On the Arrangements of the Micro-crystals in Copper and Gold deposited by Electrolysis

By

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Abstract

The arrangements of the micro-crystals in electrolysed specimens of copper and gold deposited under various conditions, were examined with X-rays, by the so-called "transmission method". The experimental results thus obtained were found to agree well with those obtained by other experimenters in many respects. But in some respects, especially with regard to the direction of the growth of the deposited copper and that of the largest face of the specimen, some slight modifications are found to be needed in the conclusions arrived at up to the present time.

Introductions

Several X-ray examinations of the crystalline structures of various electro-deposited metals have already been made. But to arrive at a harmonious conclusion, more experimental data are needed even with respect to metals of such simple and well known crystal forms as those belonging to the copper group.

The writers were therefore induced, by way of continuing the investigation carried out in this laboratory with electro-deposited silver,[1] to repeat the experiments with electro-deposited copper. Supplementary to these copper specimens, some specimens of electro-deposited gold were also examined.

It is well known that the crystal forms of these two metals, like that of silver, belong to the face centred cubic system, the length of the edge of a unit cell being respectively 3.60 Å and 4.06 Å in the cases of copper and gold.

1. H. Hirata and H. Komatsubara: These Memoirs, A, **10**, 95 (1926).

Just as in the case of the former one, the present research has been carried out by the so-called "transmission method", the heterogeneous X-rays emitted from the molybdenum anticathode of a Coolidge X-ray tube being utilized. To take the diffraction figures, the photographic plates were always placed perpendicularly to the incident beam at a distance of 3.2–3.5 cms. behind the specimen.

The experimental results thus obtained were found to be slightly different from those previously given by Glocker and Kaupp,[1] Bozorth[2] and others. In the following pages, the parts of the present experimental results which are inconsistent with those of the others, will mainly be dealt with.

Experimental Results

I. Copper.

(i) On the Formation of Irregular Arrangements: The present investigation was first performed with electrolytic copper specimens, deposited from copper sulphate solutions of various concentrations (0.5–1N.) with various current densities (0.07–0.035 amp./cm.^{2}). To obtain these specimens, a cast plate of copper, 7 cms. × 3 cms. in area, was used as anode. Parallel to this anode, a sheet of commercial electrolytic copper of the same size was suspended as the cathode.

The specimens thus deposited usually appeared in a botryoidal form of varying size (0.7–1.2 mm. in diameter). As a result of X-ray investigation, all the specimens belonging to this category were found to give rise to diffraction figures consisting of a number of Debye-Hull rings. This is in no way different from the experimental results given by Bozorth and Takeyama,[3] who suggest that the copper crystal has no marked tendency to be deposited electrolytically with any regularity.

(ii) On the Formation of Fibrous Structures: Next, the writers extended their investigation to other electrolytic copper specimens prepared at the Hidachi Factory of the Kuhara Mining Company. The conditions under which these specimens were prepared are given below:

Electrolyte: 4% Cu, 10% SO_3, and 86% H_2O (in gr. %).

1. Z. S. f. Phys., **24**, 121 (1924).
2. Phys. Rev., **26**, 390 (1925).
3. These Memoirs, A, **13**, 363 (1928).

Temperature : 37°C.
Potential difference : 0.2 volt.
Current density : 0.017 amp./cm.^{2}

Two vats, each 28 cms. × 21.5 cms. × 25.5 cms. in size, were so arranged that the electrolyte was flowing from one vat to the other at the rate of 100 c.c. per minute. A cast plate of copper 1 cm. in thickness was used as the anode. On both sides of this anode, two parallel sheets of copper 16.5 cms. × 19.5 cms. in area, were placed at a distance of 4.5 cms., as the cathodes. The concentration of the electrolyte was kept unchanged while the electrolysis proceeded by adding now and then as much water as was lost by evaporation.

As a result of the electrolysis above mentioned, the copper specimens appeared after 140 hours, in prismatic or pyramidal forms (1.5–3.5 mms. in diameter) with ragged surfaces. It is to be noted that some of the prismatic or pyramidal axes of these specimens were found to be normal to the surface of the cathode, while many others inclined obliquely to this surface. The macro-structure of the pyramidal one is reproduced in Fig. 9, Plate I.

With one of these specimens thus deposited, it was impossible to get any reliable diffraction figure. Not only would its great thickness considerably reduce the intensity of the diffracted rays, but its detachment from the cathode surface might also cause some mechanical distortions in the crystalline structure at the cut end of the specimen. It seemed, therefore, to be of fundamental importance to make the specimens such that they could be utilized in these experiments.

For this purpose, the writers were obliged to remove the outer portion of each specimen by pickling it in dilute nitric acid, before it was examined. When the specimen was pickled until it was reduced to a suitable size, a number of faces made their appearance on this specimen. Of these faces of the specimen thus formed, it was noticed that the largest one was situated nearly parallel to the direction of the prismatic or pyramidal axis, which usually remains unaltered during the process of etching.

By placing this largest face of the specimen perpendicularly to the direction of the incident X-ray beam, we usually obtained a diffraction figure in which the radiating bands predominated, as shown in Fig. 11, Plate I. To obtain this figure, Fig. 11, Plate I, the photographic plate was placed 3.2 cms. behind the specimen. This predomination of the radiating bands in the figure shows us without doubt,

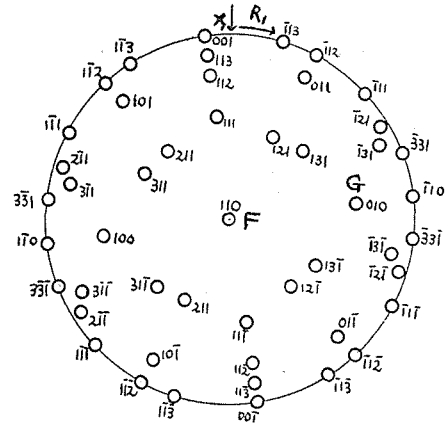
that the copper specimens under examination are mostly of the fibrous structure, as was asserted by Glocker and Kaupp.[1]

As can be seen in Fig. 11, Plate I, all the radiating bands of a diffraction pattern obtained by the procedure above mentioned, are nearly straight in the vicinity of the central spot. This indicates that the axis of the fibre is nearly perpendicular to the direction of the incident beam, and is in a direction nearly parallel to the largest face of the specimen.

Having thus assertained these facts, the writers tried to determine the direction of the fibrous axis in some of the specimens under consideration. This determination could similarly be done as performed by S. Tsuboi[2] to find out the direction of the fibres in silver deposited by the difference of electrolytic solutional pressure.

In the annexed figure, Fig. 1, the normals of various atomic planes of the copper crystal are projected, by taking one of its rhombododecahedral faces 110 parallel to the plane of the paper. This projection was not made by the ordinary method adopted in the crystallographical considerations, but is the orthogonal projection of the pole figure of the copper crystal on the equatorial plane 110, as the latter seems to be more convenient for our further consideration.

Fig. 1



Now, let us provisionary suppose that the incident X-ray beam was made to strike this copper crystal perpendicularly to its $<110>$ axis, taking the direction nearly normal to the 001 face. Then, if the copper crystal is rotated from its initial orientation above mentioned around the $<110>$ axis by a certain angle, a diffraction figure as can be obtained by the normal incidence of the X-ray beam to the axis of rotation is expected to be produced: i. e., the diffraction figure

1. Loc. cit.
2. These Memoirs, A, **11**, 271 (1928).

obtained should consist of a number of radiating bands nearly straight in the vicinity of the central spot.

By the aid of an improved Yoshida's crystallographic globe,[1] we can easily determine the position of each one of these radiating bands above stated. The curves in the annexed figure, Fig. 2, represent diagrammatically the theoretical positions of the prominent radiating bands expected to be produced on the photographic plate placed 3.2 cms. behind the specimen; and the short lines crossing these radiating bands express the calculated positions of the impression of the K_α line of Mo on the same plate.

To draw these curves in Fig. 2, we assumed that the copper crystal was rotated by some 19° around the <110> axis from its initial orientation above mentioned. The projection of this axis of the rotation <110> on Fig. 2 is represented by an arrow F, while the arrow X_1 and R_1 in Fig. 1 represent the direction of the incident beam in the initial orientation of the crystal, and that of the rotation of this crystal respectively.

If we place the original photograph[2] of Fig. 11, Plate I upon Fig. 2, in such a way that the direction represented by F and the centre of the central spot in both figures coincide with each other, a fine agreement between the two figures will easily be observed. This shows us that the orientation of each micro-crystal in the specimen giving rise to Fig. 11, Plate I can be realized by the above stated rotation of a copper crystal. Thus, it seems to be legitimate to consider that the micro-crystals are arranged in a fibrous structure, having one of the [110] axes in common; and the rotation of the micro-crystals around this common axis is about 19° from the initial orientation above mentioned. Moreover, from the indices of the atomic planes attributed to the corresponding theoretical curves in Fig. 2, the radiating bands represented by the symbols I, II, III, IV, V, VI and VII in Fig. 11, Plate I, were also found to be produced by the reflections of the atomic planes belonging to the families (111), (110), (100), (211), (311), (210) and (331) respectively.

Next, to confirm the above considerations still further, the writers investigated the interference phenomena due to the oblique incidences

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1. U. Yoshida: Japanese J. Phys., 133 (1927), and S. Takeyama: These Memoirs, A, 11, 467 (1928).

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

of the X-ray beam from several directions to the largest face of the same specimen as was used in the case of Fig. 11, Plate I. Fig. 12, Plate I is the diffraction figure taken when the axis of the fibre was tilted 20° from its vertical position towards the incident ray. To take this diffraction figure, the photographic plate was placed 3.4 cms. behind the specimen.

In the annexed figure, Fig. 3, the theoretical positions of the prominent radiating bands expected to appear in the present case, are represented by the full lines: While the shaded part of the same figure is the copy of the diffraction pattern in the original plate of Fig. 12, Plate I. As may be seen from Fig. 3, the agreement between the calculated curves and the observed ones is satisfactory.

Fig. 2

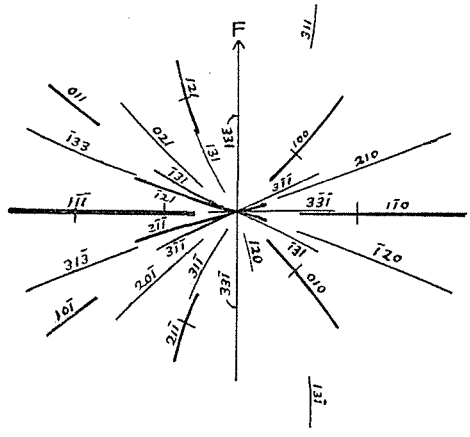
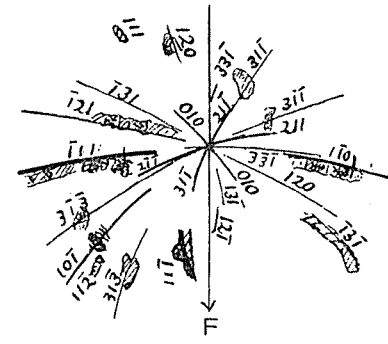


Fig. 3



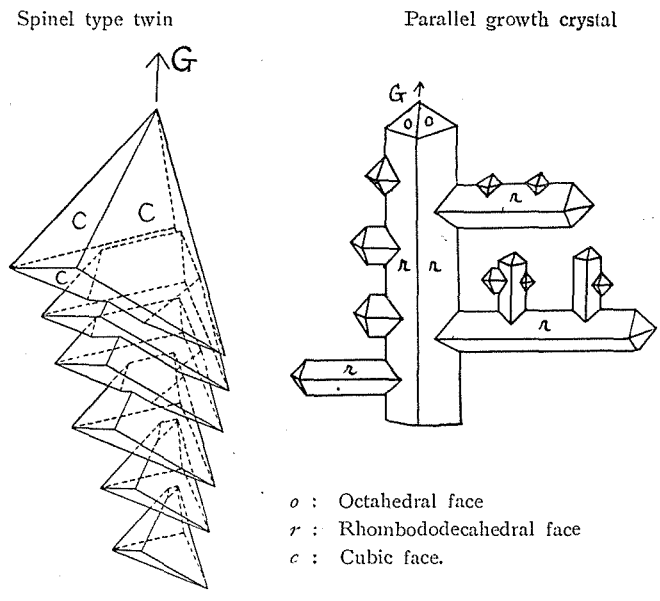
Such an agreement between two curves above mentioned was also found even in the other orientations of the largest surface of the specimen to the incident X-ray beam. Accordingly, our foregoing considerations are again confirmed, and we may conclude that the specimen giving rise to Fig. 11, Plate I has a fibrous structure, the common axis of which coincides with one of the [110] axes, and is situated in the plane of the largest face of this specimen. The direction of the maximum growth, which coincides with the pyramidal axis of the specimen, was found to make an angle of 45° with the direction of this common axis. Thus, the micro-crystal in its initial orientation is seen to be situated with one of the [100] axes in the direction nearly normal to the largest face, and another [100] axis (represented by

G in Fig. 1) in the direction parallel to the maximum growth of the specimen.

Not only the diffraction figure reproduced in Figs. 11 and 12, Plate I, but those obtained with other specimens belonging to this category were also found to be explainable by considerations similar to the above. This shows us that these specimens are of the crystalline structure nearly the same as that of the so-called " parallel growth " copper crystals (see Fig. 4); the difference between two structures above mentiond is only due to the rotation of the micro-crystals in these specimens having one of the [110] axes in common.

Here it must be remarked that the above statement is rather a general one obtained from several specimens. Here and there occasionally a few exceptions were detected: e. g., Fig. 13, Plate I, obtained

Fig. 4

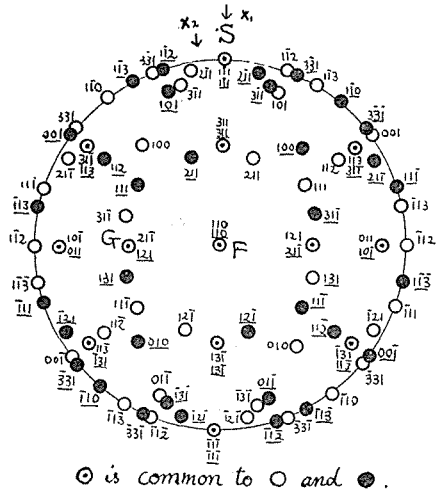


with a specimen belonging to this category, was found not to be explainable by the foregoing considerations. To take this diffraction figure, Fig. 13, Plate I, the photographic plate was placed 3.5 cms. behind the specimen.

Now, let us advance our arguments with respect to the crystalline structures of the specimens giving rise to a diffraction figure such as that reproduced in Fig. 13, Plate I.

If we suppose that two copper crystals are so situated as to form a so-called "spinel type twin" (see Fig. 4), then the orthogonal projection of these two crystals corresponding to Fig. 1 should be represented as in the annexed figure, Fig. 5. To distinguish the atomic planes of one of these crystals from those of the other, their points of projection are expressed in Fig. 5 by the white circles, and those corresponding to the other by the black ones. The points S and G in Fig. 5, are the projections of the directions represented by the same letters in Fig. 4, which coincide respectively with the normal of the flat surface and the direction of the maximum growth of the spinel twin. As can be seen in Fig. 5, the one set of points of projection expressed by the white circles is distributed in identically the same manner as in Fig. 1, while the other given by the black ones is the same as obtained on rotating Fig. 1, through an angle 180° around the direction S.

Fig. 5



Now, let us suppose that the micro-crystals in the specimens have two ideal orientations as is suggested by the two sets of points in Fig. 5; then the radiating bands, as can be seen in Fig. 13, Plate I, are given rise to by the rotations of the micro-crystals around one of the [110] axes, represented by F, in the vicinities of the two ideal orientations above mentioned. Here it may be noticed that in each one of these two ideal orientations, the micro-crystal has one of its [111] axes in the direction normal to the largest face of the specimen, and one of its [211] axes in the direction parallel to the maximum growth.

As a consequence of the foregoing supposition, Fig. 13, Plate I can be considered to be a superposition of two figures, the one being given rise to by a set of atomic planes corresponding to the white circles in Fig. 5, and the other, by those corresponding to the black ones. By calculation, it was found that the former set of atomic

planes gives rise to a diffraction figure as shown in Fig. 6a; while the latter is responsible for the formation of Fig. 6b. To draw these two figures, the angles of rotations of the micro-crystals were taken as 11° and 28° respectively in the cases of Figs. 6a and 6b from two initial orientations, and a micro-crystal in its initial orientations corresponding to Figs. 6a and 6b, was considered to be so situated that the directions represented respectively by the arrows X_1 and X_2 in Fig. 5, coincided with the direction of the incident X-ray beam.

Fig. 6

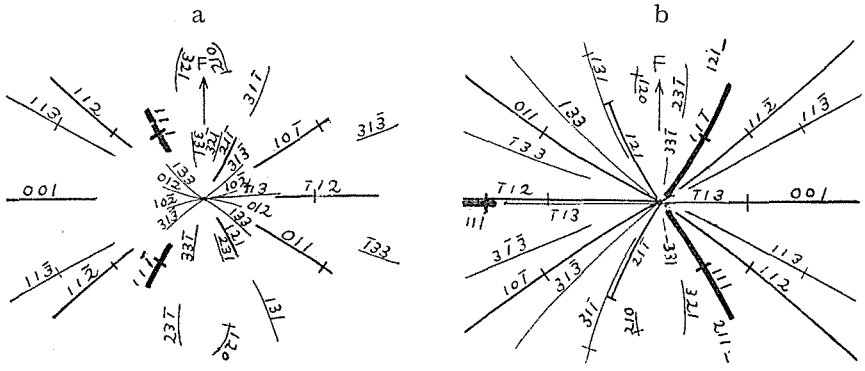
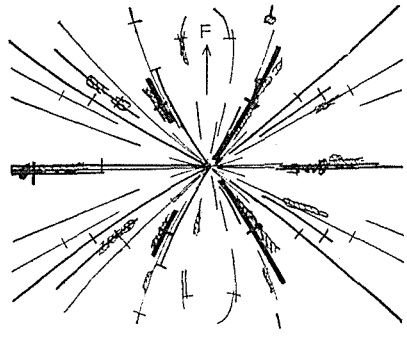


Fig. 7



This being confirmed, it is presumable that the general features of Fig. 13, Plate I must be in fine accordance with the theoretical curves obtained by combining Fig. 6a and 6b. In the annexed figure, Fig. 7, the combination of these two figures above mentioned is represented by the full lines, while the part represented by the shadow in the same figure is a copy of the diffraction pattern in the original plate of Fig. 13, Plate I. As may be seen from Fig. 7, the agree-

ment between the calculated curves and the observed ones is rather satisfactory.

Accordingly, our foregoing suppositions were confirmed as correct and we may consider that the specimen giving rise to Fig. 13, Plate I is of a fibrous structure, the common axis of which is also [110] as in the former case. Furthermore, it was found that the micro-crystals in the specimen were rotated by a small angle from a certain orientation, in which one of the (111) planes of the copper crystal is placed roughly parallel to the largest face, and one of the [211] axes lies nearly parallel to the direction of the maximum growth of the deposited copper. In short, Fig. 13, Plate I may be said to be produced by the rotations of two copper crystals so situated in relation to each other as to form a spinel type twin, around one of their [110] axes.

From our foregoing argument in connection with the specimens of fibrous structure, we arrive at the following conclusions:—

(1) The specimens under consideration consist of micro-crystals arranged in such a way that the common axis is one of the [110] axes of the copper crystal.

(2) For the majority of these specimens, the micro-crystals are rotated within a certain angle around the common axis from the initial orientation, in which one of the (100) planes of the copper crystal is situated nearly parallel to the largest face of the specimen. As the common axis makes an angle 45° with the direction of the maximum growth of the specimen, this direction of the growth is nearly parallel to the normal of another (100) plane of the micro-crystal in the initial orientation.

(3) Some of the specimens consist of micro-crystals rotated around the common axis above stated from two initial orientations. Each of these two initial orientations has one of the [111] axes in the direction parallel to the normal of the largest face of the specimen, and one of the [211] axes in the direction of the maximum growth.

The above conclusions agree well with those previously given by Glocker and Kaupp, excepting the point that one of the [100] or [211] axes, instead of the fibrous direction [110] in the previous experiments, lies roughly parallel to the direction of the specimens in the present experiments.

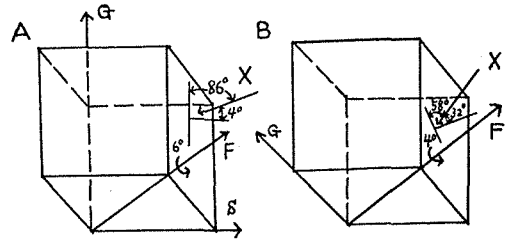
(iii) On the Formation of Single Crystals: A crystalline structure resembling more closely that of the parallel growth crystal of copper,

was observed in some of the specimens which appeared mixed with the fibrous ones, as a result of the process of electrolysis previously mentioned. The diffraction patterns obtained with these specimens, as is shown in Figs. 14 and 15, Plate II, consist of a number of somewhat elongated Laue's spots. To take these two figures, the specimen was so placed at a distance of 3.2 cms. in front of the photographic plate, so that the direction of its maximum growth became parallel to the direction represented by the arrow G on the photographic plate.

From the distributions of Laue's spots, it was found on the one hand, by making use of the Yoshida's globe, that the former figure, Fig. 14, Plate I, can be produced when the direction of the incident X-ray beam is inclined 90°, 4° and 86° respectively to the normal to the atomic planes 100, 010, 001 of a single-crystal of copper; while on the other hand, when the direction of the incident beam is inclined 32°, 19° and 84° respectively to the normals to the atomic planes 010, 011 and 100 of a single crystal, was confirmed by the distribution of Laue's spots to agree well with that of the latter figure, Fig. 15, Plate I. Moreover, the directions represented by the arrows G in these two figures, Figs. 14 and 15, Plate I, were found to coincide respectively with the normals to the atomic planes 001 and 100 within the limits of experimental error.

If we represent diagramatically the orientations of the copper crystal giving rise to Figs. 14 and 15, Plate II, the figures shown in A and B, Fig. 8, may respectively be obtained from the above considerations. It is noticed that in the orientation represented by A, the incident X-ray beam takes the direction nearly parallel to the normal of the 010 plane: But in B, the direction of the incident X-ray beam is inclined obliquely to any one of the prominent atomic planes of the copper crystal. This fact is due to the lack of the largest face of the specimen giving rise to Fig. 15, Plate II.

Fig. 8



X. Direction of the incident X-ray beam.
F. Direction of the fibrous axis.
G. Direction of the maximum growth of the specimen.
S. Direction normal to the largest face of the specimen.

From our arguments with respect to the specimens under con-

sideration, we may conclude that each one of these specimens is mostly made up of a single crystal of copper, having one of its [100] axes in the direction of the maximum growth of the deposited copper, and another [100] axis normal to the largest face (if there is any). In short, the crystalline structure of the specimens giving rise to Figs. 14 and 15, Plate II, is the same as that of the parallel growth copper crystal.

Hitherto, we have treated the diffraction patterns in Figs. 14 and 15, Plate II as ordinary Laue's figures. But strictly speaking they are not exactly so; and a slight elongation of each Laue's spot indicates the presence of a fibrous nature of weak degree. By calculation, it was found that one of the [110] axes in the specimens was also arranged parallel to the direction of the fibre, and the angle of rotation of the micro-crystals around this direction was respectively 6° and 4° in the cases of Figs. 14 and 15, Plate II.

II. Gold

The gold specimens mainly used in the present experiment were gold foils electrolytically deposited on sheets of copper, silver and gold at the laboratory of the Imperial Mint Osaka. Supplementary to these, a specimen of a spongy form prepared at the Mint was also examined.

We are not informed of the procedure adopted in the electrolysis at the Mint, excepting with regard to the specimen of spongy form. The conditions under which this spongy specimen was prepared are given below:

Electrolyte: 140 c.c. saturated water solution of $AuCl_3$, 10 c.c. HCl.
Temperature: 20°C.
Potential difference: 1 volt.
Initial current density: 0.14 amp./cm^2.

A plate of pure gold 2 mms. in thickness and 3 cms. × 3 cms. in area was used as the anode. Parallel to the anode, a sheet of gold, 0.5 mm. in thickness and 10 mms. × 2 mms. in area, was suspended as the cathode, at a distance of about 3 cms. from the anode. Owing to the increase of the volume of the electro-deposited substance, the current density through the electrolyte was found to increase gradually in the course of the electrolysis. The macro-structure of the spongy specimen thus deposited is reproduced in Fig. 10, Plate I.

Diffraction figures were taken with the electro-deposited gold

foils above mentioned. To take these figures, the specimens were so placed that the foliated surface was perpendicular to the incident X-ray beam.

The diffraction phenomena thus investigated with all the specimens of this category were found to be essentially the same. Each one of these specimens gave rise to a diffraction figure consisting of a number of Debye-Hull rings. This shows us without doubt that the arrangement of the micro-crystals in each specimen has no regularity with regard to the surface of the foil. As an example of these diffraction figures, the one obtained with gold deposited on copper plate is reproduced in Fig. 16, Plate II. To take this diffraction figure, the photographic plate was placed 3.2 cms. behind the specimen.

Next, to ascertain whether any regularity with respect to the other directions might exist or not in these specimens, the writers investigated the diffraction phenemena obtained by rotating some of the specimens under consideration, but no regularity was found; the diffraction figures obtained in this case also consisted of Debye-Hull rings. Accordingly, it was confirmed that the gold foils examined are mostly made up of an irregular aggregation of micro-crystals.

Similar investigations were carried out with the spongy specimen, and it was found that the diffraction figure given rise to by this specimen was also an assemblage of Debye-Hull rings. Thus we may conclude, that the spongy specimens are of the same crystalline structure as the electrolytic gold foils, in which the micro-crystals of gold are arranged without any regularity.

Summary.

The arguments which have hitherto been advanced with respect to electro-deposited copper and gold, lead us to the following conclusions :—

(1) As was already known, the micro-crystals of copper are deposited electrolytically without any regularity under ordinary conditions. But, under certain conditions, the micro-crystals of copper have a tendency to arrange themselves in a fibrous-like manner, having one of the [110] axes in common; and occasionally the rotation of micro-crystals of copper around this common axis is so small that they form a crystalline structure nearly the same as that of a single crystal.

(2) The direction of the maximum growth and that of the normal to the largest face in a quasi-single crystal of copper above stated,

are closely related to those in a "parallel growth" natural crystal. As one of the [100] axes of each micro-crystal in the specimen lies roughly parallel to the normal of the largest face, another [100] axis nearly coincides with the direction of the growth of the deposited copper.

(3) Most of the fibrous specimens of electro-deposited copper are of the crystalline structure nearly the same as that of a "parallel growth" crystal, excepting the presence of a fibrous nature in these specimens due to the small rotation of micro-crystals around their common axis [110]. But, some of these fibrous specimens consist of two groups of micro-crystals rotating around the same common axis as before; a micro-crystal belonging to one of these groups is so situated as to form a "spinel type twin" with another micro-crystal belonging to the other.

(4) The micro-crystals of gold have no marked tendency to deposit themselves with any regularity.

The above conclusions contradict slightly those of Glocker and Kaupp[1], who suggest that the direction of the growth of electro-deposited metals coincides with that of the fibrous axis.

In conclusion, the writers wish to express their best thanks to Professor U. Yoshida and Professor D. Uno for the interest they have taken in the experiments, and to Professor A. Matsubara for his efficacious advice on many occasions. Their thanks are also due to Dr. Y. Kimata of the Hidachi Factory of the Kuhara Mining Company, and to Dr. H. Komatsubara of the Imperial Mint, who kindly supplied many samples required for the present investigations.

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Kyoto Imperial University.

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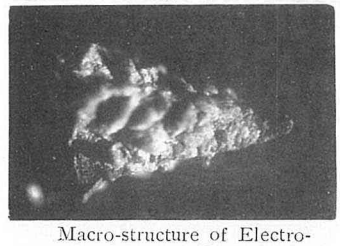
1. Loc. cit.

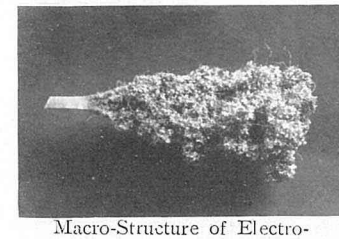
Plate I

Fig. 9



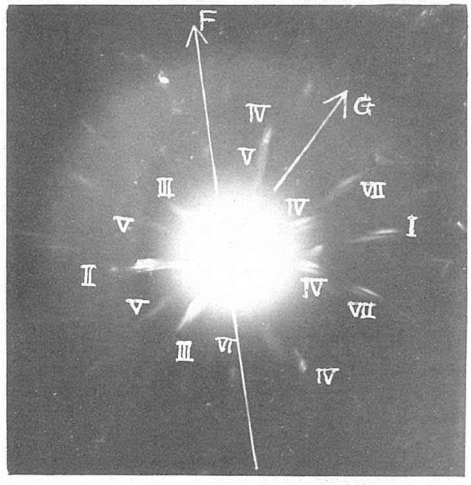
Macro-structure of Electro-deposited Copper
× 19

Fig. 10



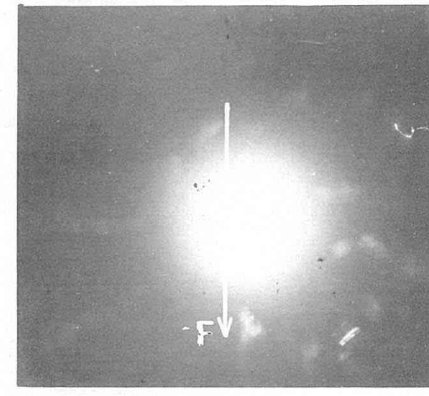
Macro-Structure of Electro-deposited Gold
1 : 1

Fig. 11



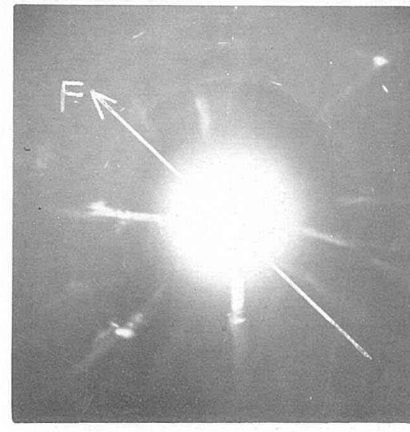
Copper

Fig. 12



Copper

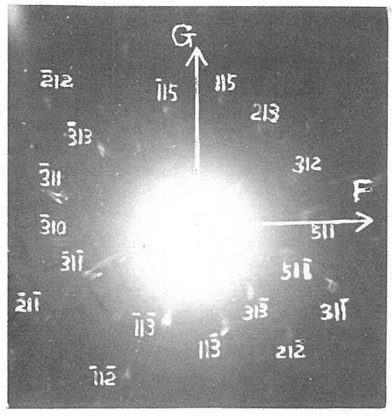
Fig. 13



Copper

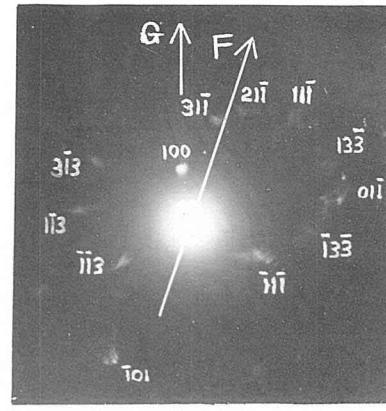
Plate II

Fig. 14



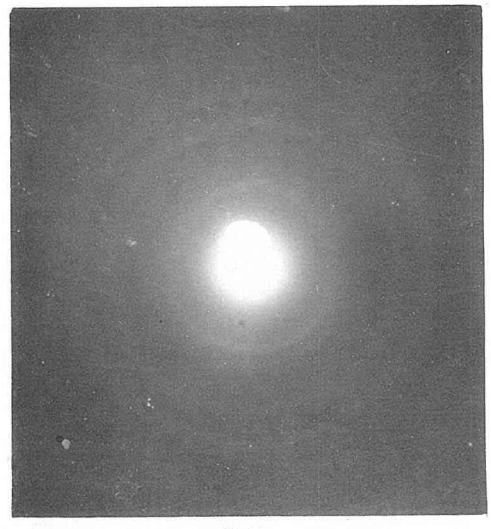
Copper

Fig. 15



Copper

Fig. 16



Gold