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Cathodic process in copper–tin deposition from sulphate solutions

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Data on cathodic processes in sulphate solutions containing Cu(II) and Sn(II) ions and H_2SO_4 with and without Laprol 2402C (OA) is given. The sequence of cathodic processes and their dependence on the electrolyte composition were determined. The presence of OA extended the range of cathodic current densities (i_c) at which a high quality alloy was obtained. Electrolysis conditions under which the cathodic process rates considerably decrease were found. This is caused by passivation of the cathode surface by the film formed. The cathode passivation is accompanied by periodic oscillations. Anodic current peaks, i.e. 'reverse' maxima, were found to occur during reverse potential sweeps. The peak values depended on the potential at which the reverse sweep began.

1. Introduction

The process of copper–tin alloy electrodeposition has been widely applied in industry [1, 2]. Either cyanic [3–5] or boron–fluoride [6, 7], or phosphate [8, 9] electrolytes have been used. These electrolytes are toxic. Sulphate electrolytes [9–12] are promising alternatives. However, due to their instability in time they are not frequently used.

Furthermore, bronze coatings of goldish colour can be obtained only when the tin content varies from 8% to 15%. Decreasing the tin content, the coatings acquire a reddish hue, whereas increasing it, they become grey–white. Since electrolyte compositions proposed in the literature operate over a narrow range of cathodic current densities (from 0.5 to $1.5\,A\,dm^{-2}$), they have not been widely used in practice.

Studies on the Cu–Sn alloy deposition mechanism in sulphate electrolytes [13–16] deal principally with separate problems. There is no systematic data in the literature. This makes comparison of data obtained in different studies difficult.

The present work describes the investigation of cathodic processes in sulphate solutions during copper and tin codeposition as related to the solution composition and electrolysis conditions.

2. Experimental data

A copolymer of ethylene oxide and propene oxide (mol. weight ~ 3200), 'Laprol 2402-C' was investigated as an organic additive (OA).

Cathodic polarization was measured employing a potentiostat (P-5827 or Pl-50-1). Sweep rates of 0.02, 0.1, 0.2, 1 and $5\,V\,s^{-1}$ were used. A saturated silver chloride electrode served as a reference electrode. The values of the cathode potentials in the Figures are given relative to the normal hydrogen electrode. The platinum cathode (area $\sim 1\,cm^2$) was plated with copper. The quantity of electricity passed was determined by copper coulometry. A copper anode ($\sim 10\,cm^2$) was used.

The copper content in both the alloy and the electrolyte was determined by titration. The tin quantity in the alloy was determined by subtracting the copper mass from that of the alloy [17, 18].

3. Results and discussion

Partial curves of copper and tin deposition calculated according to Faraday's law from the analysis data show the first process to be copper deposition (Fig. 1, curve 2). Upon reaching the cathode potential of −0.06 V, tin codeposition begins.

The potential at which copper deposition begins is +0.24 V, whereas according to the Nernst equation it should be +0.31 V. The disagreement is related to the decrease in the value of the Cu(II) activity coefficient at high H_2SO_4 concentration [19]. The initial tin deposition potential is also more positive (−0.06 V instead of −0.166 V). This is, apparently, related to the depolarization process resulting from codeposition of the alloy [1]. After the beginning of tin codeposition the total process rate increases gradually, and after the limiting rate of tin deposition is achieved (Fig. 1, curve 4), hydrogen evolution begins at the potential of −0.32 V.

As indicated by the experimental data obtained in solutions with changing concentration of Cu(II) and Sn(II), cathodic process rates are, to some extent, controlled by diffusion limitations of the Cu(II) and Sn(II) ions. The Cu(II) concentration increase is accompanied by a proportional increase in the first limiting current (i_1). Increase in Sn(II) concentration has a slight effect on the first limiting current height, while the second height increases considerably with increase in Sn(II) concentration.

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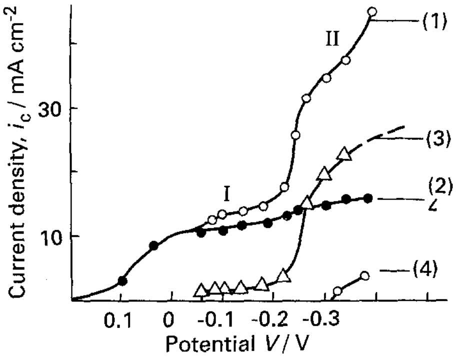

Fig. 1. Cathodic polarization in solution containing (M): 0.12 $CuSO_4$, 0.2 $SnSO_4$ and 1.0 H_2SO_4. (1) A summary curve. Partial curves of deposition process of: (2) copper, (3) tin and (4) hydrogen.

It is impossible to obtain high-quality coatings in the absence of OA. The introduction of 0.1 g dm^{-3} of OA changes the shape of the cathodic polarization curves (Fig. 2, curve 1). A considerable inhibition of copper deposition is observed in this solution (~ 0.15 V). With increase in OA concentration the cathodic process rate decreases further (Fig. 3, curves 3–5).

A small concentration of OA (Fig. 3, curve 2) considerably inhibits copper deposition. With increase in OA concentration, a new phenomenon is observed, namely, a sharp decrease in the cathode surface passivation by the film formed. This decrease begins at −0.2 V (Fig. 3, curve 3). Increasing the OA concentration, the process rate decreases more sharply. Having reached 2 g dm^{-3}, further increase in OA concentration does not change the curve shape. Therefore, 2 g dm^{-3} concentration of OA was chosen for further investigations.

Partial curves of copper and tin deposition (Fig. 2), similar to those of OA-free solution, are indicative of copper deposition taking place at the very beginning of electrolysis. The process reaches a maximum rate at the potential of −0.2 V and then the rate decreases sharply.

It should be noted that the cathode potential, at which the rate decrease was observed, reproduces fairly well. Starting at this potential, periodic oscillations reproducible both in shape and frequency were observed.

The tin deposition process starts at −0.06 and tin begins to discharge at a constant rate after the maximum rate of copper deposition is achieved. Hydrogen evolution begins at −0.4 V. There are sound reasons to believe that the cathodic process is far more complicated.

As has been demonstrated above (Fig. 3), the OA concentration and surface passivation are interrelated. Sn(II) concentration (Fig. 4) also affects the passivation process.

The greater the Sn(II) concentration, the shorter the time required to attain the rate decrease (Fig. 4(a), part 'a' of the curves). The quantity of electric current consumed prior to the passivation process is represented by the exponential curve. The first signs of cathode passivation are observed at 7 × 10^{-3} M Sn(II) concentration (Fig. 4(b)).

The observed cathodic process rate dependences on Sn(II) and OA concentrations suggest that Sn(II) ions and OA molecules take part in the cathode passivation. Electrodeposition may proceed only on free sites on the surface. Thus, the area of the active electrode surface decreases manyfold. Subsequently, Sn(II) discharges mainly on the isolated parts of the cathode surface. This is also confirmed by periodic cathode current oscillations [20] which are indicative of a competitive nature of passivation and activation processes. A similar phenomenon was observed by Loshkarev and Kriukova in an investigation of the influence on tin deposition from sulphate electrolytes [21, 22].

The experimental data (Fig. 5) show changes which take place on the electrode surface activity during electrolysis. On the reverse sweep from the point at which copper alone deposits, the back curve repeats the forward sweep curve (Fig. 5(a)). On returning the potential from the point corresponding to the lowest point of the process rate decrease (Fig. 5(b)), a high peak of current increase is observed. This is caused by the cathode surface formation. The change to the surface is clearly seen. Coatings obtained at this potential are powder-like and black.

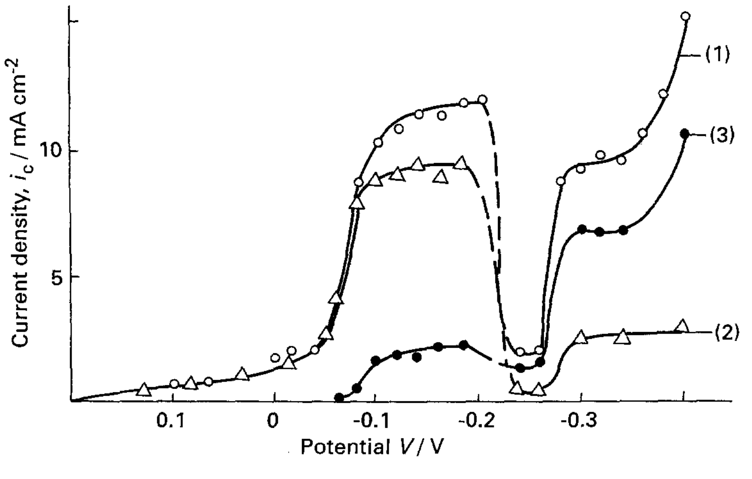

Fig. 2. Cathodic polarization in solution containing (M): 0.12 $CuSO_4$, 0.25 $SnSO_4$, 1.0 H_2SO_4 and 2 g dm^{-3} Laprol 2402C: (1) A summary curve. Partial curves of deposition process of: (2) copper, (3) tin.

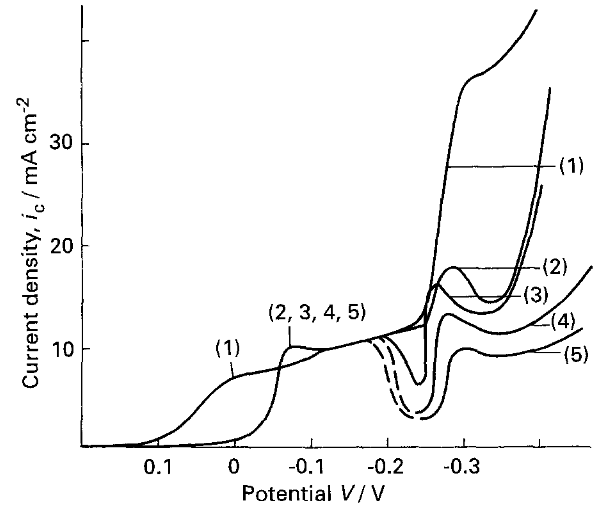

Fig. 3. Cathodic polarization in solution containing (M): 0.12 $CuSO_4$, 0.2 $SnSO_4$, 1.0 H_2SO_4, and varying concentrations of Laprol 2402C: (1) 0, (2) 0.1, (3) 0.2, (4) 0.5, (5) 2 and 5 g dm^{-3}, $v = 2 \times 10^{-3}$ V s^{-1}.

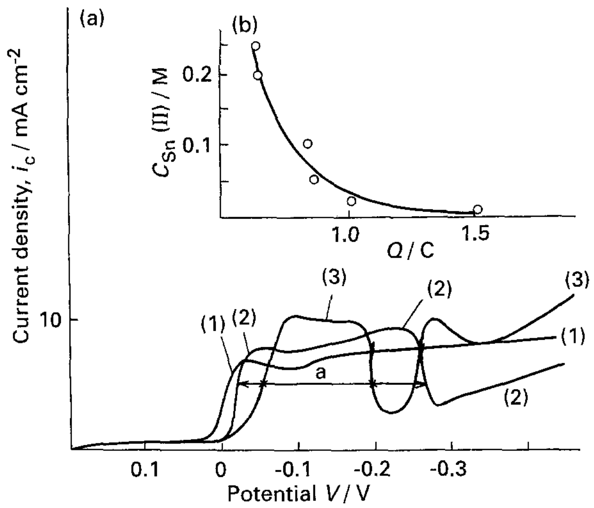

Fig. 4. Cathodic polarization in solution containing (M): 0.1 $CuSO_4$, 1.0 H_2SO_4 and 2 g dm^{-3} Laprol 2402C and varying concentrations of $SnSO_4$: (1) 0, (2) 0.02 and (3) 0.25 M, 2×10^{-3} V s^{-1} (a). The dependence of the amount of electricity (Q), passed prior to the process rate decrease, on tin concentration in the electrolyte (b).

On returning the potential from a more negative potential, a new phenomenon is observed. The anode current originates in the cathode zone (Fig. 5(c)). Even higher anodic current is observed when the potential returns after having reached more negative values (Fig. 5(d)).

Additional experimental data is needed to fully clarify the mechanism of the cathodic processes. However, the phenomena observed suggests that complex interactions between the electrode surface and solution components are taking place. For instance, compounds consisting of OA and Sn(II) may be absorbed on the cathode surface. Data on an analogous phenomenon is available in the literature (23–29].

4. Conclusions

(i) In investigating cathode polarization and partial curves in Cu(II) and Sn(II) sulphate solutions in the presence of sulphuric acid, the content of separate metal components in an alloy has been found to depend on the concentration of their ions in solutions.

(ii) The organic additive Laprol 2402C (OA) changes the nature of the cathodic polarization and extends the range of cathodic current densities at which high quality Cu–Sn coatings are obtained. Decrease in the cathodic process rate is preceded by periodic current oscillations. This phenomenon is caused by the cathode surface interaction with OA and Sn(II).

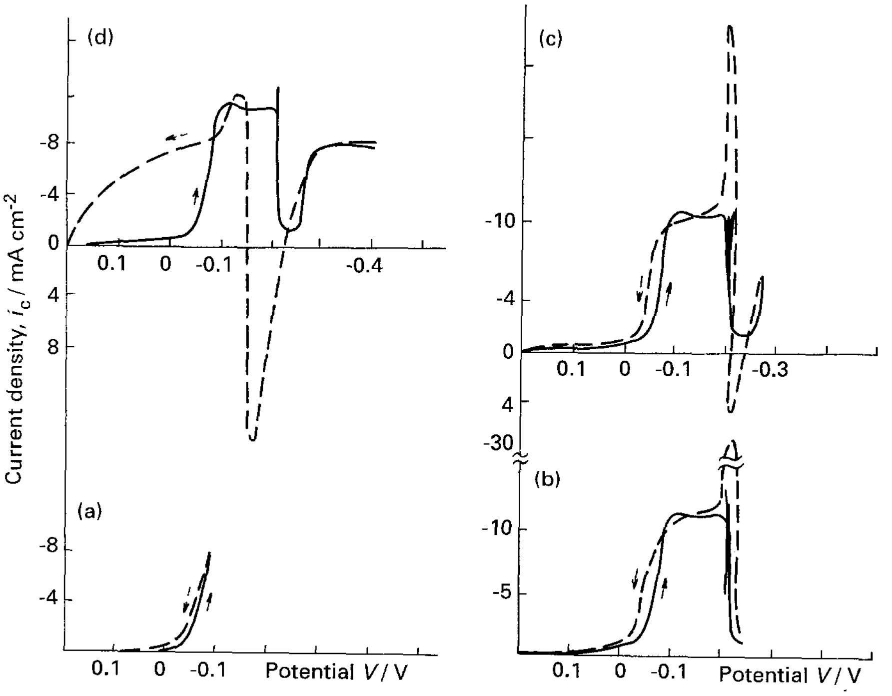

Fig. 5. Forward and retrace trend of the cathodic polarization curve in solution containing (M): 0.12 $CuSO_4$, 0.25 $SnSO_4$, 1.0 H_2SO_4 and 2 g dm^{-3} Laprol 2402C depending on the potential from which the reverse sweep begins: (a) 0.09, (b) 0.24, (c) −0.27 and (d) −0.4 V, $v = 2 \times 10^{-3}$ V s^{-1}.

(iii) An anodic current was detected in the cathode zone. The anodic current value depends on the potentials at which the reverse sweep starts.

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