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The influence of nickel ions on the long period electrowinning of zinc from sulfate electrolytes

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ABSTRACT

The effects of nickel ions on cathodic current efficiency, electrical power consumption, cell voltage and the surface morphology of deposits during the long period electrowinning of zinc from acid sulfate electrolytes are investigated in this paper. The polarization behavior of the cathode is also examined. The presence of nickel ions in the electrolytes increases the electrical power consumption, decreases the current efficiency, affects the cell voltage and produces the worse surface morphologies. The results of the experiments also show that the zinc electrodeposition process and the cathodic polarization behavior are greatly changed in the presence of nickel ions in the electrolytes.

1. Introduction

Most of the zinc all over the world is produced by the hydrometallurgy process of roasting–leaching–electrowinning (Saba and Elsherief, 2000). Along with the advancement of technology, in order to fulfill the requirement of mechanization, long period electrowinning of zinc is necessary. The deposition progress of zinc is affected by acidity, temperature, current density, the presence of impurities, and so on.

The effect of metallic impurities is complex (Tripathy et al., 2004; Mantell, 1980; Robinson and O'Keefe, 1976; Fosnacht and O'Keefe, 1980; MacKinnon et al., 1986; Ault and Frazer, 1988; Frazer, 1988; Muresan et al., 1996; Noguchi et al., 1994) during zinc electrowinning from acidic sulfate solutions. The zinc electrodepositions from baths, especially the bright plating baths, are very sensitive to impurities such as Ge, Sb, Ni, Co, Bi, Cu, As, and Sn. These impurities, besides affecting the cathodic current efficiency (CE), electrical power consumption (PC), cell voltage (CV) and deposit quality, also change the characteristics of the electrodeposited metal. Some papers (Ichino et al., 1995; Lupi et al., 2003; MacKinnon, 1994; MacKinnon and Brannen, 1991) indicated that the deleterious effect of impurities on the current efficiency of zinc deposition and surface morphology follows in the order: Ge>Sb>Ni>Co>Bi>Cu>As>Sn. Most of these metals have electrode potentials that are nobler than zinc, so these impurities could increase the tendency of pitting, thus greatly affecting the quality of cathode zinc (Robinson and O'Keefe, 1976; Frazer and Hamilton, 1986; Mohanty et al., 2001; Tripathy et al., 2003; Raghavan et al., 1999).

Nickel is one of the most injurious impurities in the electrolytes. During the electrowinning of zinc from sulfate electrolytes in the presence of nickel, a process of redissolution of the deposited metal takes place. Nickel deposits with zinc form numerous galvanic micro-batteries. Hydrogen evolves on the nickel zones and the surrounding zinc redissolves, thus causing the spongy and dark deposits. After many formation and dissolution cycles of the zinc deposits, the frequency of the cycle increases, showing that the cathode is gradually polluted by the nickel until zinc deposition can no longer occur. The hydrogen evolution decreases at higher current density and increases at higher temperature and acid concentration (Stefanov and Ivanov, 2002; Morrison et al., 1992).

The purpose of this paper is to study the influence of nickel ions on the long period electrowinning of zinc from sulfate electrolytes by analyzing the cell voltage, current efficiency, electrical power consumption, deposit morphology and cathodic polarization behavior.

2. Experimental details and methods

The electrolyte was a base electrolyte (BE) with different concentrations of nickel (added as $NiSO_4 \cdot 6H_2O$).The composition of BE was 50 g L^{-1} of Zn^{2+} and 110 g L^{-1} of H_2SO_4. The cathodes were aluminum strips, the anodes were Pb–Ag alloy sheets in the electrowinning experiment and the electrode was platinum in the polarization experiment.

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The deposit morphologies were examined using a scanning electron microscope (SEM), and the content distributions of element in micro-area were examined by electron probe X-ray micro analysis (EPMA). The SEM and the EPMA instruments were all produced by Shimadzu, Japan.

The electrochemical workstation PARSTAT 2263 which was produced by the EG&G company of America was used for measuring the cathode polarization curves. The initial potential and final potential of the cathode polarization curves were 1.36 V and 1.6 V, respectively.

3. Results and discussion

3.1. Current efficiency, power consumption and cell voltage

Experiment conditions: BE with various concentrations of nickel ions. Current density, 500–550 A m^{-2}. Electrowinning temperature, 40 °C. Electrowinning period, 48 h.

The effects of nickel ions on the CE and PC for 48 h zinc deposition are shown in Fig. 1 and the effects on the CV are shown in Fig. 2.

The data presented in Fig. 1 showed that the CE decreased and the PC increased during the process of 48 h zinc electrowinning as the nickel ions concentration increased in the electrolytes. But there were no significant variations when the nickel ions concentration was lower than 0.2 mg L^{-1} in the electrolytes. The decreasing trend of CE and the increasing trend of PC were very significant when the concentration of nickel ions was more than 0.2 mg L^{-1}. It was far from the need of 48 h zinc electrowinning while the nickel ions concentration in the electrolytes exceeded 0.2 mg L^{-1}.

As shown in Fig. 2, the CV could keep stable when the nickel ion concentration in the electrolytes was between 0 and 0.2 mg L^{-1} during the process of 48 h zinc electrowinning. With the increase of the nickel ion content in the electrolytes, the CV got more and more unstable, it indicated that the resolution of zinc deposits got more and more serious.

3.2. Deposit morphology

The zinc deposits were the product of the 5 h zinc electrowinning at a current density of 500–550 A m^{-2}. The deposit morphologies were inspected by SEM.

Fig. 3 illustrates the micro-area photograph of zinc deposits for the base electrolyte (BE). The zinc deposits obtained from nickel-free zinc sulfate electrolytes were smooth, bright and compact. The addition of nickel to the electrolytes affected the deposit morphology. The higher the nickel ion concentration in the electrolytes was, the worse the deposits will become (see Fig. 4). At high nickel ion concentration (≥0.5 mg L^{-1}) in the electrolytes, the morphologies of deposits were very rough and unconsolidated. It was because the hydrogen evolution became obvious in the presence of nickel in the electrolytes.

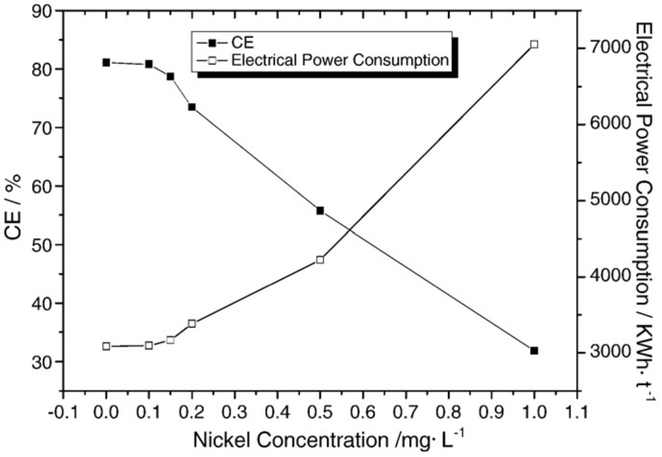

Fig. 1. Effect of nickel ions on the CE and PC for 48 h zinc electrowinning.

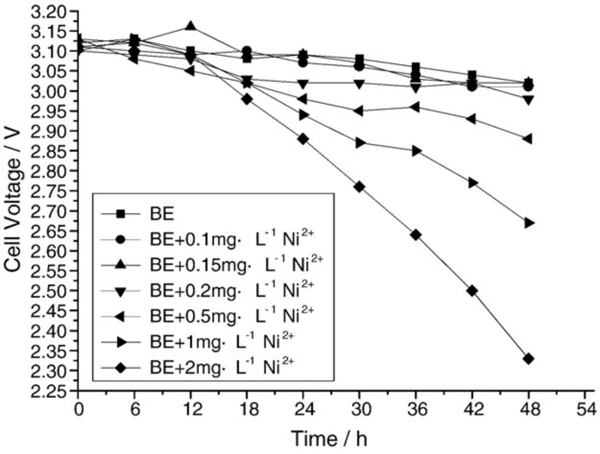

Fig. 2. The trend line of CV for 48 h zinc electrowinning.

Fig. 5 shows the micro-area photographs of the base electrolyte in the presence of 1 mg L^{-1} and 3 mg L^{-1} nickel ions at the plate-burning region. As shown in Fig. 5(1), the surface of zinc deposits developed some holes with round shape. The holes in Fig. 5(2) have the same shape as the ones in Fig. 5(1), but they were bigger and deeper. The results further proved that the hydrogen evolution became more and more obvious with the increase of nickel ion concentration in the electrolytes. EPMA revealed that the content of nickel in the plate-burning regions was much more than in non-plate-burning regions. The main reasons for this phenomenon were the hydrogen evolution and zinc resolution.

The photos of deposits for 48 h electrowinning of zinc are shown in Fig. 6. The holes caused by hydrogen evolution were more and were deeper in a nickel ion concentration-dependent manner. The results also indicated that the small change of nickel ions could induce the serious deterioration of deposit quality during the long period electrowinning of zinc. The induction periods of hydrogen more direct-viewing reflected the effects of the nickel ions in the electrolytes on the long period electrowinning of zinc (Table 1).

3.3. Polarization behavior

The cathodic polarization of the nickel ions during the electrowinning of zinc was investigated by recording current–potential curves using linear sweep voltammetry. Linear sweep voltammetry is a convenient technique for measuring zinc deposition polarization behavior. Linear sweep voltammograms basing on the BE with

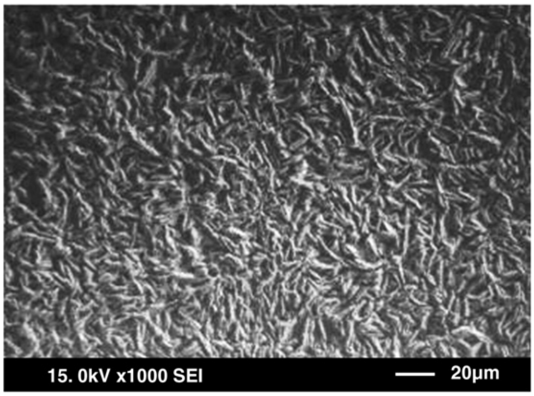

Fig. 3. SEM photograph of base electrolyte (BE).