Influence of decyl glucoside on the electrodeposition of tin

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Abstract: The aim of the present study was to improve an electrochemical deposition bath for tin coating an acidic sulphate medium by addition of decyl glucoside. The effects of this additive on the deposition kinetics were examined by electrochemical methods, namely voltammetry and galvanostatic tin-layer formation, while scanning electron microscopy and X-ray diffraction analysis allowed the determination of the morphological and structural modifications resulting from the addition of this new surface active agent. The presence of the examined additive induced an increase of the activation energy and of the overvoltage of the reduction of stannous ions. From the morphological point of view, a marked decrease in the grain size of the deposit was achieved in the presence of the additive. The preferential crystal growth axes was also changed from Sn (200) without additive to Sn (112) with the additive.

Keywords: tin, electrodeposition, decyl glucoside, voltammetry, X-ray diffraction, scanning electron microscopy.

INTRODUCTION

Tin coatings have largely been used in industry to improve corrosion resistance or enhance appearance and/or solderability. In acidic solutions, tin is electrodeposited with a small activation overpotential.1,2 Porous or dendritic deposits are usually obtained. A lead compound is often added to inhibit the reduction of the stannous species and increase the polarization reaction.3 To avoid pollution problems, organic additives1,4–11, or surfactants2,12–18 are commonly used to improve the deposit morphology.

A new class of organic compounds, alkylpolyglucosides, are biodegradable and non toxic. These compounds find application as emulsifying agents, hydrolysing agents of proteins,19 and vectors of medicines.20

In the present work, the effect of decyl glucoside on tin deposition was investigated because of its high solubility in aqueous solutions and excellent biodegra-
dability. A kinetic investigation was carried out using cyclic voltammetry and chronopotentiometry, while structural characterization was performed by X-ray diffraction and scanning electron microscopy.

EXPERIMENTAL

A classical three-electrode cell was used. The bath temperature was kept at 20 ± 1 °C. The working electrode was a disc of iron or copper, the surface of which was polished with SiC paper down to 1200 grade. The reference electrode was a saturated calomel electrode and the counter electrode was a platinum wire.

A PG P201 potentiostat connected to a computer was used. The surface tension was measured by means of a Kruss K12 tensiometer with a precision of 0.1 mN m⁻¹. The morphology was examined using a LEO 1530 FEG-microscope. X-Ray diffraction was performed in θ/2θ geometry using a diffractometer with a cobalt anticathode.

The solutions of tin sulfate and sulphuric acid were prepared using analytical grade chemicals. Their pH was close to 1.1, as in industrial applications. The basic electrolyte, denoted (a), contained stannous sulfate (0.14 mol dm⁻³) and sulphuric acid (0.56 mol dm⁻³). The electrolyte labeled (b) contained stannous sulfate and sulfuric acid in the same concentrations as electrolyte (a) and 10⁻³ mol dm⁻³ of decyl glucoside.

The additive was decyl glucoside with a molar mass of 390 g mol⁻¹. It is a surfactant agent with a hydrophilic head to glucose and a hydrophobic chain with 8, 10 or 12 carbon atoms (Scheme 1). It was used as a 50 weight % aqueous solution.

RESULTS AND DISCUSSION

Determination of the critical micellar concentration (CMC) of decyl glucoside

The surface tension of the electrolyte was measured as a function of the decyl glucoside concentration in the range of 1×10⁻⁴ to 5×10⁻³ mol dm⁻³ (Fig. 1). Two regimes were observed: in the low concentration range, the surface tension de-
increased strongly. For higher concentrations, the surface tension was nearly constant. The critical micellar concentration is equal to $5.1 \times 10^{-4}$ mol dm$^{-3}$.

For the electrodeposition, electrolytes with concentrations of additive higher than the CMC were used to induce the formation of micellar aggregates of high molecular weight which are able to adsorb on the electrode surface and affect the reduction of the stannous species.

**Polarization measurements**

Continuous recordings of the cathodic potential versus the duration of the deposition of tin on an iron rotating disc electrode, at 1000 rpm, at a constant current density of $-10$ mA cm$^{-2}$ for plating solutions with and without additive are shown in Fig. 2. According to Fig. 2, in presence of additive, tin is deposited on the iron substrate with a high overpotential. The increase in the polarization in the presence of the additive is due to the micelles which block the electrode surface.

**Voltammetric investigation**

The cyclic voltammograms recorded at a scan rate of 500 mV min$^{-1}$ in quiescent electrolytes (a) and (b) are shown in Fig. 3. In both cases, a cathodic peak in the forward scan was observed at $-540$ mV. During the reverse scan, for bath (a) without additive, the current was much higher than during the direct scan, which indicates that a non-uniform deposit was formed, which dramatically increased the specific area. In the anodic scan, in both solutions an oxidation peak was observed at $-360 \pm 10$ mV.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$Q_c$/C cm$^{-2}$</th>
<th>$Q_a$/C cm$^{-2}$</th>
<th>$Q_a/Q_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>2.17</td>
<td>1.14</td>
<td>0.52</td>
</tr>
<tr>
<td>(b)</td>
<td>0.60</td>
<td>0.55</td>
<td>0.92</td>
</tr>
</tbody>
</table>

As shown in Table I, in the absence of additive, the efficiency, estimated by the
ratio of the anodic and cathodic charge, was much lower than in bath (b). This indicates that the hydrogen evolution was much more important in bath (a) and also that some of the tin deposited during the cathodic cycle might not be oxidised during the anodic cycle.

**Temperature dependence**

The voltammograms recorded at a linear sweep of 500 mV min\(^{-1}\) at various temperatures in the electrolytes with and without additive are shown in Fig. 4.

As can be seen, at a given potential, the current density increases with increasing temperature.

The lines describing the limiting current density *versus* the reciprocal temperature, are given in Fig. 5. The energy of activation calculated from the slope of these lines was found to increase from 18 kJ mol\(^{-1}\) without additive to 30 kJ mol\(^{-1}\) in the presence of additive. This increase confirms the blockage of the surface of the working electrode by molecules of the additive.
Surface morphology and crystal orientation of the electrodeposited tin

Scanning electron micrographs (SEM) and X-ray diffraction patterns of the electrodeposited tin obtained from the electrolytes with and without additive under galvanostatic conditions (–mA cm–2) on an iron disc rotating at 2000 rpm were recorded. Figure 6 shows that the presence of decyl glucoside in the bath decreases the grain size of the deposit significantly.

The X-ray diffraction patterns of the tin electrodeposited from electrolytes (a) and (b) are shown in Fig. 7. Both deposits exhibit a tetragonal structure. The film deposited from the electrolyte (a) without additive showed a strong (200) preferred orientation, whereas the layer deposited from the bath with additive (b) exhibited a strong intensity (112) diffraction peak.
Fig. 5. Logarithm of the current density versus $T^{-1}$ for the electrodeposition of tin at a potential of $-600$ mV. Data taken from Fig. 4.

Fig. 6. Scanning electron micrographs of the tin deposited from the electrolyte without decyl glucoside (i) and with decyl glucoside (ii).

Fig. 7. X-Ray diffraction patterns of the tin deposited from the electrolyte without decyl glucoside (a) and with decyl glucoside (b).
CONCLUSION

This paper presents the results of a study aimed at improving an electrochemical deposition bath for tin coating in acidic sulphate medium by the addition of decyl glucoside. The effects of this additive on the deposition kinetics were examined by cyclic voltammetry and galvanostatic thin-layer formation, while scanning electron microscopy (SEM) and X-ray diffraction analysis allowed the determination of the morphological and structural modifications resulting from the addition of this new surface active agent. It was found that the presence of the additive examined induced an increase of the activation energy and of the overvoltage of the reaction of stannous. From the morphological point of view, the additive induces a uniform deposition of tin over the entire surface and a marked improvement of the deposit was achieved, i.e., a reduction of the grain size. In the presence of additive, the electrodeposited tin had a preferred orientation with the (112) plan parallel to the surface.

ИЗВОД

УТИЦАЈ ДЕЦИЛ-ГЛУКОЗИДА НА ЕЛЕКТРОХЕМИЈСКО ТАЛОЖЕЊЕ КАЛАЈА

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Циљ рада је био да се побољша кисели сулфатни електролит за електрохемијско таложење калала додатком децил-глукозида. Ефекти овог адитива на кинетику таложења калала су испитивани електрохемијским методама цикличне волтаметрије и галваностатског таложења танког слоја метале. Утицај на морфолошке и структурне карактеристике превлачак калала је испитиван методама скинирање електронске микроскопије и дифракције X-зрака. Присуство адитива је довело до повећања енергије активације и пренапетости за редукуцију Sn(II) јона. Са морфолошке тачке гледишта, дошло је до значајног смањења величине зrna калала у присуству адитива. Такође је промењена и преференцијална кристална раван од Sn(200) без адитива на Sn (112) уз присуство адитива.

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REFERENCES