THE MORPHOLOGY OF COPPER ELECTRODEPOSITED FROM ACID COPPER SULPHATE BATH WITH Cl^- IONS ON COPPER (110) FACE

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ABSTRACT

Studies of copper electrodeposits, on to the (110) plane of copper was made from highly purified solutions of copper sulphate containing known concentration of HCl from 10^{-10} to 10^{-1} m./L. In presence of small amounts of HCl the morphology was not affected but deposition was facilitated. At higher concentration of HCl, CuCl was included in the deposit giving rise to polycrystalline deposit.

INTRODUCTION

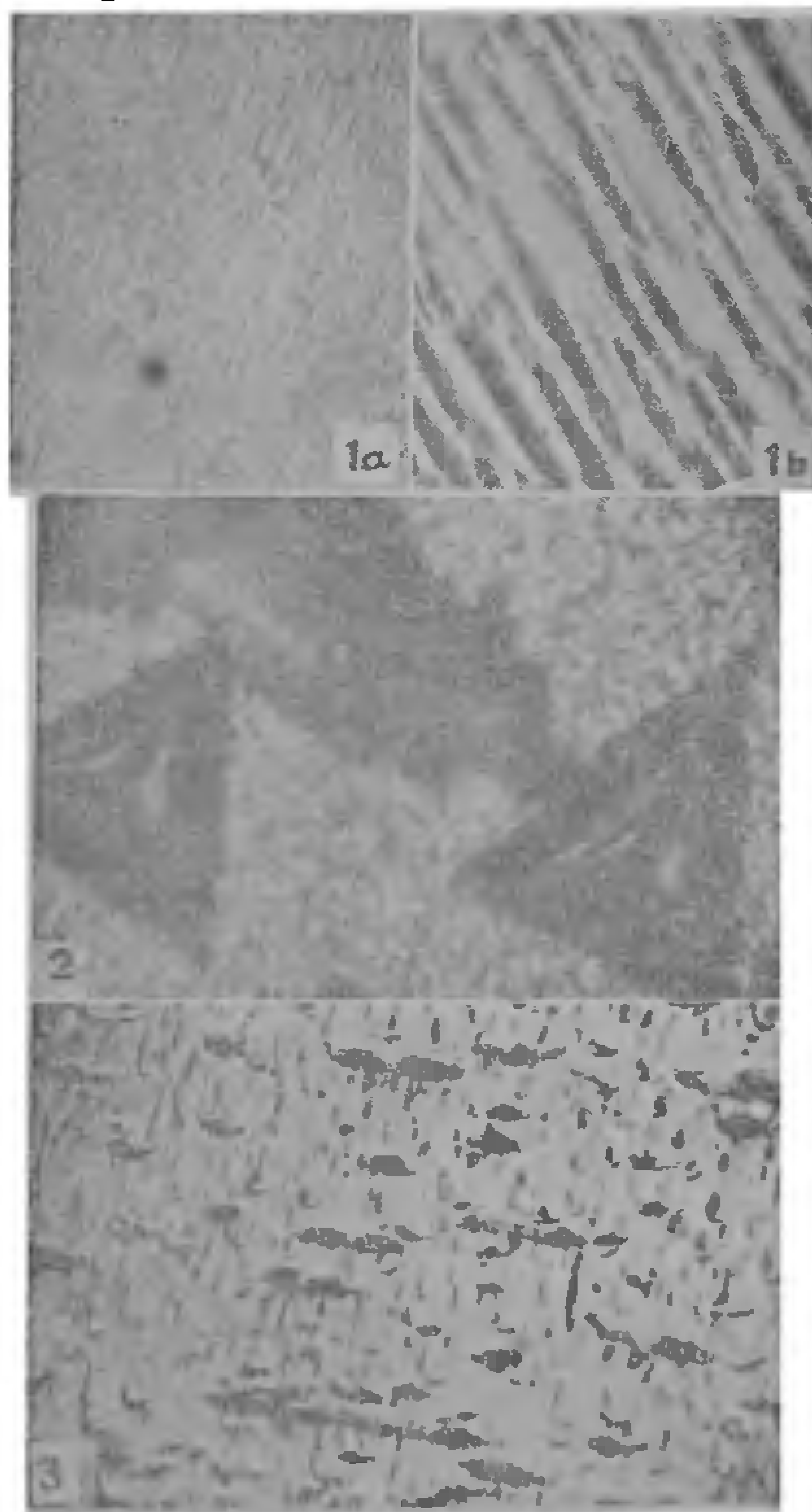
THE morphology of copper electrodeposits deposited on copper single crystal faces from pure acid copper sulphate bath has been studied.[1-4] It was observed that the morphology of deposit was influenced by the crystallographic orientation and bath conditions. Generally pyramids, layers and ridge type of growth were observed depending upon the substrate orientation and current density when deposited from very pure solutions. It was shown that the chloride ions present in bath modify the growth forms of copper electrodeposited on copper (100) face.[5] The present work was extended to study the effect of chloride ions on the morphology of copper electrodeposits deposited on (110) plane of copper.

The (110) plane was mechanically polished on emery-paper finishing with 4/0 and then electropolished in 1 : 1 H_3PO_4. The deposition was carried out at various current densities (*cd*) on the plane from $0 \cdot 25$ M $CuSO_4 + 0 \cdot 1$ M H_2SO_4 bath with a known amount of freshly distilled HCl. The thickness of the deposit was 10 C./cm.^{2} ($3 \cdot 5\,\mu$) in almost all cases. The deposit was examined under a metallurgical microscope and photomicrographs were taken. The other experimental details have been described earlier.[5]

RESULTS AND CONCLUSIONS

A ridge type of deposit was observed when copper was deposited from pure acid copper sulphate bath at all *cd* studied (2, 5, 10, 15 and 20 mA./cm.^{2}) as noticed by earlier workers.[2-4] These ridges were aligned parallel to [100] directions at 2 and 5 mA./cm.^{2}, whereas they were aligned parallel to [110] direction at or above 10 mA./cm.^{2} as observed earlier[2] and as shown in Figs. 1 (*a*) and (*b*). It was also noticed that the size of the ridges were bigger when deposited at higher *cd* (20 mA./cm.^{2}, Fig. 1 *b*).

The chloride ions would not affect the type of growth upto a concentration of 10^{-4} m./L of HCl at all *cd*. However, the direction of the ridges at or above 10 mA./cm.^{2} changed from [110] direction to [100] direction at 10^{-6} m./L of HCl, *i.e.*, the direction of the ridges would be the same as those obtained at 5 mA./cm.^{2} from very pure solution. The deposit obtained at $7 \cdot 5$ mA./cm.^{2} from pure solution showed that ridges were growing in both directions (Fig. 3). The ridges obtained at $7 \cdot 5$ mA./cm.^{2} from pure



FIGS 1–3. Fig. 1. (*a*) Ridges parallel to [100] direction when copper was deposited on Cu (110) from acid copper sulphate bath at 5 mA/cm.^{2}, × 500. (*b*) Ridges parallel to [110] direction when deposited at 20 mA/cm.^{2} × 500. Fig. 2. Polycrystalline deposit with CuCl on (110) from acid copper sulphate bath in presence of 10^{-4} m/L HCl at 5 mA/cm.^{2}, × 500. Fig. 3. Ridges growing in two directions when deposited at $7 \cdot 5$ mA/cm.^{2} on Cu (110) from acid copper sulphate bath, × 500.

solution at various thicknesses were examined. Upto 6 C./cm.^{2} the ridges were aligned along [100] direction only. At 8 C./cm.^{2}, ridges along [100] began to fade out and ridges along [110] direction began to grow. Above 15 C./cm.^{2} only ridges aligned along [110] were observed.

At 10^{-4} m./L of HCl the ridges broke up to small flat ridges. On further increase of the concentration of HCl to 10^{-2} m./L triangular pyramids of CuCl precipitated out during deposition as noticed in the case of [100] plane and a matty dull polycrystalline type of deposit resulted (Fig. 2). This transition from ridges to polycrystalline deposit was noticed at all *cd.*

The overpotential on [110] plane was always lower than on [100] plane at any corresponding *cd.* The overpotential remained constant with time except for the initial period at 2, 5, 10 and 20 mA./cm.^{2} but at 7·5 mA./cm.^{2} it increased upto a thickness of 8 C./cm.^{2} and then remained steady. The Tafel slope was 110 (± 5) mv. which shows that the r.d.s. is the charge transfer of first electron.[6] The presence of chloride ions upto a concentration of 10^{-6} m./L did not affect the value of overpotential but at 10^{-6} and 10^{-5} m./L of HCl the overpotential was very much lower than those from pure solution. For instance, the overpotential at 10 mA./cm.^{2} in pure solution was 110 (± 5) mv. whereas it was 70 (± 5) mv. at the same *cd* in presence of 10^{-6} m./L of HCl. This value of overpotential obtained in presence of chloride ions was nearer to the value of overpotential obtained at 5 mA./cm.^{2} from pure solutions. However, the Tafel slope did not change at that concentration.

When the concentration of HCl was increased further (10^{-4} m./L) the overpotential was higher than those obtained from pure solutions at corresponding *cd.* The Tafel relationship does not hold good at these concentrations of HCl as noticed by Bockris *et al.*[6]

It is noticed that the direction of ridges changes at higher *cd* from [100] to [110] in pure solution but in presence of chloride ions the direction of ridges would only be [100] even at higher *cd.* A close examination of overpotential indicates that the ridges align in [110] direction if the overpotential is below 100 mv. and in [110] direction when the overpotential is more than 100 mv. This idea is also supported by the fact that the overpotential at 7·5 mA./cm.^{2} in pure solution was between 75 and 100 mv when ridges aligned in both directions were observed. Some further experiments were carried out to test whether the direction of alignment of ridges really depends upon the overpotential.

It was observed that the presence of chloroacetic acid in copper sulphate bath increases the overpotential at all *cd* when deposited on (100) plane of copper.[7] Therefore the deposition of copper on copper (110) face was carried out from acid copper sulphate bath in presence of chloroacetic acid. It was observed that the overpotential would be more than 100 mv. even at 5 mA./cm.^{2} when the chloroacetic acid content was 10^{-2} m./L. It was also further observed that the ridges grew along [110] direction. This conclusively proves that the overpotential decides the direction of alignment of ridges.

It is known that chloride ions are highly polarisable anions and so they get specifically adsorbed on the surface. This adsorption of chloride ions may facilitate the incorporation of copper adions into crystal lattice along (100) direction without altering r.d.s. as indicated by Tafel slope. This shows that incorporation of adions is easier along [100] direction compared to [110] direction as expected since atomic density along [100] is lower than along [110]. At concentration higher than 10^{-4} m./L. of HCl the transition from ridge type of growth to random type growth takes place and CuCl precipitates out. It is possible therefore to assume that CuCl begins to get precipitated at growing centres of the plane and this obstructs the easy incorporation of copper adions as indicated by the increase of overpotential. The only alternative for copper adions is to nucleate randomly and grow which results in polycrystalline deposit.

Thus it could be concluded that the lower concentration of chloride ions facilitates the deposition without affecting the habit but higher concentration will affect the growth habit of deposition because of the inclusion of CuCl.

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