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The effect of tin on zinc electrowinning from industrial acid sulphate electrolyte

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The effect of tin on the electrowinning of zinc from industrial acid sulphate electrolyte was studied using cyclic voltammetry, X-ray diffraction and scanning electron microscopy techniques. Tin concentrations < 2 mg l^{-1} resulted in a rapid decrease in the current efficiency for 1-h zinc deposits electrowon at 430 A m^{-2}; for tin concentration > 2 mg l^{-1}, the current efficiency remained constant at about 75%. The presence of tin in the electrolyte depolarized the zinc deposition reaction and resulted in a zinc deposit having a preferred [002] orientation. The addition of glue appeared to aggravate rather than counteract the adverse effects of tin.

1. Introduction

The work described in this paper is part of an overall programme to develop a better understanding of the factors which influence zinc deposition in order to gain closer control over the process. Specifically, the objective of this work is to determine if a characteristic behaviour pattern exists for the effect of various impurities on the current efficiency and polarization for zinc deposition and on the morphology and orientation of the zinc deposits.

The concentrations of germanium, antimony or tin required to cause a given reduction in the current efficiency are almost an order of magnitude lower relative to other impurities, e.g. cobalt, nickel, cadmium and lead. Recently, reports have been published that characterized the effect of antimony [1–3] and germanium [4–7] on zinc deposition current efficiency and polarization behaviour as well as their effects on deposit morphology and orientation. Although small concentrations of these impurities drastically reduce zinc deposition current efficiency, their effect on deposit morphology and orientation and on zinc deposition polarization are quite different.

The presence of antimony in the electrolyte depolarized zinc deposition and the zinc deposit consisted of large, rounded platelets, having a preferred [002], [103] orientation [1–3]. Germanium had no effect on the morphology of 1-h zinc deposits, but the preferred orientation changed from [114], [112] for Ge-free electrolyte to [112], [110] for electrolytes containing Ge [7]. Cyclic voltammograms obtained for Ge-containing electrolytes were characterized by a shoulder on the reverse scan prior to the cross-over potential; vigorous hydrogen gassing occurred at the shoulder.

The effect of tin on zinc electrowinning has received scant attention, probably because it rarely appears in the electrolyte to any significant extent. Previously, Weaver [8] noted that 'appreciable' amounts of tin lowered the hydrogen overvoltage and reduced the current efficiency for zinc deposition. He also noted that the surface of the zinc deposit became shiny with prominant vertical ridges. Based on the standard potential for tin, $E_0 = -0.14$ V SHE and the exchange current density, $i_0 = 1 \times 10^{-8}$ A cm^{-2}, Bratt [9] predicted that tin would decrease the current efficiency for zinc deposition; 0.5 mg l^{-1} tin was found to decrease the current efficiency by 20–25%. Fukubayashi *et al.* [10] observed that 0.2 mg l^{-1} Sn resulted in a current efficiency of 62.8% for a 2-h zinc deposit. They noted that the presence of tin in the electrolyte caused an overall corrosion of the zinc and that hydrogen gas was evolved over the entire electrode.

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Since very low concentrations of tin, like germanium and antimony, are detrimental to zinc electrowinning it was felt that a detailed study of its effect might provide insight into the general mechanism of impurity behaviour. The present study was undertaken to study in detail the effect of Sn on the current efficiency and polarization behaviour of zinc deposition and its effect on the morphology and orientation of 1-h zinc deposits electrowon from industrial acid sulphate electrolyte. The interaction of tin with glue, a common additive in zinc electrowinning, was also studied.

2. Experimental procedure

2.1. *Electrolyte and apparatus*

The electrolyte was an industrial zinc sulphate solution prepared from hot zinc dust purified neutral zinc electrolyte obtained from Cominco Ltd, Trail, British Columbia. The average analysis was (in $g\,l^{-1}$): Zn 150, $MgSO_4$ 38, Mn 1.6; (in $mg\,l^{-1}$): Cd 0.2, Sb 0.02, Co 0.3, Ge 0.01, Ni 0.1, Cu 0.1, Fe 0.9, Pb 0.2, Cl 80, F 3.

Cell solutions were prepared by adding H_2SO_4, redistilled water and impurities to the electrolyte to give final concentrations of 55 $g\,l^{-1}$ Zn and 150 $g\,l^{-1}$ H_2SO_4. Animal glue was added as a concentrated solution. Tin was added as an aliquot from Fisher AA standard, 1 $g\,l^{-1}$ Sn^{2+} solution.

The electrolysis cell consisted of a 1 litre beaker fitted with a Lucite cover which had slots cut in it to mount the electrodes [3]. A three electrode assemblage consisting of a central aluminium cathode and two platinum anodes was used. The cathode was fashioned from 4.7 mm thick aluminium sheet (purity 99.6%) obtained from Cominco. It measured 31.8 mm × 136.3 mm and was mounted so that zinc deposited on both sides onto a total area of 12.9 cm^2. The anodes were cut from a 0.3 mm thick platinum sheet and measured 17.9 mm × 109.7 mm. Platinum was used to avoid lead contamination of the electrolyte from conventional Pb–Ag anodes [11].

2.2. *Electrolysis*

The electrolysis were done in a constant temperature bath at 35° C with stirring at a cathode current density of 430 $A\,m^{-2}$ for a period of 1 h. Cathode conditioning was not emphasized for the electrodeposits and was carried out only when required.

2.3. *Examination of deposits*

Sections of the zinc deposits were examined by scanning electron microscopy to determine the surface morphology and by X-ray diffraction to determine the preferred crystal orientation relative to the ASTM standard for zinc powder. Sections of certain zinc deposits were accurately weighed and dissolved in 60% HNO_3. The resulting solution was diluted with water to a total volume of 50 cm^3. The solution was analysed by atomic absorption (AA) spectrophotometry for zinc and tin with the ppm tin contained in the zinc being calculated from the AA data.

2.4. *Cyclic voltammetry*

Cyclic voltammograms were obtained using a voltage scan generator, a potentiostat and an x–y recorder for recording current vs applied potential. The voltage scan generator was used to cycle the potential from − 0.85 to about − 1.10 V vs a saturated calomel electrode. The latter limit was chosen to give a maximum current of approximately 60 mA on the forward scan; hence, there is some variation in the potential scan range. The scan was done at a rate of 1 $mV\,s^{-1}$.

The cell used for the cyclic voltammetry experiments contained 50 ml of electrolyte. The working electrode was an aluminium cathode measuring 15.4 mm × 109.5 mm × 0.8 mm thick. It was mounted so that the surface area was approximately 3.2 cm^2. The counter electrode was platinum. A saturated calomel electrode mounted adjacent to the cathode was used as the reference electrode.

Prior to each test the cathode was conditioned by polishing with 600 grit paper, washing with acetone followed by redistilled water, and patting dry with a tissue. The cathode was then put into the cell while the electrolyte was stirred. Once a steady rest potential was established the stirrer was turned off and the scan was initiated.

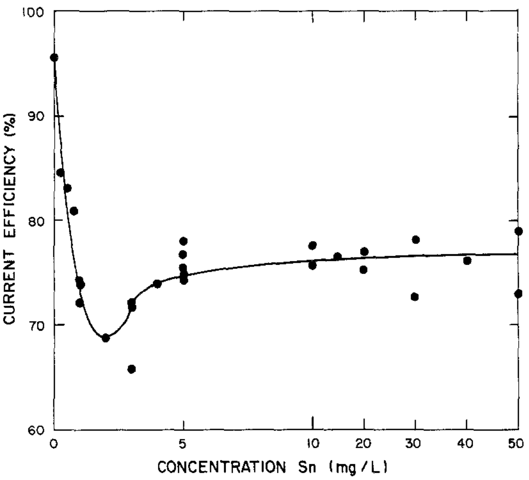

Fig. 1. The effect of increasing tin concentration on the current efficiency of 1-h zinc deposits.

3. Results and discussion

3.1. *Current efficiency*

The effect of increasing tin concentration on the current efficiency (CE) for 1-h zinc deposits electrowon at 430 A m^{-2} from industrial acid sulphate electrolyte is shown in Fig. 1. The CE decreases rapidly from ~ 96% in a tin-free medium to < 70% at 2 mg l^{-1} per litre. Subsequently, there is a small increase in the CE to about 75% at 5 mg l^{-1} Sn. The CE remains virtually constant for further increases in tin concentration to 50 mg l^{-1}.

The small increase and levelling-off of the CE for Sn > 2 mg l^{-1} coincides with a change in the preferred orientation of the zinc deposit (Table 1).

Table 1. The effect of tin and tin + glue on the preferred orientation of zinc deposits electrowon from industrial acid sulphate electrolyte

Tin (mg l^{-1})	*Glue (mg l^{-1})*	*Deposit orientation**
0.25	0.0	002
0.50	0.0	105,002
0.75	0.0	103
1.0	0.0	103
2.0	0.0	103
5.0	0.0	102
10.0	0.0	112,101
20.0	0.0	101
30.0	0.0	102
50.0	0.0	100,101
0.50	5.0	101,201
0.50	10.0	103
0.50	20.0	002
1.0	5.0	002
1.0	10.0	114
1.0	20.0	103,114,105,002
1.0	30.0	105
1.0	50.0	002

* Relative to ASTM standard for zinc powder. Electrolysis conditions: 55 g l^{-1} Zn, 150 g l^{-1} H_2SO_4, 35° C; 430 A m^{-2}

The preferred orientation changes from [002], [105], [103] for Sn < 2 mg l^{-1} to [101] for Sn > 2 mg l^{-1}. Previous work [1, 3] has shown that the [002], [103] orientations are usually associated with low CE whereas the [101] orientation corresponds to deposits electrowon at relatively high CE.

The effect of increasing glue concentration on the CE for zinc deposition from electrolytes containing 0.5 and 1.0 mg l^{-1} Sn is shown in Fig. 2. Initially, the CE decreases significantly

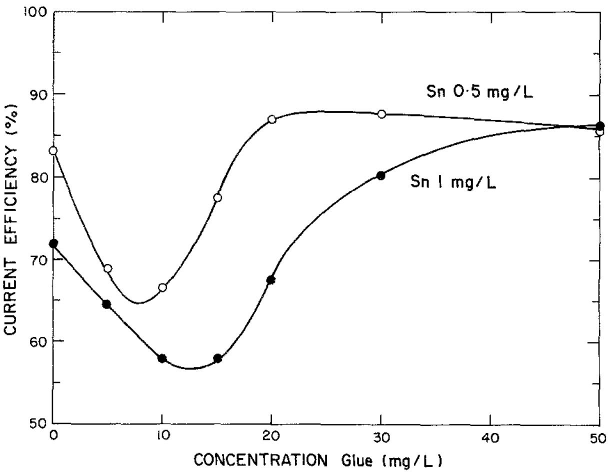

Fig. 2. The effect of increasing glue concentration in the presence of tin on the current efficiency for 1-h zinc deposits.

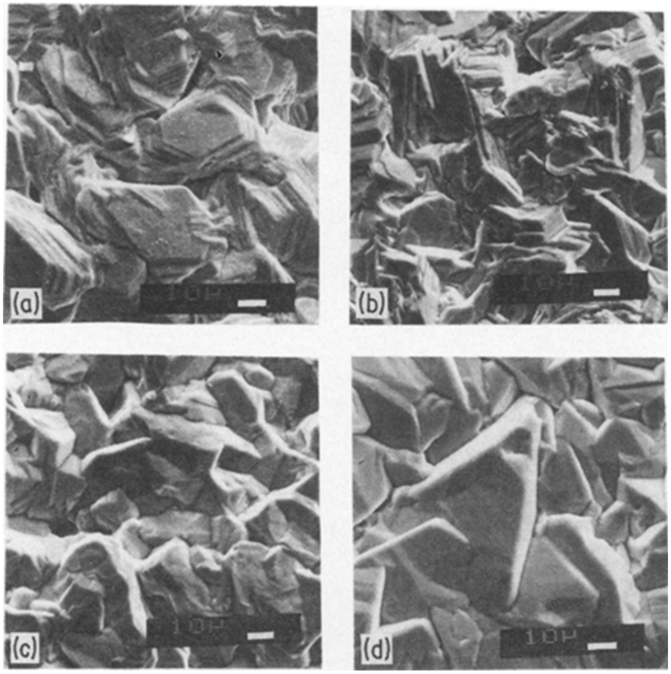

Fig. 3. SEM photomicrographs showing the effect of tin on the morphology of 1-h zinc deposits electrowon at 430 A m^{-2}. (a) 0.5 mg l^{-1} Sn; (b) 0.75 mg l^{-1} Sn; (c) 2 mg l^{-1} Sn; (d) 50 mg l^{-1} Sn.

with the addition of glue to the electrolyte, reaching a minimum level at about 8 and 12 mg l^{-1} glue for 0.5 and 1.0 mg l^{-1}, Sn, respectively. With further glue additions, the CE begins to increase and in the case of 0.5 mg l^{-1} Sn, reaches a maximum of 87% at 20 mg l^{-1} glue; at 1.0 mg l^{-1} Sn, the maximum in CE is not achieved until 50 mg l^{-1} glue is added to the solution.

3.2. *Deposit morphology and orientation*

The effect of tin on the morphology of the 1-h zinc deposits electrowon at 430 A m^{-2} from purified industrial acid sulphate electrolyte is shown in the series of SEM photomicrographs, Fig. 3. The addition of 0.5 mg l^{-1} Sn to the electrolyte results in the deposit morphology shown in Fig. 3a. As indicated the deposit consists of poorly defined hexagonal platelets oriented parallel to the aluminium cathode. This is in agreement with the X-ray diffraction (XRD) data presented in Table 1 that indicate that the preferred orientation for this deposit is [002]. Some of the platelets shown in Fig. 3a have rounded edges, and voids appear at some of the grain boundaries indicating that re-solution of zinc might be occurring.

Increasing the tin concentration to 0.75 mg l^{-1} results in the zinc deposit morphology shown in Fig. 3b. In this case the deposit also consists of stacks of poorly defined hexagonal platelets, but they appear to be oriented at a low angle to the aluminium cathode, rather than parallel to it, cf. Fig. 3a. XRD data confirm that this is the case as the preferred deposit orientation is [103] (See Table 1).

For 2.0 mg l^{-1} Sn, individual zinc platelets are no longer distinguishable, Fig. 3c, and the deposit consists of triangular-shaped grains. The preferred orientation remains [103] (see Table 1). This same morphology persists as the tin concentration is increased to 50 mg l^{-1}, Fig. 3d; however, the orientation has changed from [103] to [101], [201] preferred (Table 1).

The effect of tin in combination with various concentrations of glue on the morphology of the 1-h zinc deposits is shown in the series of SEM photomicrographs, Fig. 4. The addition of 10 mg l^{-1} glue in combination with 1 mg l^{-1} Sn results in the deposit morphology shown in Fig. 4a. Although the preferred orientation remains the same as that without glue, i.e. [103] (see Table 1), the deposit consists of well-defined hexagonal platelets. The deposit grain size is also reduced.

Increasing the glue to 20 mg l^{-1} (Fig. 4b) results in the platelets becoming oriented at a

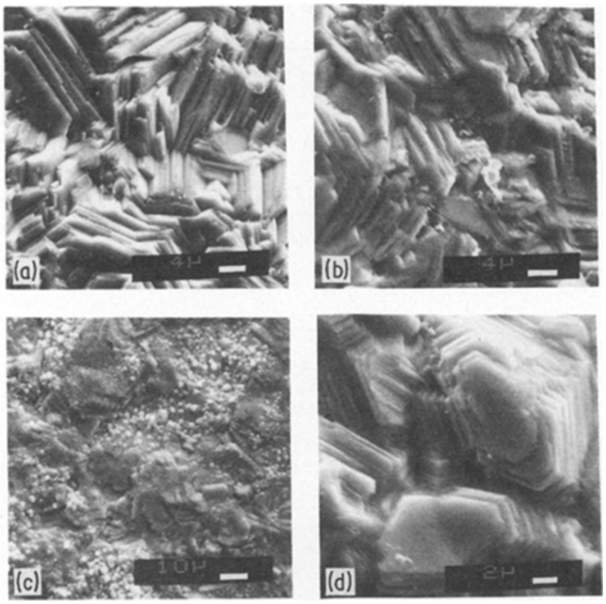

Fig. 4. SEM photomicrographs showing the effect of tin + glue on the morphology of 1-h zinc deposits electrowon at 430 A m^{-2}. 1 mg l^{-1} Sn plus (a) 10 mg l^{-1} glue; (b) 20 mg l^{-1} glue; (c) 30 mg l^{-1} glue; (d) 50 mg l^{-1} glue.

lower angle to the aluminium cathode. This is confirmed by the XRD data in Table 1, which indicate a preferred orientation of [105]. At higher glue concentrations, i.e. 30 and 50 mg l^{-1}, the zinc platelets became oriented parallel to the aluminium cathode, Fig. 4c, d; the preferred orientation is [002] (Table 1).

Although the presence of glue reduces the deposit grain size, it does not counteract the effect of tin as it does antimony [1–3]; in fact, glue in the presence of tin enhances the [002] deposit orientation.

3.3. *The effect of tin on zinc deposition polarization*

The cyclic voltammograms obtained for zinc deposition for electrolytes containing 1 mg l^{-1} Sn and 1 mg l^{-1} Sn + 30 mg l^{-1} glue are compared to that obtained from the addition-free electrolyte in Fig. 5. With reference to Fig. 5, a cycle starting from Point A (– 0.85 V vs SCE) goes through a region of low current until Point B where zinc deposition commences. The current increases to Point C where the scan is reversed. The current then decreases, reaches zero at Point D where it becomes anodic corresponding to the dissolution of deposited zinc. The anodic peak is reached at E and dissolution is compelte on return to A.

Comparing the curves in Fig. 5, it is obvious that the current for initial deposition of zinc becomes appreciable at different cathodic potentials (decomposition potentials), indicating a difference in the degree of zinc deposition polarization. The presence of 1 mg l^{-1} Sn in the electrolyte results in a significant decrease in the potential for zinc deposition, resulting in a depolarization of the reaction. This behaviour is similar to that previously reported for antimony [2, 3] where it was observed that depolarization of the zinc deposition reaction resulted in a deposit morphology consisting of large, poorly-

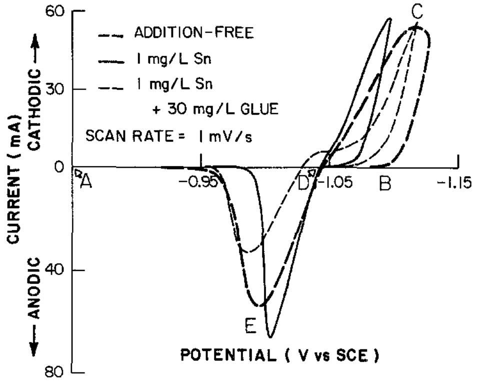

Fig. 5. Cyclic voltammograms showing the effect of tin and tin + glue on zinc deposition polarization.

defined hexagonal platelets aligned at low angles to the aluminium substrate and having a preferred [002] orientation; the CE also decreased. Similar results were observed in this work for electrolytes containing tin, cf. Table 1 and Fig. 3.

The presence of glue in combination with tin in the electrolyte results in an increase in the zinc decomposition potential relative to that of tin alone, but it remains less than that of the addition-free electrolyte, (dashed curve of Fig. 5). This behaviour is different from that observed for antimony–glue combinations [2, 3] where it was found that similar glue levels counteracted the depolarizing effect of antimony and resulted in a zinc deposit having morphologies and orientations similar to those of the addition-free deposit. Increasing the glue concentration from 30 to 50 mg l^{-1} did not significantly increase the decomposition potential beyond that indicated in Fig. 5 (dashed curve); in fact, the curves were almost identical in shape.

Thus, the polarization curves indicate that the addition of glue is not effective in counteracting the detrimental effects of tin. This finding is in agreement with the observed morphology and orientation data which showed that the presence of tin + glue enhanced the basal type morphology and [002] preferred orientation, cf. Fig. 4 and Table 1. Further, as described earlier, glue concentrations < 30 mg l^{-1} actually decreased the CE for zinc deposition when the electrolyte contained 1 mg l^{-1} Sn. The addition of > 30 mg l^{-1} glue, however, resulted in an increase in CE (cf. Fig. 2) that may be related to the increase in zinc deposition polarization relative to that obtained for tin alone (Fig. 5).

Another significant difference in the curves shown in Fig. 5, particularly for the tin + glue case, is the potential at which the descending branch crosses the zero-current axis (crossover potential). The crossover potential occurs at or near the reversible potential of the system so that any departure is generally caused by impurity currents, side reactions such as hydrogen evolution or perhaps the dissolution of an alloy phase, e.g. Zn–Sn alloy. Analysis of the zinc deposits confirmed that tin co-deposited with zinc. The data presented in Table 2 indicate that for electrolytes containing > 15 mg l^{-1} Sn, the tin content of the zinc deposit increases rapidly. For electrolytes containing < 15 mg l^{-1} Sn, the tin content of the zinc deposits was below the AA detection limit, i.e. < 1 mg l^{-1}.

Table 2. Tin content of zinc deposits as a function of tin added to the electrolyte

Tin added ($mg\ l^{-1}$)	*Tin in deposit (ppm)*
1	< 200
5	< 200
10	< 200
15	< 200
20	380
30	1400
40	3300
50	2700

Electrolysis conditions: 55 g l^{-1} Zn, 150 g l^{-1} H_2SO_4, 35° C, 430 A m^{-2}

The cyclic voltammogram obtained for the electrolyte containing 1 mg l^{-1} Sn had a small shoulder just prior to the crossover potential. In the presence of glue (dashed curve of Fig. 5), the shoulder became a large plateau as the crossover potential was shifted to a more positive value relative to that for addition-free electrolyte. Enhanced hydrogen evolution occurs over the plateau region.

The plateau region was investigated further using an electrolyte containing 1 mg l^{-1} Sn and 10 mg l^{-1} glue, a combination which resulted in a minimum in the CE vs glue concentration curve, Fig. 2. The first scan, Fig. 6, was also characterized by a shoulder region prior to the crossover potential. During the second scan (dashed curve of Fig. 6), the potential was held constant for a

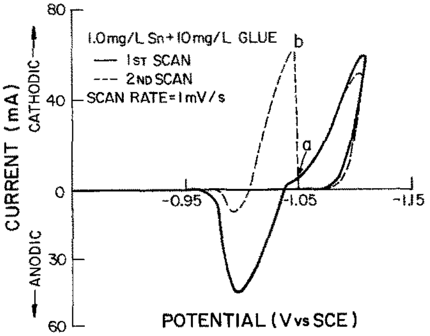

Fig. 6. Cyclic voltammograms showing the effect of tin + glue on zinc deposition polarization; (---) potential held at – 1.05 V vs SCE.

short time, about mid-way on the shoulder, Point a. The current increased rapidly and at Point b, the potential scan was resumed. The increasing current (Points a to b) was accompanied by vigorous hydrogen gassing at the cathode. After resuming the scan at Point b, the anodic peak was considerably reduced, indicating that much of the deposited zinc had dissolved while the potential was held at Point a. A possible explanation for this phenomenon is that an autocatalytic cycle is set up in which hydrogen is evolved at impurity (tin) sites, and zinc metal redissolves:

$$2H^+ + 2e \longrightarrow H_2 \qquad (1a)$$

$$Zn \longrightarrow Zn^{2+} + 2e \qquad (1b)$$

4. Conclusions

The presence of < 2 mg l^{-1} Sn in industrial acid-zinc sulphate electrolyte results in a rapid decrease in the CE for 1-h zinc deposits. The addition of tin to the electrolyte depolarizes the zinc deposition reaction, causing a predominantly [002]-oriented deposit. Similar behaviour has also been reported for small concentrations of antimony [1–3] and germanium [4–7]. For tin concentrations > 2 mg l^{-1}, the CE remains constant at about 75%; this behaviour coincides with a change in deposit orientation from [002], [103] to [101], [201] and with an increase in the tin content of the zinc deposit. The addition of glue to an electrolyte containing small concentations of tin, i.e. 1 mg l^{-1}, aggrevates the detrimental effect of tin, resulting in a further decrease in CE and a strongly preferred [002]-oriented deposit. Also, the presence of tin, with or without glue, results in a shoulder on the reverse scan of the voltammogram that is associated with enhanced hydrogen evolution.

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