

ELECTRODEPOSITION OF COPPER ON COPPER SINGLE CRYSTAL (100) FACE IN PRESENCE OF CHLORIDE IONS*

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ABSTRACT

Observations of copper electrodeposits on to the (100) plane of copper was made from highly purified solutions of copper sulphate containing known concentration of hydrochloric acid from 10^{-10} to 10^{-1} m/L. In pure solutions at current densities of 5 and 10 mA/cm.² layers and pyramids were noticed. In the presence of hydrochloric acid of concentration 10^{-9} to 10^{-5} m/L there is a gradual decrease of distance between successive steps. At 10^{-4} m/L of HCl there was the breaking of layers giving rise to ridge type of growth. With the increase of concentration to 3.5×10^{-3} m/L pyramids appear again. On increasing the concentration of HCl to 10^{-2} m/L there was the formation of triangular pyramids of cuprous chloride and on still increasing the concentration, polycrystalline type of deposit was noticed. The transition from layer to ridge, ridge to pyramids and to polycrystalline deposit occurs at all c.d. studied but the critical concentration of HCl needed for the transition depends upon the current density.

INTRODUCTION

THE mechanism of electrocrystallisation of copper on copper single crystals when deposited from pure acid copper sulphate bath is fairly understood.^{1,2} It is known that the anions, specially halide ions, affect the electrode kinetics.^{3,4} Some studies have been carried out to investigate the role of chloride ions in copper refining⁵ and hydrogen overpotential on copper electrodes.⁶ However, in these cases only polycrystalline bases of copper are used. The authors⁷ studied the effect of chloride ions on the morphology of electrodeposits at lower current density.

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The purpose of this study is to find the effect of chloride ions on the morphology and overpotential at various current densities when copper is deposited from acid copper sulphate bath in presence of various amounts of chloride ions. It is noticed that there is transition from layer type of growth to ridge type and ridge type changes to pyramidal growth and then to polycrystalline deposit.

EXPERIMENTAL

Electrolytic Bath

All the glass vessels were soaked in acid mixture (1 : 1) (nitric : sulphuric acid) overnight and washed with distilled water and rinsed with conductivity water. Copper sulphate (A.R.S.M.) was crystallised twice from conductivity water. The twice crystallised copper sulphate was washed and dissolved in conductivity water. The concentrated solution was pre-electrolysed cathodically for twelve hours: at a constant c.d. of 10 mA/cm.². The pre-electrolysed solution was treated with activated charcoal and neutral alumina and was set aside with occasional shaking for twelve hours and filtered. Sulphuric acid (A.R.) and hydrochloric acid (A.R.) were distilled separately and treated with charcoal. A bath of composition 0.25 M copper sulphate and 0.1 M sulphuric acid and of desired concentration of hydrochloric acid was prepared and transferred to the electrolytic cell.

Cathode Preparation

(100) face of copper single crystal was mechanically polished on 4/0 emery paper using ethyl alcohol as lubricant. It was cleaned well with alcohol and washed with conductivity water. This was electropolished in 1 : 1 orthophosphoric acid for 30 minutes at a cell potential of 1.2 volts. The surface was washed first with 10% orthophosphoric acid and then with conductivity water. The crystal was transferred to the electrolytic cell immediately.

Procedure

The electrolytic cell consisted of three compartments as shown in Fig. 1. The cathode was placed in the middle compartment. Copper foil (A.R.), nearly 40 times to that of cathode, was washed with dilute nitric acid and with conductivity water and used as anode. Copper was deposited on platinum wire from acid copper sulphate bath at 1 mA/cm.² for 30 minutes. It was washed well with conductivity water and used as reference electrode. The electrodeposition was carried out at a known constant current density

to an average thickness of 10 C/cm.^2 at 25° C . The galvanostatic condition was maintained by using $\approx 90 \text{ v}$ dry battery and with resistors. The over-potential was recorded at regular intervals using V.T.V.M. with reference to freshly prepared copper electrode with an accuracy of $\pm 5 \text{ mV}$. The cathode was taken out after the deposition without switching off the current and washed with conductivity water and then with alcohol. The surface appearance of the deposit was examined under phase contrast microscope and microphotographs were taken.

RESULTS

Morphology

At 2 mA/cm.^2 —At 2 mA/cm.^2 a layer type of deposit is obtained when copper was deposited on (100) face from very pure solution. This is a characteristic deposit of copper at low current densities.⁸ The distance between the layers becomes smaller and the layers catch up with neighbouring layers and become longer (Figs. 2 and 3) when the concentration of hydrochloric acid in the bath is increased from 10^{-10} to 10^{-4} m/L . There is transition from layer type to ridge type of deposit as the concentration of hydrochloric acid is increased to $2.5 \times 10^{-4} \text{ m/L}$. The deposit consists of layers and striations near the steps as seen in Fig. 4. These striations extend as ridges and layers almost disappear and there is a gap between one set of ridges and another set at $5 \times 10^{-4} \text{ m/L}$ hydrochloric acid (Fig. 5). The deposit was completely transformed into ridge type in presence of 10^{-3} m/L hydrochloric acid (Fig. 6). The direction of ridges is perpendicular to the layers. When $3.5 \times 10^{-3} \text{ m/L}$ of hydrochloric acid is added to the bath occasional very big pyramids are growing along with the ridges. The pyramids break up to four parts and there is a drag in the direction of the ridges as shown in Fig. 7. As the concentration is increased to $4 \times 10^{-3} \text{ m/L}$ hydrochloric acid triangular pyramids with dendrites are growing in the background of flat ridges⁷ (refer Fig. 10). More dendrites grow as the concentration of hydrochloric acid is increased. The deposit is polycrystalline at concentration 10^{-1} m/L of hydrochloric acid (Fig. 8) and the deposit appears dirty grey and non-uniform.

At 5 mA/cm.^2 —The type of growth at this current density is the same as at 2 mA/cm.^2 except that the distance between layers is large. The addition of hydrochloric acid to the bath brings about the same type of change in growth as at 2 mA/cm.^2 up to 10^{-4} m/L . At 10^{-4} m/L of hydrochloric acid, the layers become short and cone type. There are tooth-like striations at the steps, all in one direction which grow as ridges when the con-

centration of hydrochloric acid is increased to 10^{-3} m/L as shown in Fig. 6 already. Occasional pyramids appear in the background of ridges as noticed at 2 mA/cm^2 . Triangular pyramids and the dendritic growth is observed at a higher concentration of hydrochloric acid (10^{-2} m/L) compared at 2 mA/cm^2 . At 10^{-1} m/L of hydrochloric acid the polycrystalline deposit was obtained and the deposit was grey and not smooth and does not adhere to the substrate firmly.

At 10 mA/cm^2 —The deposit obtained from pure solution consists of layers and small pyramids.⁸ When the concentration of hydrochloric acid in the bath is 10^{-4} m/L, the layers become short and coney and there are striations at the steps. The ridge type of deposit is obtained at concentration of 10^{-3} m/L hydrochloric acid. The deposit consists of a large number of small pyramids which are dragged in the direction of ridges (Fig. 9) when the concentration of hydrochloric acid is 10^{-2} m/L. Mostly, triangular pyramids with twinning appear (Fig. 10) which become dendritic at concentration of 10^{-1} m/L. It is noticed that the polycrystalline deposit occurs at a higher concentration of hydrochloric acid compared to lower current density which does not adhere firmly to the substrate.

At 15 mA/cm^2 —There are pyramids (some are truncated) in a background of layer in the deposit when copper is deposited at 15 mA/cm^2 from pure solution. When the concentration of hydrochloric acid is increased to 10^{-3} m/L there are more truncated pyramids (Fig. 11). At 10^{-2} m/L hydrochloric acid very large number of small clear pyramids with slight dragging are observed (compare Fig. 9). At 10^{-1} m/L hydrochloric acid small triangular pyramids with tendency for the dendritic growth are observed.

At 20 mA/cm^2 —The deposit was similar to that at 15 mA/cm^2 except that there are more pyramids. As the concentration of hydrochloric acid is increased, the deposit consists of only pyramids most of them truncated. At 10^{-2} m/L hydrochloric acid more pyramids grow on the truncated pyramids. When the concentration is increased to 10^{-1} m/L hydrochloric acid occasional triangular pyramids appear, but the dendritic growth is not clear as observed at lower current densities. The deposit is also very rough.

Further, it is noticed that the size of triangular pyramids decreases with increase of current density. It is elsewhere shown by the authors⁹ that the cuprous chloride precipitates out as triangular pyramids when copper (polycrystalline or single crystal surface) is immersed in acid copper sulphate bath containing chloride ions.

Overpotential

The reproducibility of the overpotential curves varies with the amount of hydrochloric acid. Hence it is only possible to give a qualitative evaluation of the results obtained. The overpotentials at all current densities in pure solution initially increase and attain a constant value² (Fig. 12). The initial overpotential at all current densities in presence of chloride ions is higher than in the pure solution at given c.d. At lower current densities (2.5, and 10 mA/cm.²) the overpotential decreases with time and reaches a steady state at a concentration less than 10⁻³ m/L and more than 10⁻⁴ m/L. However at concentration 10⁻³ m/L where ridge type deposit grows, the overpotential remains constant throughout the deposition. When chloride ion concentration is more than 10⁻² m/L the overpotentials are fluctuating. At 15 and 20 mA/cm.² the potential below 10⁻⁴ m/L increases initially and reaches a steady state. When ridge type of deposit is growing, when the chloride concentration is 10⁻³ m/L the potential again remains almost constant. At higher concentration of hydrochloric acid the potentials are not steady.

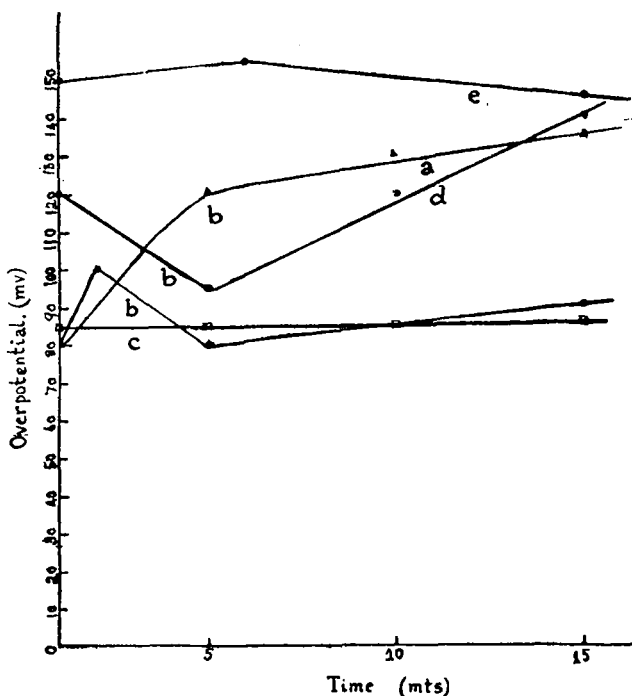


FIG. 12. Deposition at 10 mA/cm.² (change of overpotential with time). (a) Pure solution, (b) 10⁻⁴ m/L HCl, (c) 10⁻⁵ m/L HCl, (d) 10⁻³ m/L HCl, (e) 10⁻² m/L HCl,

The η - $\log i$ relation is linear in pure solution with the slope $120 \pm \text{mV}$ (Fig. 13). The Tafel relationship approximately holds good in presence of chloride ions also with the slope of about 120 mV . When ridge type of growth is observed in presence of $1 \times 10^{-3} \text{ m/L}$ of HCl the relationship is linear and the Tafel slope is $120 \pm 5 \text{ mV}$. At higher concentration of HCl there are deviations from Tafel relationship. This may be because the surface is covered partly by cuprous chloride.

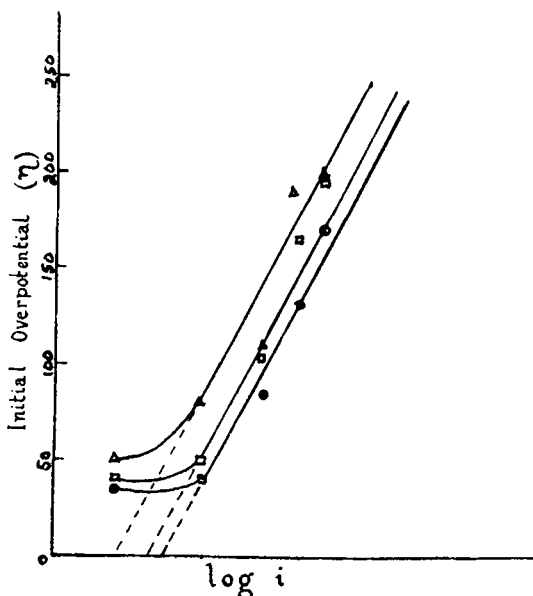


FIG. 13. Tafel lines in presence of HCl and pure solution. Pure solution, ○. 10^{-3} m/L HCl , □. 10^{-4} m/L HCl , △.

There is not much change in the i_0 values obtained which indicates no change in the mechanism of the electrochemical reaction.

DISCUSSION

Bockris and co-workers^{4, 10, 11} have extensively studied the mechanism of copper deposition reaction and have established that the rate determining step is first charge transfer in the range of current densities studied by us.

The reaction could be written as follows :



The available data of overpotential measurements in presence of chloride ions, though insufficient, indicate that there is no change in the mechanism of the reaction. However, the fact that the initial overpotential at all current densities in presence of chloride ions is higher than those from pure solutions, show that the diffusion and incorporation of adions are abstracted without affecting the rate-determining step.

The chloride ion is a highly polarisable ion and it may get specifically absorbed on the surface of the copper electrode at lower concentrations affecting the movement of layers which is indicated by the fact that the distance between layers is narrowed down as the concentration of chloride ions is increased. When the concentration is increased higher than 10^{-4} m/L there is a possibility of the precipitation of cuprous chloride as its solubility is 1.1×10^{-3} m/L.¹² The cuprous chloride precipitated out may block the diffusion of adions to the sink sites. These adions then may diffuse easily in (110) or (100) face. As $\langle 110 \rangle$ are directions of easiest surface diffusion¹³ and they crystallise at most favourable deposition sites which are alligned in this direction.¹⁴ Thus the transition to ridge type may take place. At higher current densities (10 and 15 mA/cm.²) and at 10^{-2} m/L hydrochloric acid the initial overpotentials are 120 and 240 mV respectively. The adions may acquire sufficient energy under these conditions and crystallise as pyramids at favourable sites by displacing the blocking cuprous chloride. However, cuprous chloride may affect only the bunching mechanism. The cuprous chloride at higher concentration of hydrochloric acid codeposits in large quantities and thus may block all the growth sites. Under these conditions deposition of copper takes place by randum nucleation which produces only polycrystalline deposit. The transition of layer growth to other types is mainly due to the inclusion of cuprous chloride.

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EXPLANATION OF PLATES

PLATE IX

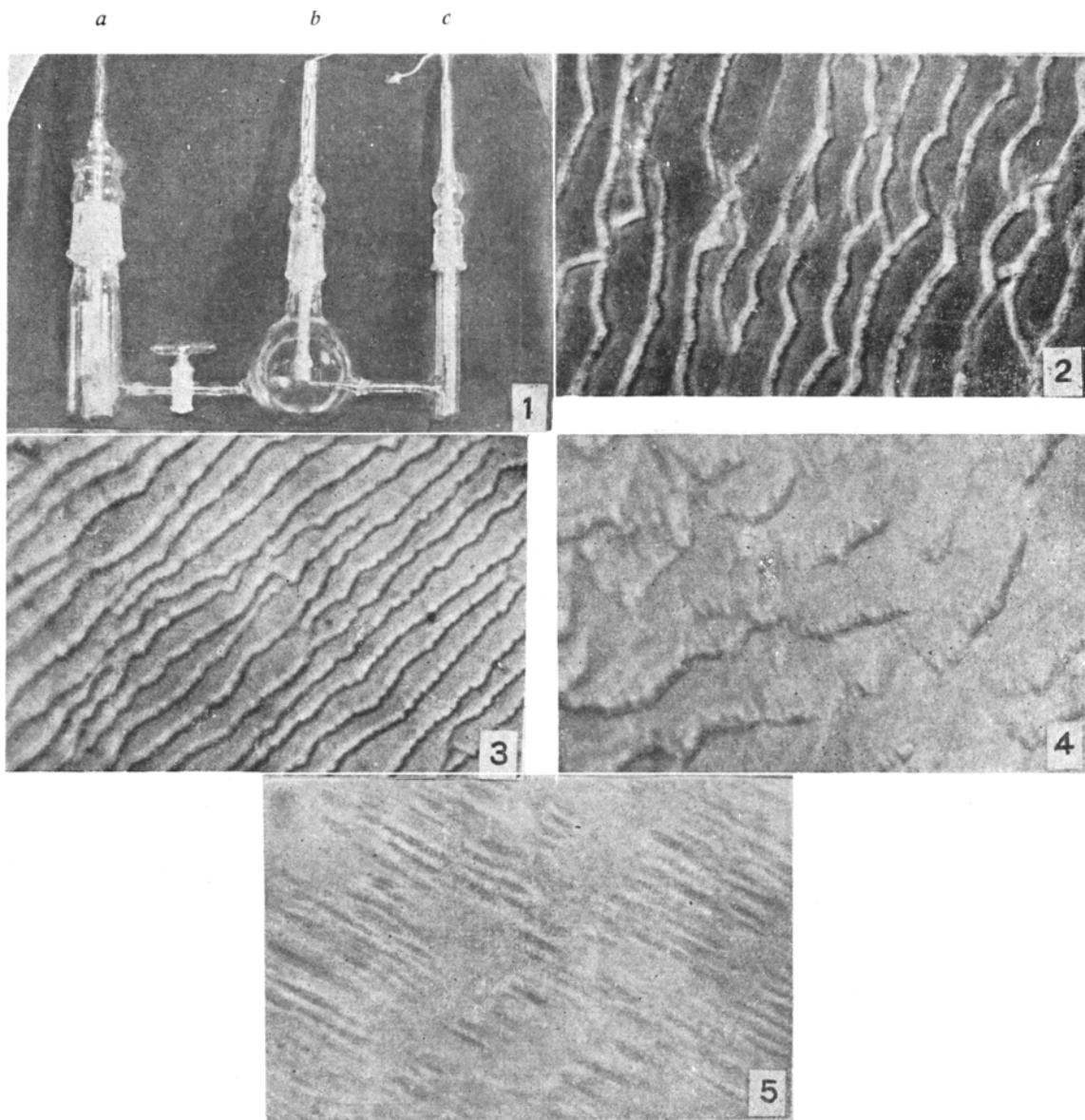
FIGS. 1-5

- FIG. 1. Electrolytic cell, (a) Anode, (b) Test electrode, (c) Reference electrode.
- FIG. 2. Copper deposited on Cu (100) from acid copper sulphate bath at 2 mA/cm.² (× 500).
- FIG. 3. Shortening of layers on the (100) plane at 2 mA/cm.² with 10⁻⁴ m/L HCl (× 500).
- FIG. 4. Transition from layers to ridges on the (100) plane at 2 mA/cm.² with 2.5 × 10⁻⁴ m/L HCl (× 500).
- FIG. 5. Layers changing into ridges on the (100) plane at 2 mA/cm.² with 3.5 × 10⁻⁴ m/L HCl (× 500).

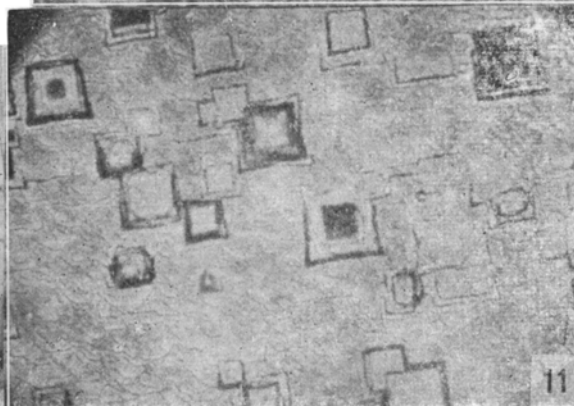
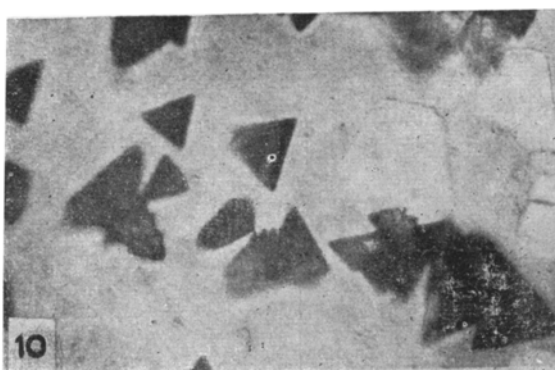
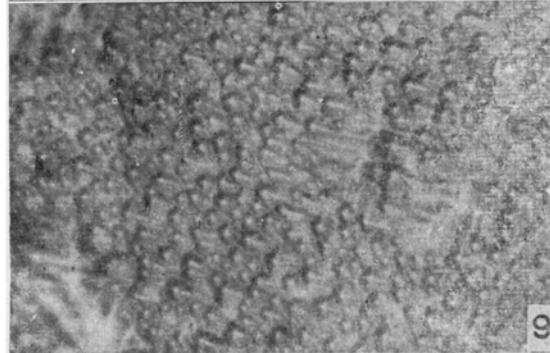
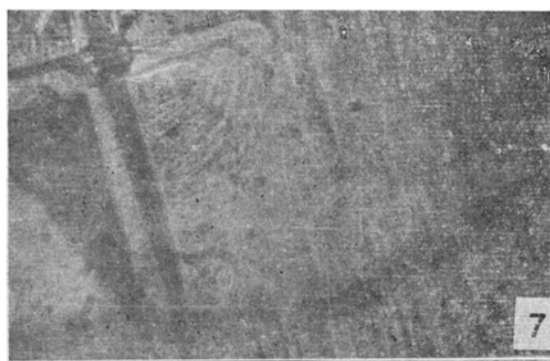
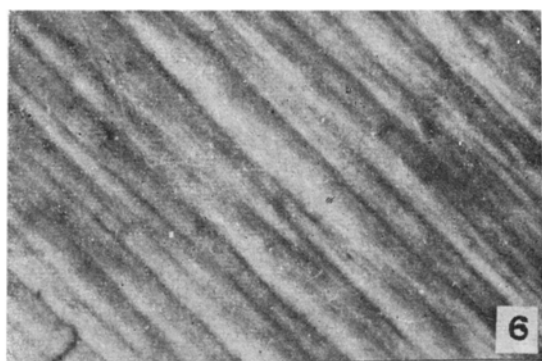
PLATE X

FIGS. 6-11

- FIG. 6. Ridge type of growth on the (100) plane at 2 mA/cm.² with 10⁻³ m/L HCl (× 500).
- FIG. 7. Ridges and breaking up of pyramids on the (100) plane at 2 mA/cm.² with 2.5 × 10⁻³ m/L HCl (× 500).
- FIG. 8. Polycrystalline on the (100) plane at 2 mA/cm.² with 10⁻¹ m/L HCl (× 500).
- FIG. 9. Formation of small pyramids on (100) plane at 10 mA/cm.² with 10⁻² m/L HCl (× 500).
- FIG. 10. Triangular pyramids of CuCl with twinning on the (100) plane at 10 mA/cm.² with 10⁻¹ m/L HCl (× 500).
- FIG. 11. Truncation on pyramic on the (100) plane at 15 mA/cm.² with 10⁻² HCl (× 500).



FIGS. 1-5



FIGS. 6-11