

GROWTH OF Cu_2Cl_2 AND Cu_2Br_2 ON SINGLE CRYSTAL FACES AND POLYCRYSTALLINE COPPER DURING DISSOLUTION IN $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ *

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ABSTRACT

Cu_2Cl_2 and Cu_2Br_2 precipitate and crystallise in the form of triangular pyramids and dendrites when Cu is immersed in aerated, acid CuSO_4 solution containing HCl or HBr. The critical concentration of HCl or HBr for this precipitation depends on the surface of the copper: Polycrystalline $< (110) < (100) < (111)$. In the deaerated solution there is no precipitation of Cu_2Cl_2 or Cu_2Br_2 even at a high concentration of HCl or HBr when only preferential etching occurs.

INTRODUCTION

It has been shown that Cl^- ions present in an electrolytic bath modify the habit of copper electrodeposited on the (100) face.¹ Triangular pyramids and dendrites were observed when copper was deposited at 2 mA/cm^2 from an acid CuSO_4 bath containing $4 \times 10^{-3} \text{ M-HCl}$. It was pointed out by Bertocci² that under these circumstances there is a possibility of precipitation of Cu_2Cl_2 which tends to crystallise in the form of triangular lamellae during deposition. The purpose of the present work was to investigate the precipitation of Cu_2Cl_2 and Cu_2Br_2 on the (100), (110) and (111) faces of copper single crystal and on polycrystalline copper in aerated and deaerated solutions.

EXPERIMENTAL

All glass vessels were immersed in an acid mixture ($\text{HNO}_3 + \text{H}_2\text{SO}_4$, 1:1) overnight and then washed with distilled water followed by conductivity water. The solution was prepared using conductivity water, and pre-electrolysed for 12 hours at 10 mA/cm^2 . The pre-electrolysed solution was then

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treated with activated charcoal and neutral alumina. H_2SO_4 , HCl , HBr (all of A.R. grade) were redistilled separately and treated with activated carbon. A bath of composition $0.25 \text{ M CuSO}_4 + 0.1 \text{ M H}_2\text{SO}_4$ with the desired concentration of HCl or HBr was then prepared.

The single crystal was introduced into Tygon tube so that only the desired surface was exposed. This surface was mechanically polished on emery paper and electropolished³ in H_3PO_4 . Purified N_2 was bubbled through solution containing various amounts of HCl for one hour just before each experiment. The specimen was immersed in the solution (aerated or deaerated) for 30 minutes, removed and washed with conductivity water and then with alcohol. The dried surface was examined under a metallurgical microscope. All the experiments were carried out at $25 \pm 0.5^\circ \text{C}$.

RESULTS

Polycrystalline copper.—Electropolished polycrystalline Cu became etched when immersed in an aerated solution containing HCl upto a concentration of $1 \times 10^{-3} \text{ M}$. At $2.0 \times 10^{-3} \text{ M HCl}$ dark specks of Cu_2Cl_2 in the background of etched surface were observed (Fig. 1). When the concentration of HCl was increased to $2.5 \times 10^{-3} \text{ M}$ some triangular pyramids were observed in the background of etched surface (Fig. 2). Dendrites of Cu_2Cl_2 began appearing at a concentration of $3 \times 10^{-3} \text{ M}$ (Fig. 3). Many dendrites appeared at a concentration of $4 \times 10^{-3} \text{ M}$ when the surface was immersed for a short time.

The precipitation of cuprous bromide occurred on a electropolished surface of copper even at $1.5 \times 10^{-4} \text{ m/L}$ of hydrochloric acid but the definite shape was not observed (Fig. 1). When the concentration was raised to $1.75 \times 10^{-4} \text{ m/L}$ of hydrobromic acid, dendrites with triangular pyramids appeared (*cf.* Fig. 3). The duration of immersion of the surface for growth of cuprous bromide decreased as the concentration was increased as observed in case of cuprous chloride.

(110) face of copper single crystal.—There was no precipitation of cuprous chloride when the electropolished (110) surface was immersed in an acid copper sulphate solution. At a $3 \times 10^{-3} \text{ m/L}$ of hydrochloric acid, dark specks of cuprous chloride were observed and at $3.25 \times 10^{-3} \text{ m/L}$ triangular pyramids were observed. When the concentration was increased to $3.5 \times 10^{-3} \text{ m/L}$ of hydrochloric acid many triangular pyramids with occasional dendrites grew. More dendrites with triangular pyramids appeared as the concentration was increased to $4 \times 10^{-3} \text{ m/L}$ and only dendrites grew when the concentration was greater than $4.5 \times 10^{-3} \text{ m/L}$.

When (110) surface was immersed in the deaerated solution there was no precipitation of cuprous chloride and the surface remained bright. At a concentration of 5×10^{-3} m/L of hydrochloric acid the surface was preferentially etched giving ridge type of surface as shown in Fig. 4.

With hydrobromic acid a large number of triangular pyramids appeared at 1.75×10^{-4} m/L and very big pyramids appeared when concentration was 2×10^{-4} m/L. Dendritic growth was observed when the concentration in the solution was raised to 2.5×10^{-4} m/L.

(100) *face of copper single crystal*.—The (100) surface of copper crystal was not affected when immersed in acid copper sulphate bath containing upto 3×10^{-3} m/L of hydrochloric acid except some etch pits and the surface remained very bright. When the concentration of hydrochloric acid was 3.25×10^{-3} m/L specks of cuprous chloride were observed (*cf.* Fig. 5). Occasional triangular pyramids began to grow at 3.5×10^{-3} m/L of hydrochloric acid (Fig. 6). Triangular pyramids with twinning appeared as in Fig. 7 at 4×10^{-3} m/L of hydrochloric acid. Very big dendrites appeared at 4.5×10^{-3} m/L of hydrochloric acid as in Fig. 8 and there were no triangular pyramids. It was also observed that the dendrites began to grow at the apex of the triangular pyramids. Whenever cuprous chloride pyramids appeared the surface was greenish-dull and on keeping it became green.

The (100) surface was not affected in any way upto a concentration of 6×10^{-3} m/L of hydrochloric acid when immersed in a deaerated solution. At a concentration of 6.5×10^{-3} m/L the (100) surface was preferentially etched and regular pyramidal pits appeared as shown in Fig. 9. The surface was very bright indicating that there was no precipitation of cuprous chloride but the surface was preferentially etched.

Similarly, when (100) surface was immersed in acid copper sulphate solution containing hydrobromic acid there was no precipitation of cuprous bromide till the concentration of hydrobromic acid was raised to 1.5×10^{-4} m/L and at 1.75×10^{-4} m/L very big triangular pyramids appeared. When concentration of hydrobromic acid was raised to 2×10^{-4} m/L triangular pyramids with dendrites appeared.

(111) *face of copper single crystal*.—The (111) surface was not at all attacked till the concentration of hydrochloric acid was 3.5×10^{-3} m/L and at this concentration small dark specks of cuprous chloride were observed (Fig. 5). Occasional triangular pyramids grew at 4×10^{-3} m/L of hydro-

chloric acid. Many triangular pyramids with occasional dendrites appeared when the concentration was raised to 4.5×10^{-3} m/L.

There was no precipitation of cuprous chloride on (111) face when it was immersed in deaerated solution. There was no indication of preferential etching even at a concentration of 6.5×10^{-3} m/L of hydrochloric acid.

The cuprous bromide began to precipitate on (111) surface when the concentration was 1.75×10^{-4} m/L (Fig. 5) but had no regular shape. Triangular pyramids with occasional twinning began to grow when concentration of Hydrobromic acid was increased to 2×10^{-4} m/L. At 2.5×10^{-4} m/L of Hydrobromic acid more irregular dendrites with triangular pyramids grew.

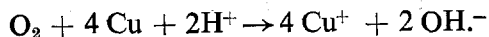
DISCUSSION

The solubility of cuprous chloride and cuprous bromide are 1.1×10^{-3} and 2.0×10^{-4} m/L respectively.⁴ When hydrochloric acid or hydrobromic acid is added to the acid copper sulphate solution there is no indication of the precipitation of cuprous chloride or bromide. When electropolished copper surface is immersed, copper dissolves in the solution as indicated by the etched surface. While dissolving in aerated solution the Cu ions may accumulate in the diffusion layer at the interface. When the accumulation of cuprous ions reaches a critical concentration the solubility of cuprous chloride (or cuprous bromide) is exceeded and there is precipitation. These may crystallise out as triangular pyramids. When the solution is stirred rigorously there is no precipitation of cuprous chloride as the Cu^+ may be transported outside the diffusion layer. It is very significant that there is no precipitation of cuprous chloride on (100) face even at a concentration of 6.5×10^{-3} m/L of HCl in deaerated solution but (100) face is preferentially etched.

The interesting point is that the precipitation occurs first in aerated solution. The reason is not immediately evident as Cu^+ ions should be produced at the surface even in deaerated solution by the reaction.



The only possible conclusion is that the reaction $\text{Cu}^{++} \rightarrow \text{Cu}^+ + e$ is too slow and does not provide enough Cu^+ ions to exceed the solubility of CuCl or CuBr . This conclusion is in agreement with findings of Bockris and Mattsson.⁵ The presence of dissolved oxygen in solution may play a prominent role in producing more of Cu^+ ions by the reaction



This reaction provides enough Cu^+ ions to precipitate CuCl or CuBr .

It is very significant that the critical concentration of hydrochloric acid or hydrobromic acid required for the cuprous chloride or cuprous bromide growth increases with atomic density of the surface as seen in Tables I and II. The density of triangular pyramids and the growth of dendrites also depend on the crystal planes, for a given concentration of hydrochloric acid or hydrobromic acid. The dendrites of cuprous chloride or cuprous bromide on (111) plane appear comparatively at higher concentration of hydrochloric acid or hydrobromic acid in the solution.

TABLE I

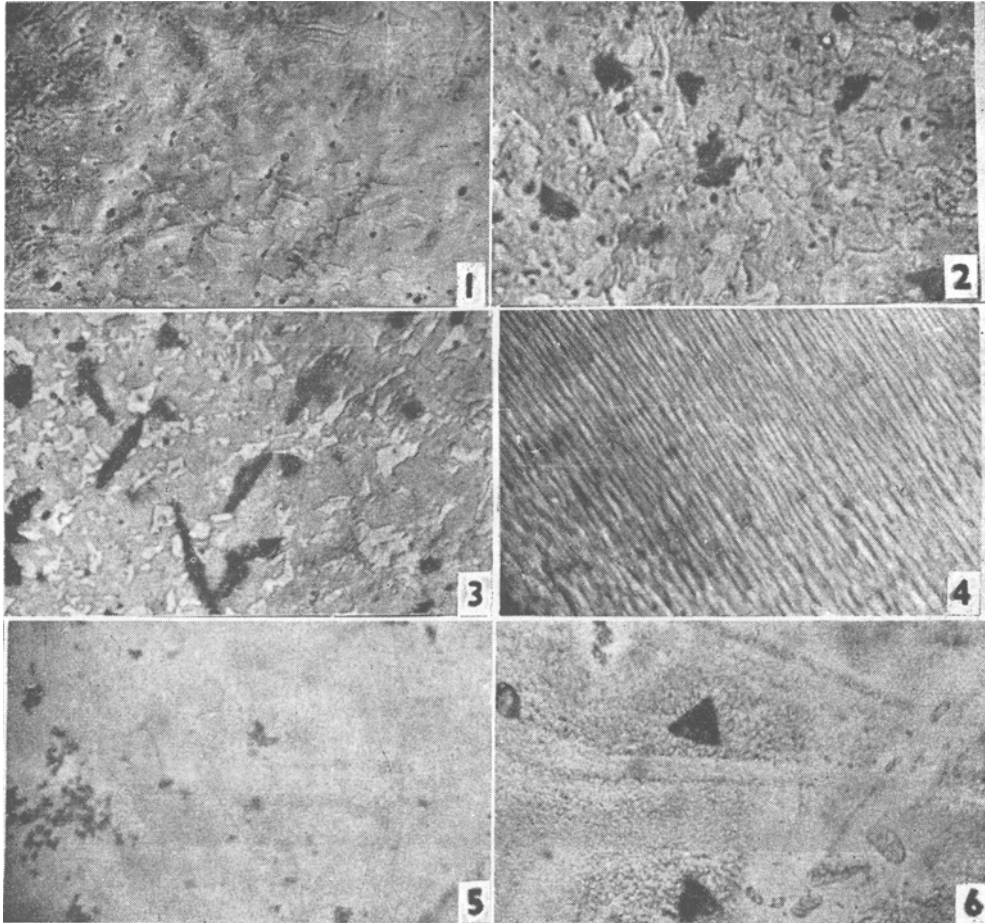
Deposition of cuprous chloride on polycrystalline and single crystals of copper

Concentration of HCl	Polycrystalline copper	Face of copper		
		(110)	(100)	(111)
2.0×10^{-3} m/L ..	Specks
2.5×10^{-3} m/L ..	Pyramids
3×10^{-3} m/L ..	Dendrites	Specks
3.25×10^{-3} m/L	do.	Pyramids	Specks	..
3.5×10^{-3} m/L ..	Many dendrites	Pyramids and occasional dendrites	Few pyramids	Specks
4×10^{-3} m/L ..	More dendrites	Pyramids and dendrites	Pyramids with twinning	Occasional pyramids
4.5×10^{-3} m/L	Dendrites	Dendrites	Pyramids with occasional dendrites

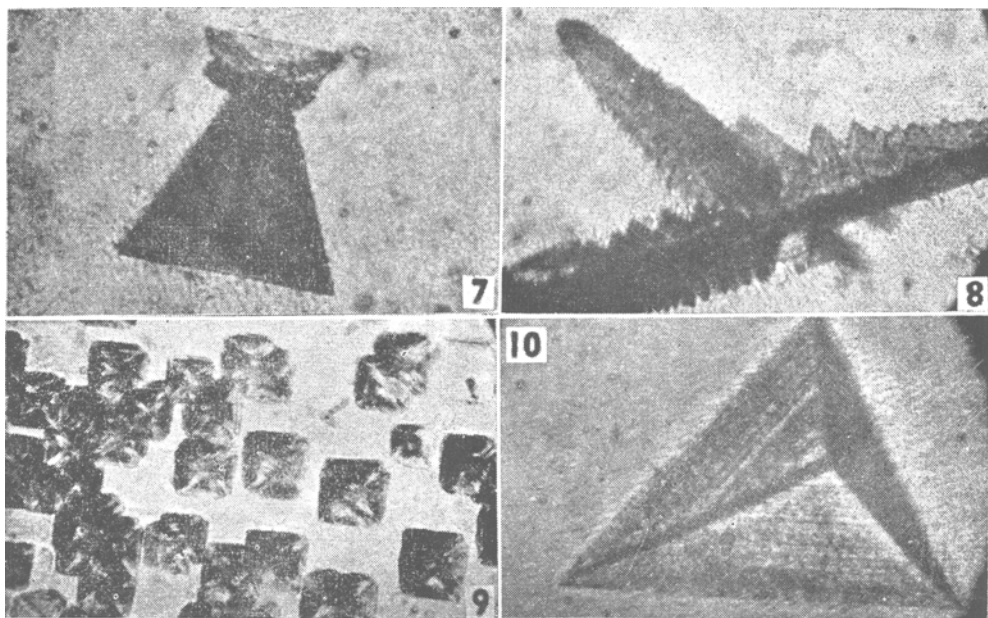
TABLE II

Deposition of cuprous bromide on polycrystalline and single crystals of copper

Concentration of HBr	Polycrystalline copper	Face of copper		
		(110)	(100)	(111)
1.5×10^{-4} m/L ..	Specks
1.75×10^{-4} m/L	Pyramids	Pyramids	Occasional pyramids	Specks
2×10^{-4} m/L ..	Dendrites	More pyramids	Few pyramids	Occasional pyramids
2.5×10^{-4} m/L ..	More dendrites	Dendrites	Pyramids	Pyramids
3×10^{-4} m/L ..	Dendrites	do.	Dendrites	Dendrites



FIGS. 1-6. Fig. 1. Dark specks of cuprous bromide on the polycrystalline base at 1.5×10^{-4} m/L of HBr ($\times 500$). Fig. 2. Triangular pyramids in the background of etched surface on polycrystalline base at 2.5×10^{-3} m/L HCl ($\times 500$). Fig. 3. Dendrites of cuprous chloride on polycrystalline base at 3×10^{-3} m/L HCl ($\times 500$). Fig. 4. Preferential etching of (110) surface in deaerated solution at 5×10^{-3} m/L HCl ($\times 500$). Fig. 5. Specks of cuprous chloride on (111) surface with a concentration of 3.5×10^{-3} m/L HCl. Fig. 6. Triangular pyramids on (100) surface at 3.5×10^{-3} m/L HCl ($\times 500$).



FIGS. 7-10. Fig. 7. Twinning of triangular pyramids on (100) surface at 4×10^{-3} m/L HCl ($\times 500$). Fig. 8. Dendritic growth on (100) surface at 4.5×10^{-3} m/L HCl ($\times 500$). Fig. 9. Preferential etching (100) surface in deaerated solution at 6.5×10^{-3} m/L HCl ($\times 500$). Fig. 10. Very big triangular pyramids of cuprous bromide on (100) surface at 1.75×10^{-4} m/L of HBr.

The fact that the critical concentration of hydrochloric on hydrobromic acid to get a precipitation of cuprous chloride or cuprous bromide on polycrystalline copper surface is low shows that the polycrystalline surface dissolves in acid copper sulphate solution at a faster rate. These results indicate the rates of dissolution of copper in acid copper sulphate solution is as follows:

Polycrystalline > (110) > (100) > (111).

It could be concluded that the presence of oxygen is necessary for the precipitation of cuprous chloride or cuprous bromide.

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