Crystal Forms of Single Crystals of Copper, Part I. Crystals produced by the Stress-Annealing Method

By

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Abstract

The outer crystallographic forms of the copper crystals obtained by the stress-annealing method in vacuo, and those developed by etching were examined in the present experiment. It was found that the crystal faces developed depended on the manner of treatment of the surface of the crystal. The fine structures of the etching figures were also observed. Polysynthetic twinning relation of the spinel type was detected in the part of the crystal which showed banded structures.

Introduction

The X-ray method has enabled great progress to be made in the investigation of the inner atomic or molecular structures of crystals. The outer forms of metal crystals too have been studied by many authors from both the theoretical and the experimental sides. But no harmonious conclusion has yet been attained, as the majority of the experimental researches are mainly concerned with the poly-crystalline specimens of metals. Consequently systematic examination of the outer structures of single crystals of metals is desirable. One part of the experiments on single crystals of copper, which were prepared under various conditions, are reported in this paper.

The Method of producing Copper Crystals

All the single crystals of copper used in this experiment were produced by the stress-annealing method. A plate of pure electrolytic copper of the size of $70 \times 15 \times 1.5$ mm.[3] was annealed in a vacuum furnace at about 700°C. for a day. Subsequently it was elongated by about one per cent., and was again heated in the vacuum furnace at about 800°C. for ten hours or thereabouts. By this procedure several large single crystals, as shown in Fig. 1 of the plate were produced in the copper plate. But not one of these crystals was perfectly single in the strict sense, since it consisted of a number of so-called twins as was observed by Carpenter and Tamura.[1]

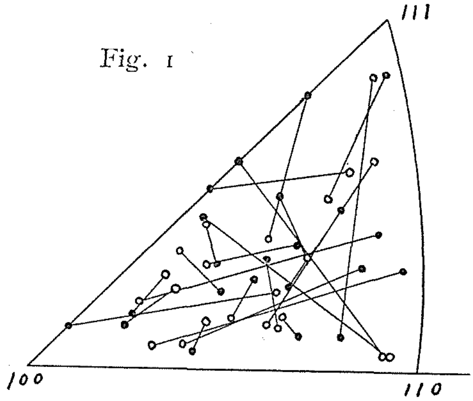
Next a stretching of a very slight degree was imparted to the crystals thus prepared. They were then annealed for the third time in the vacuum furnace at circ. 900°C. for a day or two, and finally they were cooled very slowly in the furnace. By this procedure the writer was able to make several large crystals grow, which contained no twins, or only a few if any. A photograph of the copper crystals thus formed in a plate is reproduced in Fig. 2 of the plate.

Orientations of the Crystals

The crystallographic orientation of the crystals obtained by the method described above was determined by treating the Laue-spots taken with the crystal with the crystallographic globe[2]. The writer examined whether or not the crystallographic orientation depended upon the direction of the stretching imparted to the specimen; and also whether or not some simple relation with regard to the crystallographic orientation exists among the crystals thus produced.

Fig. 1 is a stereographic representation of the crystallographic orientation of the crystals thus examined. In this figure the direction of the surface normal of the specimen and the stretching direction are denoted by a dot and a small circle respectively; and the line joining a dot and a small circle indicates that they belong to the same crystal. Since

Fig. 1



1. Carpenter and Tamura: Proc. Roy. Soc., **113**, 28 (1927)
2. U. Yoshida: Jap. J. Phys., **4**, 133 (1927); S. Takeyama: These Memoirs, **12**, 257 (1929)

the distribution of these dots and small circles is, as is seen in Fig. 1, quite at random, we may conclude that the dependency of the crystallographic axes upon the direction of stretching and the relative crystallographic orientation among different crystals are, if any, so complex that we can not detect any simple regularity in the stereographic projection.

Outer Forms of the Crystals

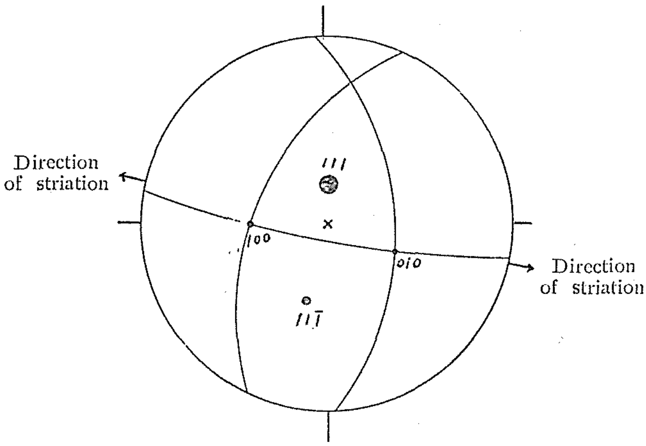
According to Dana[1] the observed forms of native copper crystals are (100), (110), (111), (410), (211), etc. The writer examined, in three ways, the outer forms of the single crystals of copper obtained, (1) by taking the Laue-photograph, (2) by the reflection of light and (3) by observing with a microscope.

When a specimen of a copper plate that contains several single crystals is rotated while illuminated by a light, each crystal shines brightly at a certain orientation. This means that certain facets are developed on the surface of the crystal and they reflect the illuminating light when and only when they are brought to the orientation which calls forth the reflection. From this point of view the writer determined the angular distribution of the normals to these facets by a reflection goniometer which was the same, in principle, as that used by B. Fujita.[2] By comparing the orientation of the surface normals of the facets with that of the crystallographic axes which was determined from the Laue-photographs, the crystallographic indices of the facets were determined on the crystallographic globe.

The result of the experiments made on about fifty crystals showed that the faces forming the outer form of the copper crystals were octahedral, or cubic, or a combination of these two; and no face of other indices was observed. Further the writer estimated roughly the breadth of these faces by comparing the blackening effects of the reflected beams on a photographic plate, assuming the reflective power of different faces to be nearly the same.[3] The result of observation made on one of the crystals is illustrated stereographically in Fig. 2. In this figure the center of the projection corresponds to the direction of the normal to the flat surface of the copper plate, and the

1. Dana: A System of Mineralogy (1914)
2. B. Fujita: These Memoirs, **12**, 159 (1929)
3. This simple method was first devised by Mr. S. Tsuboi

Fig. 2

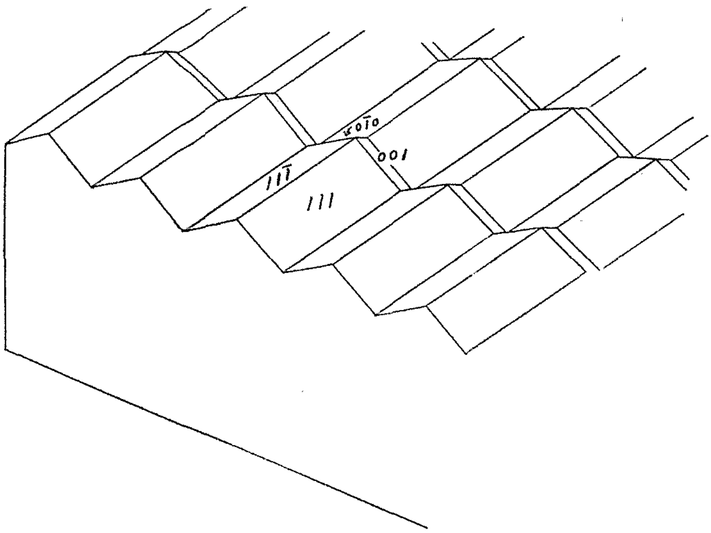


circular dots represent the direction of the normals to the crystal faces characterised by the indices annexed. The size of these dots indicates approximately the relative breadth of the respective crystal faces as was estimated by the method mentioned above.

With the method of the optical reflection only, it is impossible to perceive completely what kind of aggregation these crystal faces will make on the surface of the crystallized plate. But further microscopic observation indicates clearly this aspect. In the microphotograph shown in Fig. 3 of the plate we can see numerous parallel striations, whose direction corresponds to that of the edge of two adjacent octahedral faces which are observed by the method of optical reflection. As the writer could observe a similar appearance in many cases, it seems to him that the copper crystal has a habit of developing in a parallel growth-like aggregation of two octahedral faces along the surface of the copper plate when the crystal is made to grow by annealing in vacuo.

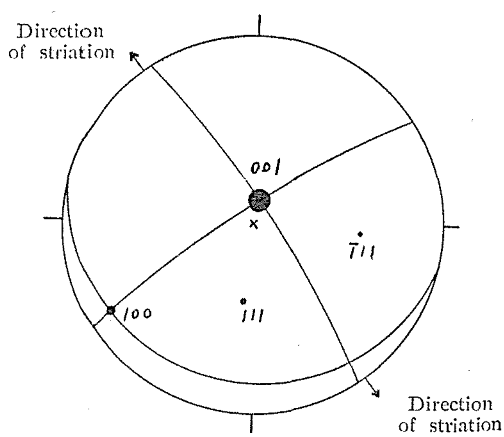
It has already been mentioned that some of the crystals may have, as their outer form, a combination of octahedral and cubic faces. It was detected by observing the surface of such crystals with a microscope, that the secondary striations ran parallel to each other across the main ones. These secondary striations are inclined to the direction of the main ones at a constant angle. The direction of these secondary striations was confirmed to correspond to that of the edges of the octahedral and the cubic faces, whose orientations were determined by optical reflection. Thus the outer form of the combination is supposed to be probably like that shown in Fig. 3.

Fig. 3



Of about fifty crystals examined there were several which consisted of a parallel growth-like aggregation of the cubic faces as the main striations. Such an appearance of the crystal seems to be especially predominant when one of the cubic faces takes the orientation nearly parallel to the flat surface of the copper plate, as shown in Fig. 4.

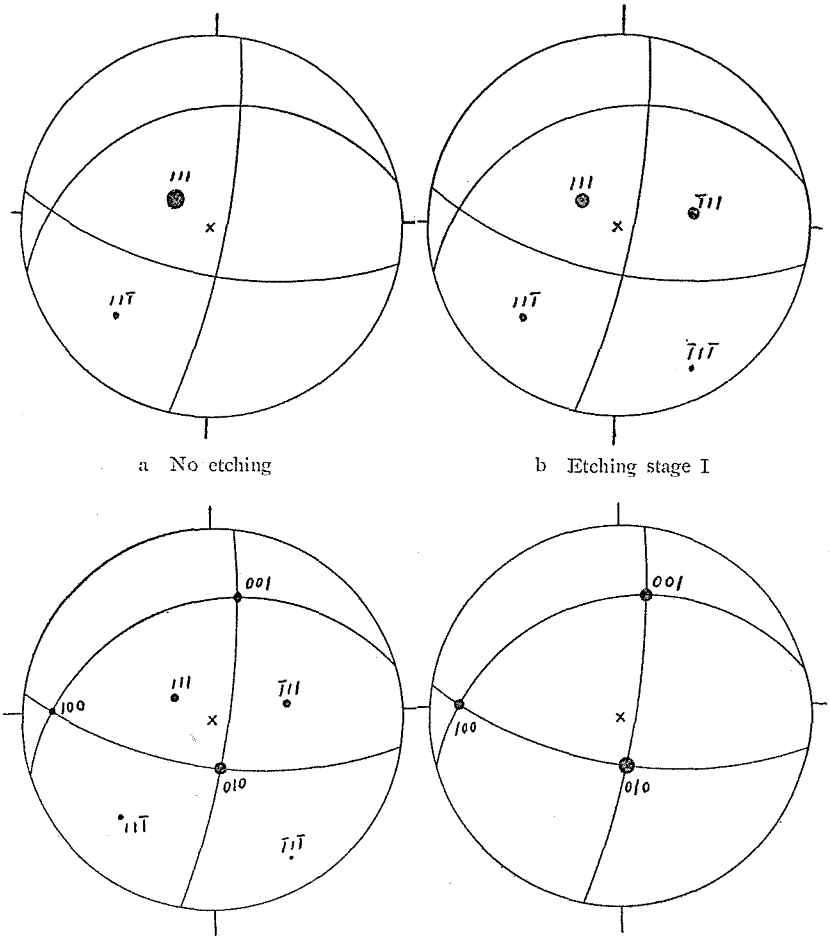
Fig. 4



The Effect of Etching

It was already been observed that with a single crystal of aluminium[1] cubic or dodecahedral facets are developed by etching, while with a single crystal of nickel[2] octahedral ones are developed, although these two metals belong to the face-centred cubic lattice type. The writer first examined the facets developed when the single crystals of copper were immersed in nitric acid diluted with distilled water (about 1 : 5

Fig. 5



a No etching

b Etching stage I

c Etching stage II

d Etching stage III

1. B. Fujita: loc. cit.
2. Davisson and Germer: Phys. Rev., **30**, 710 (1927)

in volume). The indices of the crystal facets thus developed were determined by the method of optical reflection.

The etching pattern changed gradually with the degree of etching. When a crystal, whose faces are shown stereographically in Fig. 5, a, was immersed into the etchant, many other facets were developed with the progress of the etching. In Fig. 5, b, c, d indicate the indices of the facets thus developed at successive stages of the etching process. At an early stage octahedral faces, including the initial ones, were generally developed; and a great number of pyramidal forms were observed under the microscope, as shown in Fig. 4 of the plate. These octahedral faces, however, diminished gradually in size as the etching process proceeded; and, in turn, cubic faces appeared and developed more and more, so that at last these octahedral faces ceased to be observable, only the cubic faces being left, as is shown in Fig. 5, d.

The above description is only an outline of the general features revealed by the etching. Actually the process exhibited somewhat different features with the orientations of the crystals and with the conditions of the etchant. With a crystal which had such an orientation that one of the (111) faces was nearly parallel to the flat surface of the copper plate, this octahedral face did not readily disappear even with prolonged etching. This face was made to disappear, however, with concentrated nitric acid.

It was also observed that sometimes there appeared (311), (511), (210) and (310) faces at an early stage of the etching process. But these faces were very unstable and did not show any trace of their presence when the etching process was advanced a little further. When alcohol solution of nitric acid was employed, instead of the water solution, these unstable faces never appeared from the beginning. In the alcohol solution the octahedral faces were also dissolved more easily than in the water solution, and the stable cubic faces were developed immediately after a slight advance of the etching process. Dodecahedral faces were never detected in etchants of normal concentration, but they appeared when the surface of the crystal was etched violently with a very concentrated etchant.

Recently, Zwicky[1] and others put forward the theory of the mosaic structure in a crystal, and Zwicky insisted that a fine structure of etching figures on a metallic single crystal would be observed as

1. Zwicky: Proc. Nat. Acad. Sci., **15**, 816 (1929)

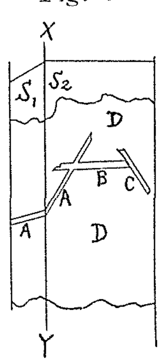
a consequence of the presence of the mosaic structure. Afterwards it was observed by Goetz[1] that there appeared such a mosaic pattern when a cleavage surface of a Bi-single crystal was etched by nitric acid. In the present case, such fine structures of etching figures on the surfaces of the single crystals of copper were also observed when the orientation of the crystal was such that one of the octahedral or of the cubic faces was nearly parallel to the flat surface of the copper plate. In the former orientation the fine structure was of a triangular pattern, and was rectangular in the latter, as can be seen in Figs. 5 and 6 of the plate respectively.

More detailed research is of course required to decide whether these patterns are due to the mosaic structure or not. It may be possible that the size and the regularity of these two patterns depend very much upon the degree of etching, as was experienced by Goetz in the case of the single crystal of bismuth.

Twinning of the Copper Crystals

That copper crystals often exhibit banded structures or so-called twin-lamellae was observed by Carpenter and Tamura.[2] They pointed out that these structures were a result of twinning on the 111-plane of the spinel type. Some of the single crystals of copper prepared by the writer contained also, as mentioned before, several such banded structures, the breadth of which amounted from one-tenth to about one millimeter.

Fig. 6



The appearance of a crystal which contains three such bands is sketched in Fig. 6, where A, B and C represent three bands. And a microphotograph taken at a place where two such bands are in contact is reproduced in Fig. 7 of the plate. The crystallographic orientations of the mother crystal D and the band A were determined by the X-rays, and are plotted on a stereographic projection in Fig. 7, in which the plane of the paper corresponds to the flat surface of the copper plate. The orientations of the atomic planes (100) of the band A are represented by broken lines, and those of the mother crystal are represented by the full lines. It

1. Goetz: Proc. Nat. Acad. Sci., **16**, 99 (1930)
2. Capenter and Tamura: Proc. Roy. Soc., **113**, 161 (1927)

will be seen from the figure that both crystals have the normal to one

Fig. 7

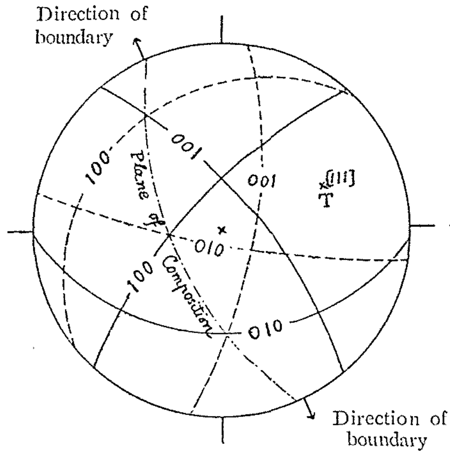
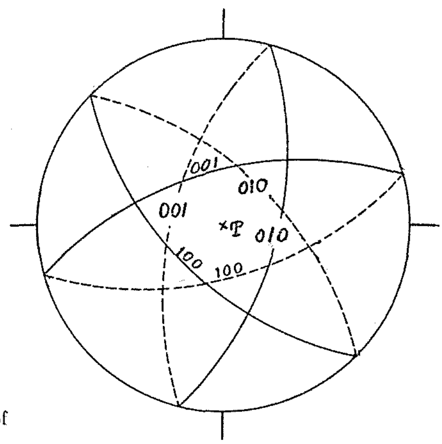


Fig. 8

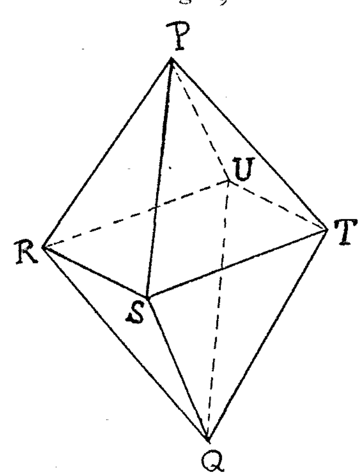


of the octahedral faces in common at the point marked T.

The crystallographic orientations of A and D are represented again in Fig. 8, the normal to the common octahedral face being taken as the centre T of the stereographic projection. Since Fig. 8 shows a symmetrical figure of six-fold symmetry, one can easily know that one orientation can be obtained from the other by rotating it through 60° about the normal to the common octahedral face.

The banded crystal is bounded by parallel straight lines on two adjacent orthogonal surfaces S_1 and S_2 of the specimen, as is shown in Fig. 6. This shows that the twinning has a plane of composition. The direction of the normal to this plane of composition can be easily determined from the inclinations of the band A to the line XY in Fig. 6 on both surfaces S_1 and S_2. The result of the measurement shows that the direction of this normal coincides with the point T in Fig. 7. Hence the banded crystal exhibits a

Fig. 9



polysynthetic twinning of the spinel type. Other banded crystals B and C, were seen also to have the similar twinning relation to the mother crystal D as A. But the planes of composition of these twinnings are not the same one octahedral face but three successive octahedral faces of the mother crystal. For example, if PQRSTU in Fig. 9 is an octahedron in the orientation of the mother crystal D, then the planes of composition of A, B and C are the faces PRS, PST and PTU respectively.

When single caystals of copper were prepared by the method mentioned before, it frequently happened that two adjacent crystals were in contact with a straight line as their boundary on the surface of the copper plate. The result of examination, to find whether such two crystals were in twinning relation or not, showed that there were three classes of contacts. In the first, the two crystals exhibited a twinning of the spinel type like that of the banded crystal. In the second, the two were mutually in contact with a certain common crystallographic plane, and one orientation was obtained by rotating it against the other about the common crystallographic axis, which was the normal to the plane of contact, through a definite angle. For example, a 110-face was a plane of contact and the angle of rotation was that between the [111]-and [110]-axes which were nearest to each other. In the third, the two were merely in contact by chance, perhaps, with any crystallographic planes.

When two copper crystals were in contact in one plane, the majority of the contacts were of the first class, but several cases belonging to the second were also detected. The writer observed also the contact belonging to the third case, but only rarely. At any rate, we must be very cautious in treating two crystals as a twin which are merely in contact with a straight line on the surface of the copper plate.

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida under whose kind guidance the present experiment was carried out.

Fig. 1 (Full size)

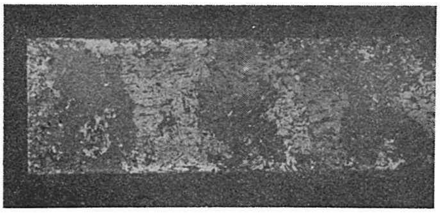


Fig. 2 (Full size)

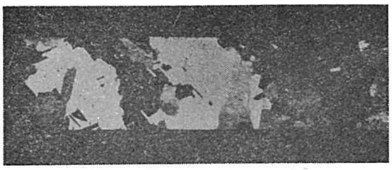


Fig. 3 (× 500)

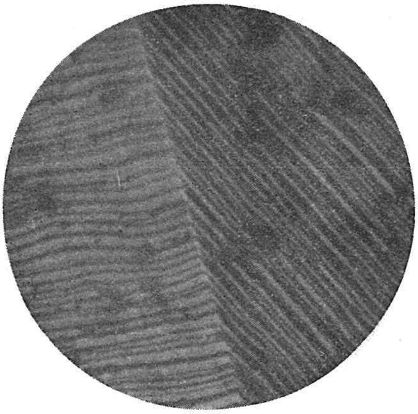


Fig. 4 (× 100)

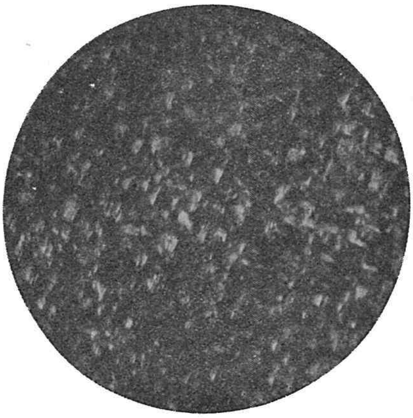


Fig. 5 (× 100)

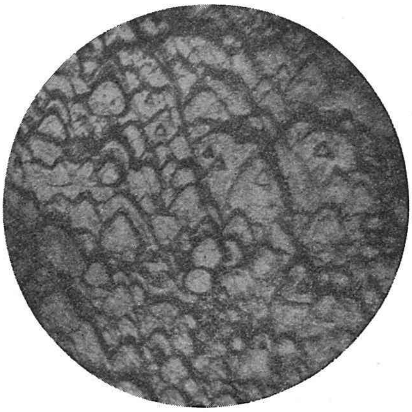


Fig. 6 (× 100)

Fig. 7 (× 50)