Crystal Forms of Single Crystals of Copper, Part II. Crystals deposited on the Surface of a Single-Crystal-Plate by Electrolysis

By

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(Received August 7, 1930)

Abstract

An attempt was made with success to some extent, to cause a single crystal of copper to grow by electrolytic deposition. The inner and outer structures of the crystals thus obtained were investigated roentgenographically and optically. It was observed that, under favorable conditions, the deposited copper consisted of a nearly perfect single crystal of the same orientation as that of the mother crystal at an early stage of deposition. As the deposition process proceeded, however, the deposited copper was found to consist of micro-crystals having the orientations scattered more or less from that of the mother crystal.

Introduction

Many investigations on the crystalline structure of electrodeposited metals have heretofore been made, and it has been ascertained that the micro-crystals of metals have a tendency, to some extent, to arrange themselves in some regular way. In these researches, however, the attention was mainly concentrated on the influence of the composition of the electrolyte or on the working conditions of the electrolysis, and a little on the structure of the metals used as the cathode. The present writer was thus induced to try electrodeposition on a single-crystal-plate of the same metal as that to be deposited. The result of the experiment made with copper is briefly described below.

Procedure in Deposition

An acid still bath was employed in this experiment. The composition of the electrolyte used was as follows: 90 gms. of pure copper sulphate, 17 c.c. of sulphuric acid (specific gravity 1.84) and 450 c.c. of distilled water. The single-crystal-plates of copper used as the cathode were produced by the method reported in the previous paper[1]. Since the plate contained generally several single crystals, the other portion on the surface of the plate than that of a single crystal was carefully covered with paraffin wax. An electrolytic copper plate was used as the anode.

It was found after some experiments that to get the best result it was fundamentally important to maintain the electrolyte as pure as possible. For this purpose the following procedure was adopted:—The two electrode-plates were electrically connected to two terminals of a commutator, pickled for a little while in 10% alcohol solution of nitric acid, rinsed well in distilled water and then they were transferred immediately to the plating bath. The electric current was made by the commutator to flow in the reversed direction during the first few minutes, and then to flow in the normal direction for ten hours or thereabouts; the current density was about 5 milliamp./sq. cm. The temperature of the bath was that of the room, and was found to be about 15°C. or so. The current density and the concentration of the electrolyte employed in the present experiment were so selected as to get the best result in making the copper crystal grow by electro-deposition.

Inner Structures of the Crystals

The inner crystal structure of the copper sheets deposited by the procedure mentioned above was investigated by X-rays. First an examination was made, by the special rotating crystal method devised by the writer[2], to see whether the deposited copper was composed of a single crystal or not. As a result of this examination it was ascertained that the electrodeposition made the mother crystal used as the cathode to grow nearly as a perfect single crystal during the early stage of the plating, by keeping the crystallographic orientation unaltered. But the deposition did not produce the single crystal after its thickness amounted to about 0.5 mm. or more.

Next, the writer investigated by the Laue-diagram method the changes in the crystal structure accompanying the progress of the

1. These Memoirs, **13**, 353 (1930)
2. These Memoirs, **11**, 399 (1928)

plating. The copper was deposited on a single-crystal-plate of copper till the deposited portion became a quarter of a millimeter in thickness. Then the portion of the mother crystal was etched off with nitric acid, in order that no mechanical destruction of the crystal structure should occur in the deposited portion. From deposited sheet thus separated, three test pieces were prepared by appropriate etching, which corresponded to the earliest, the intermediate and the latest stages of plating respectively. Laue-photographs were taken by setting the test pieces perpendicular to the beam of the X-rays from the molybdenum target of a Coolidge tube. Figs. 1, 2 and 3 in Plate I are the Laue-diagrams taken respectively from the three test pieces mentioned above.

The pattern in Fig. 1 is quite identical with that of the mother crystal, though it is not reproduced, while in Fig. 2 radiating bands appear beside the spots observed in Fig. 1. In Fig. 3, moreover, each spot is more or less diffused and elongated; and a few spots corresponding to the atomic planes of complex indices, such as (315), (123), etc., ceased to appear. From these photographs we may conclude generally that the deposited sheet under examination is nearly a single crystal, having the same crystallographic orientation as the mother crystal, though the orientation deviates very slightly in the layer deposited later.

Next, another electrodeposition on a single-crystal-plate of copper was made until the thickness of the deposited layer amounted to about half a millimeter; then the specimen was etched by nitric acid from the mother crystal side, the outer portion of the newly deposited layer, of about a quarter of a millimeter in thickness, being left undamaged. Laue-photographs were again taken with three test pieces prepared as before from the undamaged deposited portion. Fig. 4 in Plate I is the Laue-diagram of the mother crystal and Figs. 5 and 6 in Plate I and Fig. 7 in Plate II are those obtained respectively with the layers situated successively from the mother crystal side. We can detect in Fig. 5 that the spots, which correspond to the atomic planes of simple indices, are diffused to some extent in concentric rings and radials. These aspects become more distinct in Fig. 6; and at last in Fig. 7 almost the concentric rings alone appear. These changes in the appearance of the Laue-diagrams show that the deposited copper is not composed of a single crystal in the portion under examination, but of micro-crystals arranged in orientations somewhat scattered from that of the mother crystal.

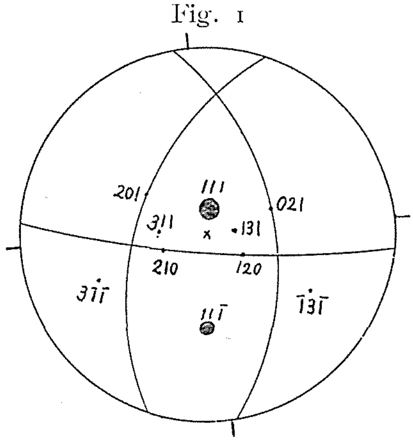
Next, the writer studied whether the micro-crystals were arranged in a fibrous manner or not. Good Laue-diagrams to determine the axis of the fibre could hardly be obtained because of the difficulty of adjustment of the proper degree of etching on the one hand, and the probable dependency of the axis of the fibre upon the orientation of the mother crystal on the other hand. A suitable photograph, however, was obtained and is reproduced in Fig. 8, Plate II. The Laue-diagram of the mother crystal in this case is shown in Fig. 9, Plate II.

It is seen from Fig. 8 that the orientations of the micro-crystals are seen to be scattered within several degrees around that of the mother crystal, having a difinite crystallographic direction as a common axis of the fibre. And the direction of this common axis is found to be parallel to that one of the [100]-axes of the mother crystal which makes the least inclination to the surface of the mother crystal.

Outer Structures of the Crystals

The method of optical reflection revealed that, as long as the electrodeposited layer is a perfect single crystal, its outer form is composed of two predominant octahedral planes and several inferior atomic planes, such as (311)-and (120)-planes. These atomic planes developed by electrodeposition are stereographically represented in Fig. 1.

Fig. 1



It was observed under the microscope that the surface of the single crystal thus developed consisted of a number of parallel ridges, having the spacing several times wider than that of the striations on the single crystal produced by the stress-annealing method. These ridges were mainly formed of the two predominant octahedral planes observed by optical reflection. Fig. 10 in Plate II is a microphotograph of such ridges.

As the electrodeposition advanced a little, however, granular depositions began to appear on the ridges, as is shown in Fig. 11, Plate II. When the electrodeposition advanced still further, these granular depositions covered the whole surface, as is seen in Fig. 12,

Plate II; and the deposition was composed of microcrystals oriented rather at random.

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

Plate I

Fig. 1

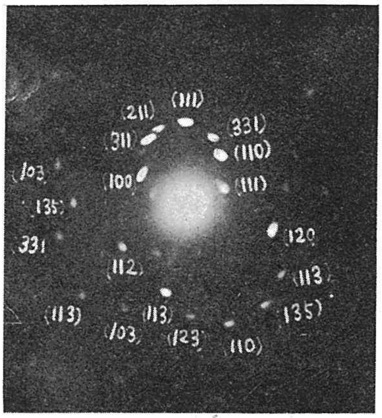


Fig. 2

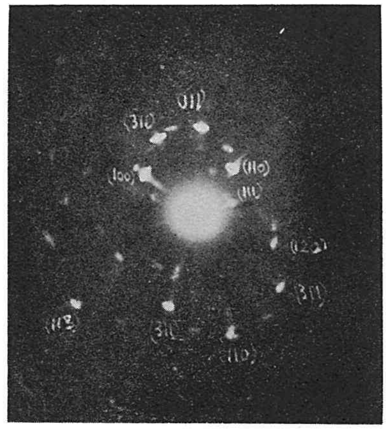


Fig. 3

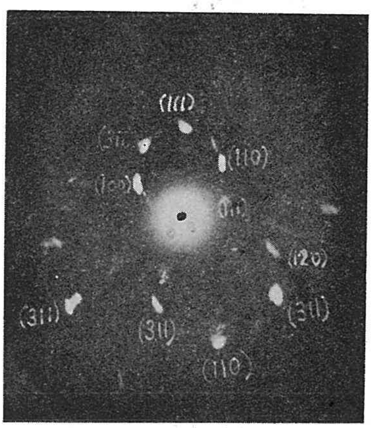


Fig. 4

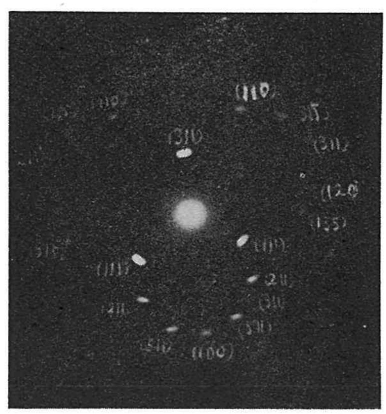


Fig. 5

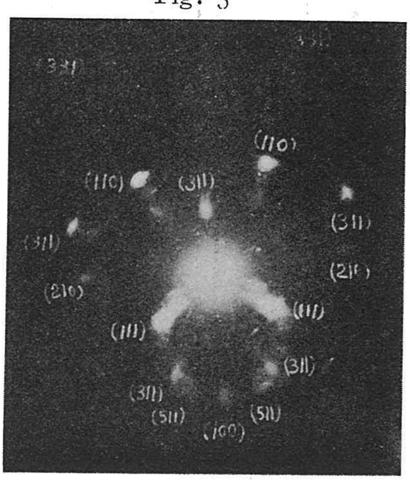


Fig. 6

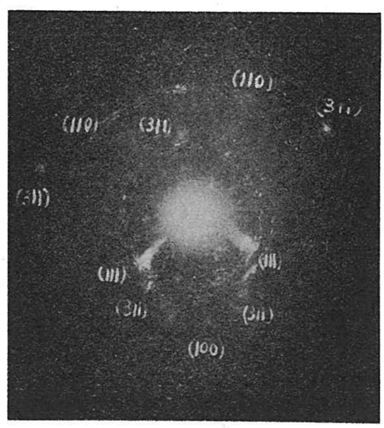


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Plate II

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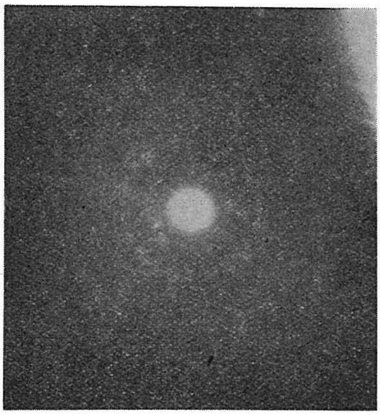

Fig. 8

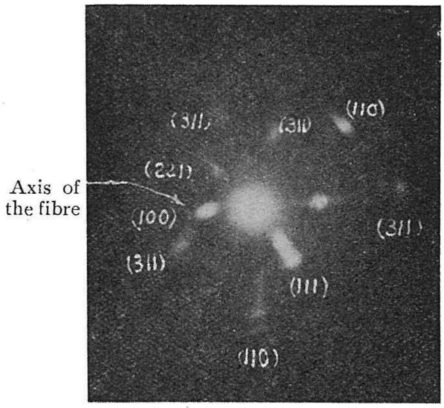

Fig. 9

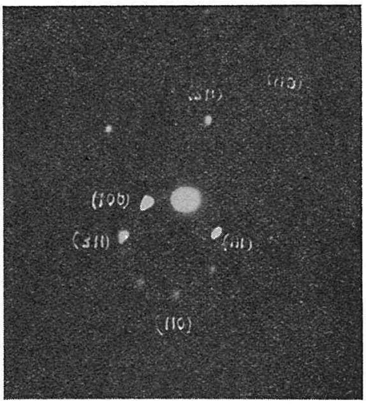

Fig. 10 (×300)

Fig. 11 (×75)

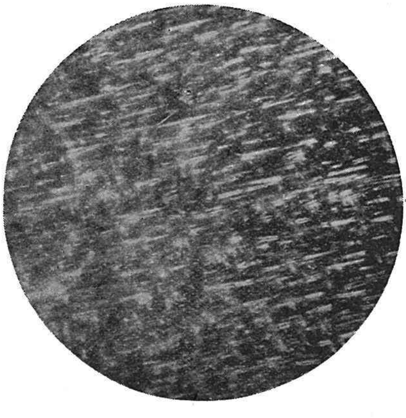

Fig. 12 (×50)