The effect of cadmium on zinc deposit structures obtained from high purity industrial acid sulphate electrolyte

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The effect of cadmium on cathodic zinc crystal growth was studied in high purity industrial electrolyte, with and without additives, in an attempt to establish a correlation between morphology, polarization and the extent of cadmium contamination. Cadmium additions to acid zinc sulphate electrolyte did not have a significant effect on the zinc deposit orientation but did substantially refine the deposit grain size. The refinement in deposit grain size is directly related to the level of cadmium in the zinc deposits. Cadmium, in combination with glue and optimum amounts of glue and antimony, also reduced the deposit grain size: the preferred deposit orientation remained (1 1 2) with a slight tendency to (1 0 1) at high glue concentrations. Cadmium in combination with antimony resulted in an increased depolarization of zinc deposition and a basal (0 0 2) deposit orientation. Lead additions to zinc electrolyte containing cadmium resulted in increased deposition overpotentials and intermediate to vertical deposit orientations.

1. Introduction

Zinc electrocrystallization from acid sulphate electrolyte is affected by a number of process parameters, including the presence of impurities and organic colloids in the electrolyte. Recent fundamental studies on zinc electrolysis [1--5] have shown that there is a definite correlation between zinc deposit morphology and the type and concentration of additives and/or impurities present in the electrolyte. These studies further revealed that the characteristic zinc deposit morphology changes, which result from the presence of impurities and/or additives in the electrolyte, are associated with particular zinc deposition overpotential conditions. Lead and cadmium are both found as impurities in zinc electrolyte and are known to affect adversely zinc electrowinning by contaminating the cathode zinc.

The effect of lead on the electrocrystallization of zinc was discussed in a previous publication [5]. Zinc deposits contaminated with lead were found to have characteristic morphologies and orientations which were dependent on the amount of lead present in the zinc deposits and to a lesser extent on the presence of other impurities such as antimony and glue in the deposits. Increasing lead in the zinc deposits progressively changes the orientations from (1 1 2) to (1 0 1) to (1 0 0) to, finally, a poorly crystalline (0 0 2) structure.

A relationship was shown to exist between the effect of lead contamination on zinc deposit morphology and orientation, and on the overpotentials associated with zinc electrodeposition in the presence of lead. Deposition overpotentials increased for conditions which gave increased lead contamination of electrodeposited zinc. Antimony or glue additions to the electrolyte decreased the observed overpotential effects.

The effect of cadmium on the electrocrystall-
lization of zinc has received scant attention. Fukubayashi et al. [6] briefly studied the effect of cadmium on zinc crystallization using synthetic acid sulphate electrolytes containing 65 g l\(^{-1}\) Zn and 200 g l\(^{-1}\) H\(_2\)SO\(_4\). At 40° C, zinc deposits obtained at 807 A m\(^{-2}\) from electrolytes containing 2.5-50 mg l\(^{-1}\) Cd showed a preferred (0 0 2), (1 0 2), (1 0 3) orientation. They reported that impurities such as Cd usually gave fine facets with increasing amounts of cadmium; sometimes a pitted or waffled structure was obtained, the degree of waffling being dependent on the amount of cadmium and the electrolysis time. For solutions containing 50 mg l\(^{-1}\) Cd, the presence of Cd was detected in the pitted regions of the zinc deposit by non-dispersive X-ray analysis.

The present work was undertaken to study the effect of cadmium alone and in combination with other impurities and additives on the morphology and orientation of zinc deposits obtained from industrial acid sulphate electrolyte; a further objective was to determine the effect of Cd on the polarization behaviour of zinc deposition.

2. Experimental

2.1. Materials and apparatus

The electrolyte was prepared from hot-zinc-dust purified neutral zinc electrolyte obtained from Cominco Ltd. It had the following average analysis: Zn 150 g l\(^{-1}\), MgSO\(_4\) 38 g l\(^{-1}\), Mn 1.6 g l\(^{-1}\), Cd 0.2 mg l\(^{-1}\), Sb 0.02 mg l\(^{-1}\), Co 0.3 mg l\(^{-1}\), Ge 0.01 mg l\(^{-1}\), Ni 0.1 mg l\(^{-1}\), Cu 0.9 mg l\(^{-1}\), Pb 0.2 mg l\(^{-1}\), Cl 80 mg l\(^{-1}\), F 3 mg l\(^{-1}\). Cell solutions were prepared by adding H\(_2\)SO\(_4\) and water to neutral electrolyte to give concentrations of 55 g l\(^{-1}\) zinc and 150 g l\(^{-1}\) H\(_2\)SO\(_4\). Antimony additions were made to the electrolyte as a potassium antimony tartrate solution and animal glue was added as a concentrated solution. Cadmium was added to the electrolyte as a cadmium sulphate solution and lead as a solution of lead acetate. One hour zinc deposits were prepared from zinc electrolytes containing various concentrations of cadmium, antimony, glue and lead. The electrolysis cell and electrode assembly have been described in detail in previous publications [4, 5].

Pt anodes were used in order to avoid lead contamination of the zinc deposits [4, 5]. The anodes were cut from 0.01 cm thick Pt sheet and measured 15.2 x 2.5 cm. The cathodes which measured 15.2 x 3.2 x 0.32 cm thick were fabricated from commercial purity Al sheet (99.6%) obtained from Cominco and were mounted in the cell so that the total deposit area was 10.2 cm\(^2\).

2.2. Electrolysis

Operating conditions of 430 A m\(^{-2}\) and 807 A m\(^{-2}\) and 35° C were used for the tests. Some tests were also done at 215 A m\(^{-2}\) to confirm certain trends.

2.3. Deposit examination

Sections of deposits were examined by X-ray diffraction (XRD) to determine their preferred orientation relative to the ASTM standard for zinc powder and by scanning electron microscope (SEM) to determine their surface morphology. Selected deposits were also analysed for their cadmium content by atomic absorption spectrophotometry and for their lead content by the Dithiazone method.

2.4. Cyclic voltammetry

The cyclic voltammetry tests for the evaluation of the effect of cadmium in the electrolyte on the overpotential associated with zinc electrodeposition onto aluminum were described in a previous publication [5].

3. Results and discussion

3.1. Characterization of the cadmium effect

3.1.1. ‘Addition-free’ and ‘balanced’ electrolytes.

Unlike impurities such as antimony and lead [4, 5], cadmium additions to the ‘addition-free’ acid zinc sulphate electrolyte (i.e., containing no additions of antimony and glue) did not result in significant changes in the zinc deposit orientation but did decrease the zinc platelet size. The effect of cadmium on the morphology of zinc deposits obtained from ‘addition-free’ electrolyte is shown in Figs. 1a–c inclusive. Fig. 1a shows the morphology of the characteristic zinc deposit structure which has been discussed in detail in a previous...