each micro-crystal seems to be such as represented in Fig. 5.

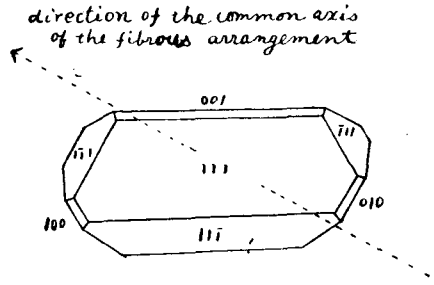

Fig. 5

A Laue-photograph taken with the specimen obtained in a 2% solution is shown in Fig. 4, Plate I. The identity of the essential feature of this photograph with that of Fig. 3, Plate I indicates that the concentration of the solution has no appreciable influence on the crystalline structure of the deposits.

Cadmium

In a spongy mass of cadmium, separated out in a solution of cadmium sulphate by putting a piece of zinc into it, there are several thin plates with metallic lustre. The specimens of such thin plates obtained in a 1% and in a 3% solution of cadmium sulphate were examined in the present experiment.

Under microscopic observation, the specimen shows a dendritic structure, the fine branches of which make an angle of about 60° to each other, as is seen in Fig. 5, Plate I.

The direction of growth of the specimen, deposited in a 1% solution, was set vertically, and a horizontal beam of X-rays from a molybdenum target was made to strike the specimen normally to its flat surface. A Laue-photograph, thus obtained, is reproduced in Fig. 6,

Plate I. The diffraction pattern in this figure consists of many Laue-spots, which are elongated only a little in radial directions. This fact indicates that the specimen can be looked upon as being nearly composed of a few single crystals. The analysis of the Laue-spots, by the aid of the globe and the spherical scale, shows that the specimen consists of two hexagonal crystals of cadmium in different orientations, as was observed in the lead deposits.

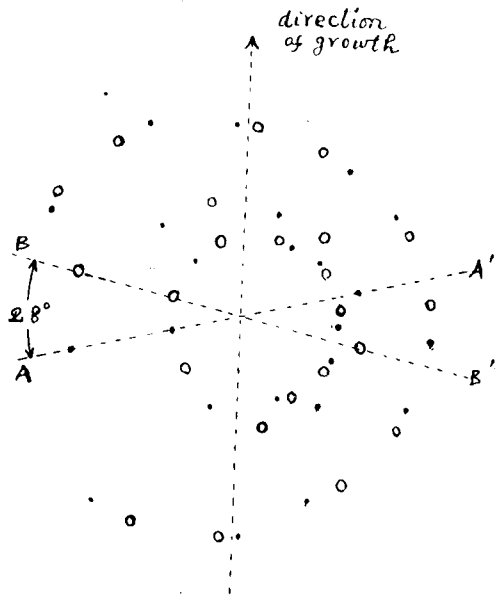

Fig. 6

Fig. 6 is a sketch of Fig. 6, Plate I, where the dots and the small circles represent the two sets of Laue-spots belonging respectively to the two crystals in different orientations. It became clear from the analysis that, for the two crystals in different orientation, the [0001] axis of the hexagonal crystal of cadmium is parallel to the normal to the flat surface of the deposit, and that the direction of growth is nearly parallel to the $[21\bar{3}0]$ axis for the two crystals. In Fig. 6 the broken lines AA′ and BB′ are in the direction of the $[\bar{1}100]$ axes of the two crystals in different orientations respectively, which correspond to the dots and the small circles. Thus the orientation of one crystal is obtained from the other by rotating it through an angle of about 28° around the [0001] axis, which is

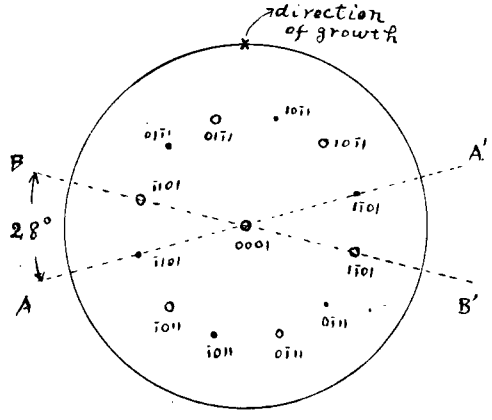

Fig. 7

common to two crystals.

The results obtained with the light reflection method, which was used in the case of lead, are shown in Fig. 7 by stereographic projection. Here the dots represent fhe direction of the normals to the reflecting planes on the incident side of the specimen for the x-rays, and the small circles represent those on the emergent side. Thus, as in the case of the lead deposit, the crystallograhphic orientation is different for the crystals on the two flat surfaces of the deposits. The [0001] axis is common to the two orientation, and the [$\bar{1}$100] axes of these two orientations make an angle of about 28° to each other. This is in fine accordance with the results obtainded with the X-rays.

Similar experiments made on different specimens obtained under the same conditions, show that the angle between the [$\bar{1}$100] axes of the crystals in two layers take various values between 22° and 28°.

As to the crystal faces developed actually as the outward form of the cadmium crystal, the results obtained above indicate that they are (0001) and (10$\bar{1}$1) faces.

Experiments were also carried on specimens deposited out in a 3% solution, but no appreciable influence of the difference of concentration could be detected.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida of Kyoto Imperial University for his kind guidance and encouragement during the research.

Shiga Normal School,
May 8, 1929.

Plate I

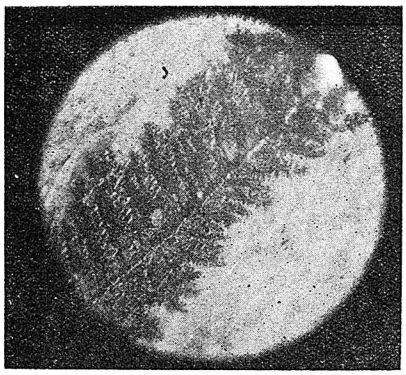

Fig. 1 (magnification 100)

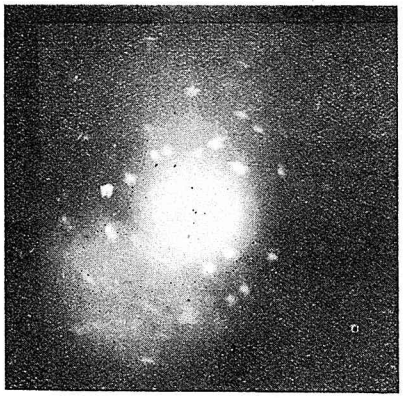

Fig. 2

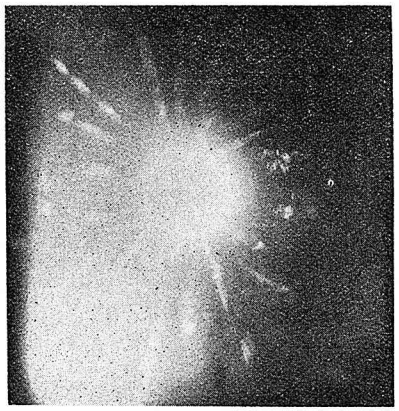

Fig. 3

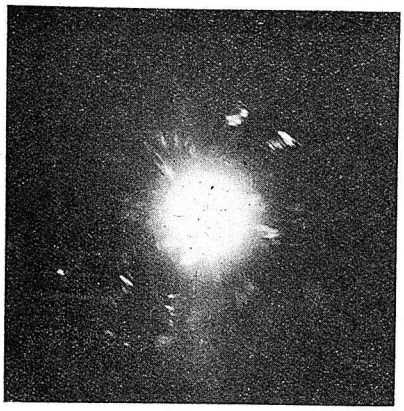

Fig. 4

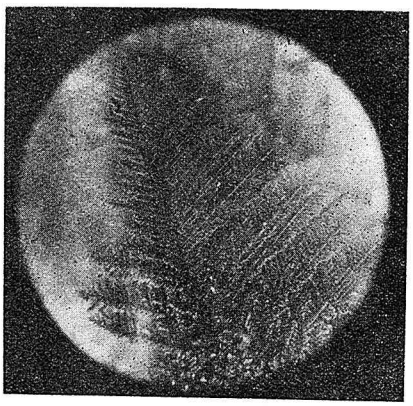

Fig 5. (magnification 100)

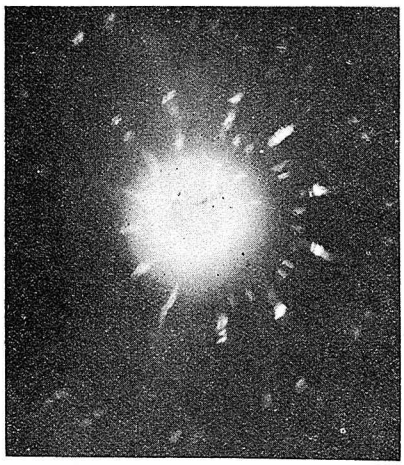

Fig. 6