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 $3.5 \times 10^{-3}$ 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 refining$^{5}$ and hydrogen overpotential on copper electrodes.$^{6}$ However, in these cases only polycrystalline bases of copper are used. The authors$^{7}$ 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/cm². 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/cm² 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