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Electrodeposition of copper on the copper (1 0 0) face in the presence of 2-mercaptoethanol

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Observations were made of the morphological changes which occur during the electrodeposition of copper on the copper (1 0 0) plane from an acid sulphate bath and in the presence of known concentrations of 2-mercaptoethanol at various current densities. At lower current densities, there was a transition from layers to ridges and then to polycrystalline growth with increasing concentration of 2-mercaptoethanol. At higher current densities the change was from pyramids to truncated blocks, then to ridges and finally to a polycrystalline deposit. The electrokinetic parameters have been correlated with these morphological changes and transport mechanisms have been proposed for different concentrations of the addition agent.

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1. Introduction

The favourable effects of organic addition agents on the properties of electrodeposits have been known for a number of years [1, 2]. A few workers [3, 4] have investigated the effect of sulphur compounds during the electrodeposition of metals and have noted the effects on the kinetics of the deposition process and the morphology of the electrodeposits. However, very few attempts have been made to understand the transport mechanisms in the presence of addition agents in the bath and to identify the products formed during the process.

In the present work, for the first time, the morphological and electrochemical effects brought about by 2-mercaptoethanol, the reaction pathway and the degradation products formed during the electrodeposition of copper on the copper (1 0 0) plane from an acid sulphate bath have been investigated. The compound reduces the overpotential and causes the morphological changes which occur during the deposition process. The changes in morphology and the electrokinetic parameters in the presence of 2-mercaptoethanol have been explained by different transport mechanisms at different concentrations of the addition agent.

2. Experimental procedure

The experimental procedure was described in detail earlier [5]. An atomically smooth (1 0 0) face of copper (checked by X-ray diffraction) was prepared by electropolishing in a phosphoric acid bath at a cell potential of 1.2 V [6]. An electrolytic bath of composition 0.25 mol dm^{-3} $CuSO_4$ in 0.1 mol dm^{-3} H_2SO_4 was prepared and 2-mercaptoethanol (Fluka, AG) of desired concentration was used. The deposition was carried out at 2, 5, 10 and 15 mA cm^{-2} to a thickness corresponding to 3.6 μm with a coulombic charge of 10 C cm^{-2}. The cathodic overpotential was measured with reference to a freshly prepared copper electrode to an accuracy of ± 5 mV using an Elico digital pH meter. The concentration polarization correction has been incorporated by taking the difference in the values of the overpotential with and without stirring. The ohmic overpotential was removed using a Luggin's capillary in the deposition cell. The surface morphology of the deposits was examined under a phase contrast microscope at a magnification of x 625 and photomicrographs were obtained.

The solid obtained when a high concentration of 2-mercaptoethanol was added to acid copper sulphate solution was separated and purified, and

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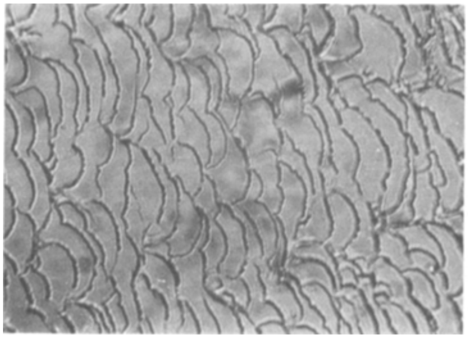


Fig. 1. Layer type of deposit on copper (1 0 0) plane from acid copper sulphate bath at 2 mA cm^{-2} (Magnification 625 ×).

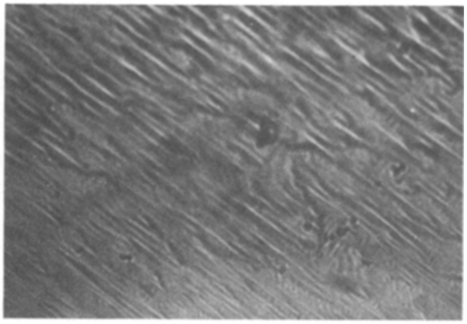


Fig. 3. Ridge type of growth on copper (1 0 0) plane from acid copper sulphate bath with 10^{-8} mol dm^{-3}, 2-mercaptoethanol at 2 mA cm^{-2} (Magnification 625 ×).

an infra-red spectrum of the solid was obtained (Carl Zeiss UR 10 infra-red Spectro-photometer).

3. Results

3.1. *Surface morphology*

3.1.1. At 2 mA cm^{-2}. A characteristic layer type of deposit was observed when copper was electrodeposited on the copper (1 0 0) face from pure solution (Fig. 1). Up to a concentration of 10^{-10} mol dm^{-3} of 2-mercaptoethanol there was very little change in the growth habit. As the concentration of 2-mercaptoethanol was gradually increased, the distance between the layers became less and less (Fig. 2). At a concentration of 10^{-8} mol dm^{-3}, the broken layers disappeared completely and ridge growth was seen (Fig. 3). When the concentration of the addition agent was further increased to 2 x 10^{-6} mol dm^{-3}, the deposit became completely polycrystalline (Fig. 4). At a concentration of 10^{-5} mol dm^{-3} dark pyramids were observed in the background of the polycrystalline deposit.

3.1.2. At 5 mA cm^{-2}. The type of growth at this current density in pure solution was same as that obtained at 2 mA cm^{-2}, except that the distance between the layers was greater. When the concentration of 2-mercaptoethanol was gradually increased up to 10^{-9} mol dm^{-3} the distance between the layers became less. At a concentration of 10^{-8} mol dm^{-3}, the layers became short and cone-shaped, and there was a tendency for these to break up into arrow-like growths all in one direction (Fig. 5) with tooth-like stiations at the steps. When the concentration was increased to 10^{-7} mol dm^{-3}, the layers changed completely to a

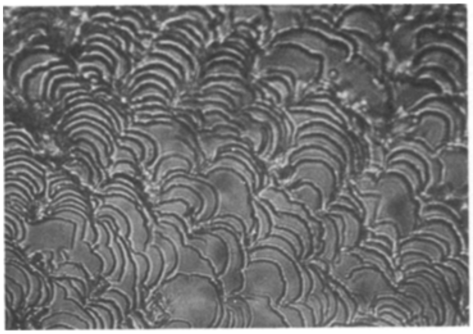


Fig. 2. Small layers on copper (1 0 0) plane from acid copper sulphate bath with 10^{-9} mol dm^{-3}, 2-mercaptoethanol at 2 mA cm^{-2} (Magnification 625 ×).

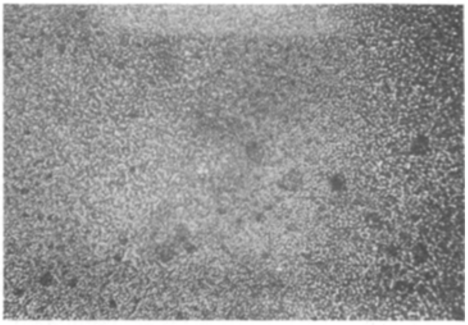


Fig. 4. Polycrystalline deposit on copper (1 0 0) plane from acid copper sulphate bath with 2 × 10^{-6} mol dm^{-3} 2-mercaptoethanol at 2 mA cm^{-2} (Magnification 625 ×).

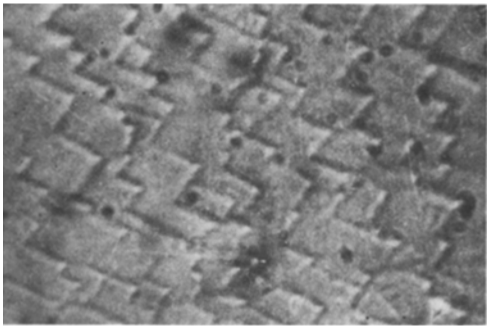


Fig. 5. Layer type of growth giving rise to an arrow type of growth in the [1 1 0] direction during the electrodeposition of copper on the copper (1 0 0) face from an acid sulphate bath with 10^{-8} mol dm^{-3} 2-mercaptoethanol at 5 mA cm^{-2}.

ridge type of growth. At a concentration of 2×10^{-6} mol dm^{-3}, a polycrystalline deposit was obtained. When the concentration was increased to 10^{-5} mol dm^{-3} dark pyramids were seen in the background of the polycrystalline deposit.

3.1.3. At 10 mA cm^{-2}. The deposit obtained at this current density consisted of layers and small pyramids (Fig. 6). At a concentration of 10^{-10} mol dm^{-3} 2-mercaptoethanol, the number of pyramids decreased and layers were observed. At a concentration of 10^{-9} mol dm^{-3} the number of pyramids decreased further, and layers and truncated pyramids continued to grow. When the concentration of the addition agent was 10^{-8} mol dm^{-3}, the pyramidal growth disappeared completely and the distance between the layers became less. As the concentration was increased to 10^{-7} mol dm^{-3}, only ridge-type growth was seen. When the concentration was 2×10^{-6} mol dm^{-3}, the deposit became polycrystalline. At a concentration of 10^{-5} mol dm^{-3}, dark pyramids were seen in the polycrystalline background.

3.1.4. At 15 mA cm^{-2}. In pure solution, non-symmetrical pyramids and truncated pyramids were seen in the background of the layers at this current density. At a concentration of 10^{-10} mol dm^{-3} of 2-mercaptoethanol, there was not much change in the growth habit of the deposit except that the size of the pyramids increased and the number of pyramids decreased. When the concentration was increased to 10^{-9} mol dm^{-3}, more truncation of the pyramids was observed. The layers disappeared and the pyramids became symmetrical. At 10^{-8} mol dm^{-3} only square truncated pyramids were observed (Fig. 7). When the concentration of 2-mercaptoethanol was 10^{-7} mol dm^{-3}, ridge growth was observed. At a concentration of 2×10^{-6} mol dm^{-3}, the deposit became completely polycrystalline. When the concentration of 2-mercaptoethanol was further increased to 10^{-5} mol dm^{-3}, dark pyramids were seen in the background of the polycrystalline deposit.

3.2. *Overpotentials*

The overpotential in pure solution increased with time and attained a steady value at all the current densities studied. In the presence of 2-mercaptoethanol the overpotential value was always less than that of the pure solution at a corresponding

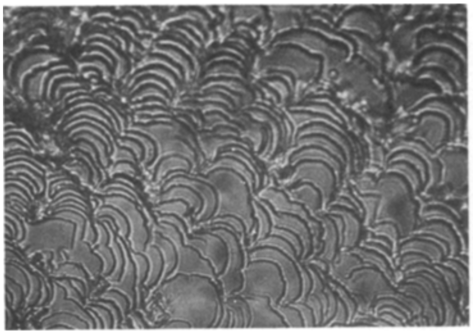


Fig. 6. Layers and small pyramids on copper (1 0 0) plane from acid copper sulphate bath at 10 mA cm^{-2} (Magnification 625 X).

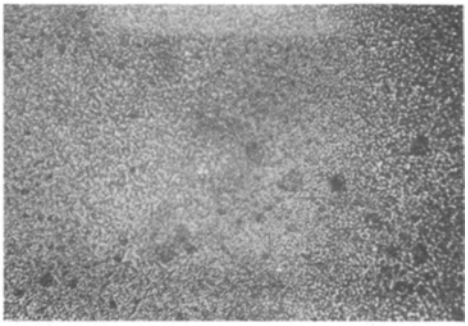


Fig. 7. Truncated pyramids on copper (1 0 0) plane from acid copper sulphate bath with 10^{-8} mol dm^{-3}, 2-mercaptoethanol at 15 mA cm^{-2} (Magnification 625 X).

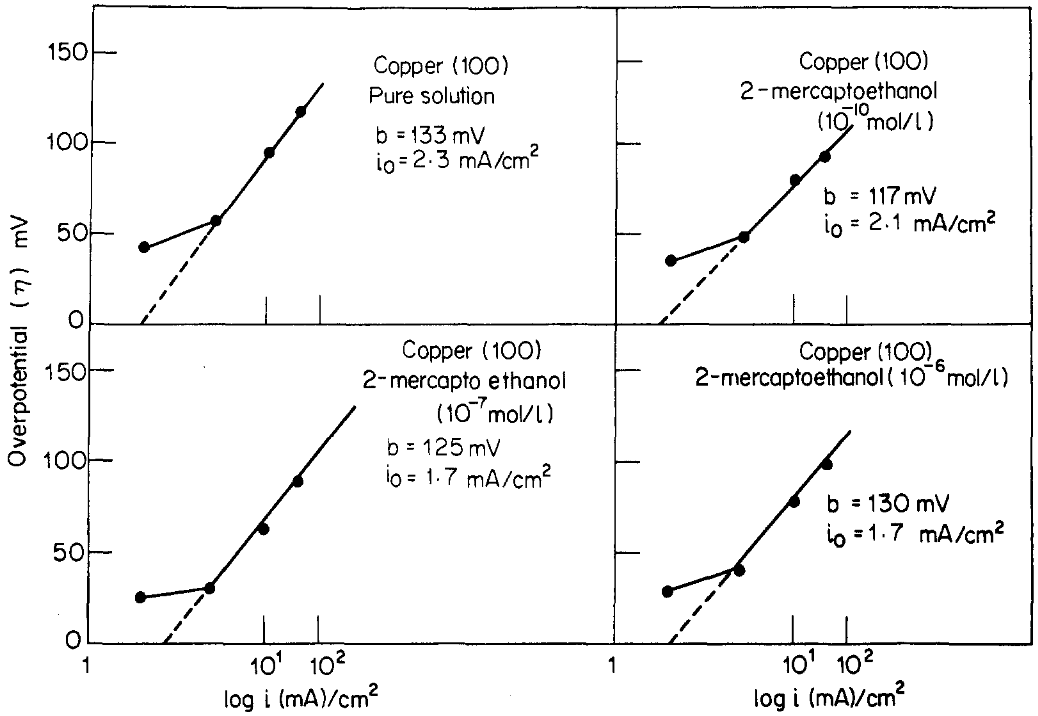


Fig. 8. The Tafel relationship for electrodeposition of copper on the copper (1 0 0) plane from pure solution and in the presence of 2-mercaptoethanol.

current density. During layer growth, the overpotential decreased with time and attained a steady value. When pyramids formed, the overpotential decreased with time and reached a steady value. The overpotential was almost steady during the formation of ridge-type growth. The Tafel relationship holds good only at low concentrations of 2-mercaptoethanol. There was a decrease in the value of i_0 in the presence of 2-mercaptoethanol (Fig. 8). At very high concentrations of 2-mercaptoethanol the Tafel relationship does not hold well.

3.3. *Infra-red spectra*

In the spectrum of 2-mercaptoethanol there is an absorption peak at 2550 cm^{-1} corresponding to the stretching vibration of the –S–H group. In the spectrum of the compound obtained with copper sulphate solution and 2-mercaptoethanol, this peak is absent.

4. Discussion

The observed $2RT/F$ value for the Tafel slope in pure solution on the copper (1 0 0) plane is in accordance with mechanism:

$$\mathrm{Cu^{2+} + e \xrightarrow{Slow} Cu^{+}}$$

$$\mathrm{Cu^{+} + e \xrightleftharpoons{Fast} Cu}$$

as found by Conway and Bockris [7]. The Tafel slope in the presence of low and moderate concentrations of 2-mercaptoethanol is found to be 130 ± 5 mV. This shows that there is no change in the reaction path, i.e. the first electron transfer step is the rate determining step.

The overpotential value during deposition in the presence of the addition agent is less than that of the pure solution at the corresponding current density studied. This indicates that 2-mercaptoethanol stimulates the discharge process.

As 2-mercaptoethanol contains a highly polarizable –S–H group [8] it may bring about rapid changes at the metal–solution interface, in complex-ion formation, in cathodic incorporation of foreign absorbates and changes in crystallographic properties during deposition [9]. At higher concentrations, precipitation can also take place.

At low concentrations of 2-mercaptoethanol the following transport mechanism may take place

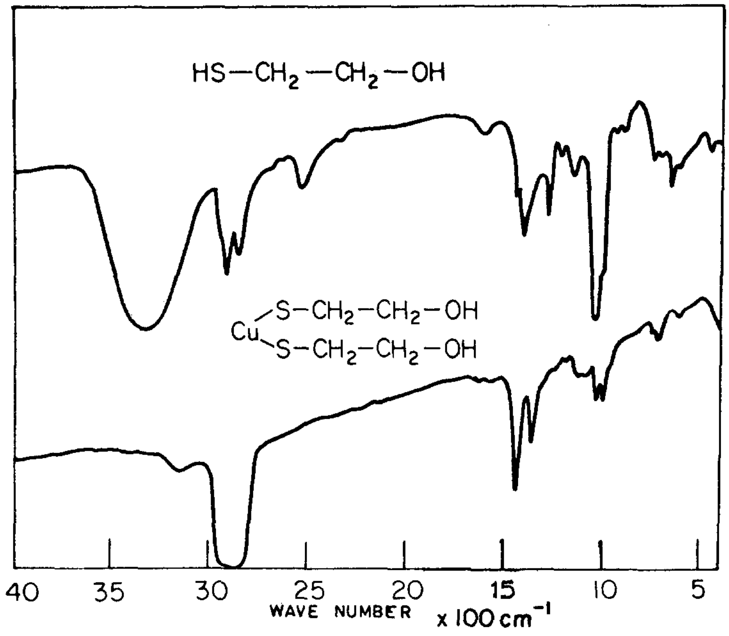


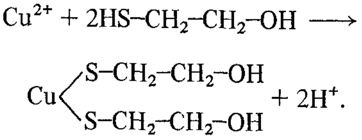
Fig. 9. Infra-red spectra of 2-mercaptoethanol and copper mercaptide.

across the metal–solution interface:

$$Cu^{2+} + HS{-}CH_2{-}CH_2{-}OH \longrightarrow [Cu{-}(S{-}CH_2{-}CH_2{-}OH)]^+ + H^+.$$

The compound formed in the above reaction may degrade to give Cu^+ ions, thereby facilitating the cation transfer at a faster rate, resulting in a decrease in the overpotential.

At moderate concentrations of 2-mercaptoethanol, as indicated by the infra-red spectra (Fig. 8), the transport mechanism may take place through the formation of copper mercaptide:



$$Cu^{2+} + 2HS{-}CH_2{-}CH_2{-}OH \longrightarrow Cu\begin{cases} S{-}CH_2{-}CH_2{-}OH \\ S{-}CH_2{-}CH_2{-}OH \end{cases} + 2H^+.$$

The copper mercaptide may be absorbed on to the surface of the copper electrode, affecting the movement of the steps, so that the distance between the layers decreases as the concentration of 2-mercaptoethanol is increased. The precipitation of copper mercaptide at the metal–solution interface obstructs a considerable number of growth sites and finally hinders growth so much that the old layer stops growing and a new layer starts to grow instead. Thus, with an increase in the concentration of 2-mercaptoethanol the layers are shortened. Further, the copper mercaptide may interfere with the diffusion of adions to kink sites. These adions then may diffuse easily in the [1 1 0] direction of the (1 0 0) face. As [1 1 0] are directions of easiest surface diffusion they crystallize at the most favourable deposition sites (Fig. 10) aligned in this direction [10]. At higher current densities, however, the adions may acquire sufficient energy to crystallize as pyramids at favourable sites by displacing the blocking copper

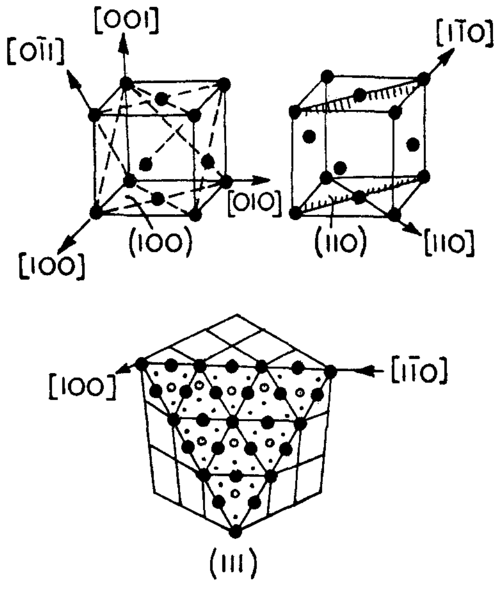
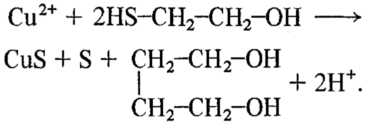


Fig. 10. Structure of a copper (1 0 0) single crystal.

mercaptide. As the concentration of 2-mercaptoethanol is increased, the copper mercaptide may be adsorbed on the apexes of the pyramids. Thus the vertical growth of the pyramids may be hindered leading to truncated pyramids. Further growth may occur laterally, giving rise to layer growth with the gradual disappearance of pyramids. At still higher concentrations of 2-mercaptoethanol, the copper mercaptide may co-deposit in large quantities and thus block all the growth sites. Under these conditions deposition of copper takes place by random nucleation which produces only a polycrystalline deposit.

At very high concentrations of 2-mercaptoethanol, the transport mechanism may be affected by the precipitation of CuS.



$$Cu^{2+} + 2HS{-}CH_2{-}CH_2{-}OH \longrightarrow$$

$$CuS + S + \begin{array}{l} CH_2{-}CH_2{-}OH \\ | \\ CH_2{-}CH_2{-}OH \end{array} + 2H^+.$$

CuS is precipitated in the form of dark triangular pyramids [11].

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References

[1] A. Seiter, H. Fischer and L. Albert, *Electrochim. Acta* **2** (1960) 97.
[2] L. L. Shrier and J. W. Smith, *Trans. Faraday Soc.* **50** (1954) 393.
[3] S.C. Barnes, *J. Electrochem. Soc.* **111** (1964) 296.
[4] K. Subramanian and S. Nageswar, *Surf. Technol.* **9** (1979) 103.
[5] S. Nageswar and T. H. V. Setty, *Proc. Indian Acad. Sci. LXVII Sec. A* **VIII (4)** (1968) p. 178.
[6] P. Jacquet, *CR Acad. Sci.* **201** (1935) 1473.
[7] B. E. Conway and J. O. M. Bockris, *Electrochem. Acta* **3** (1961) 340.
[8] J. M. West, 'Electrodeposition and Corrosion process', Van Nostrand Reinhold, Eastborne, New York (1970) p. 123.
[9] H. Fischer, *J. Electrochem. Soc.* **354** (1967) 169.
[10] N. Hackerman and H. N. Simpson, *Trans. Faraday Soc.* **52** (1956) 628.
[11] E. S. Dana, 'A Text Book of Mineralogy', John Wiley & Sons, Chichester (1948) p. 429.