Copper electrodeposition from sulfate solutions—Effects of selenium

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A B S T R A C T

The upshot of the presence of selenium in the electrolytic solution as an impurity over a concentration range of 0 to 1000 mg dm^{-3} during the electrodeposition of copper from sulfate solutions has been investigated in the present study. Higher concentrations of selenium (>50 mg dm^{-3}) in the copper sulfate solutions significantly reduce the current efficiency and quality of the copper electrodeposits and increase the energy consumption of the electrodeposition process. Cyclic voltammetric studies revealed that selenium, when present in the solution, affects the deposition and dissolution behavior of the cathodic copper significantly. The presence of selenium in the electrolytic bath polarizes the cathode and decreases the cathodic and anodic currents considerably. In the presence of higher concentrations of selenium (~1000 mg dm^{-3}), the co-reduction of selenium was observed. The order of relative diffraction intensity was changed from (111) > (200) > (220) to (111) > (220) > (200) without affecting the preferred plane of crystal growth of copper (111). However, distinguished peaks of selenium were observed for the deposits obtained at an individual impurity concentration of 1000 mg dm^{-3} in the solution in support of the observation made during polarization studies. Scanning electron micrographs revealed that the presence of selenium in the acidic copper sulfate bath develops a non-uniform and porous structure with indistinct grain boundaries instead of a compact and smooth deposit as obtained from pure solutions. At higher selenium concentrations, the copper deposits are induced with cracks and ultimately give rise to powdery deposits. The effect of selenium is worse when copper electrodeposition is carried out at 60 °C.

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1. Introduction

Copper is an essential service material and is environmentally friendly. The increased demand on the production of copper is due to the rapid growth in the sectors like infrastructure, construction, electrification, information, telecommunication, etc. The world's copper production has increased significantly over the years. This has caused severe depletion of the primary copper ore reserves. Thus, to meet the future worldwide growing demand of copper, there is no other option left than conserving the metal by maximum the recycling of secondaries and wastes in addition to the available primary resources of copper (Agrawal and Sahu, 2010; Amer, 2002; Queneau and Gruber, 1997; Tripathy et al., 2005). This has led the focus of many researchers to develop technologies for recycling the secondary resources such as mill scale, scrapped brass and bronze, auto radiators, shredder pickings from auto bodies, motors, and electrical components, spent etchant and pickling solutions, circuit boards, spent catalyst, slags, anode slimes, etc., for the recovery of copper (Amer, 2002). Nearly 40% of the total copper used in the world is produced from secondary resources.

Anode slime is one of the important secondary resources of copper, which is obtained as a by-product during electrolytic refining of copper due to the settling of more noble metals such as gold, silver, tellurium,

selenium, etc., present in the impure copper anode at the bottom of the cell (Bilson, 1978; Jorgenson, 2002; Wang et al., 2003). It can be processed through different methods of extraction for the recovery of copper (Agrawal and Sahu, 2010; Amer, 2002). If treated through hydro- and electrometallurgical processing route using sulfuric acid leaching, the generated leach liquor may get contaminated with several impurities including selenium and tellurium. Unless rigorous purification of the leach liquor is carried out, these impurities may enter the electrodeposition circuit. Solvent extraction is widely used as the purification method for the leach liquor so as to separate copper from various metallic impurities. However, when the electrodeposition setup is coupled with solvent extraction unit, a close circuit forms and possibility of contamination of the solution with these impurities would continuously increase as the impurities may build up during subsequent copper electrodeposition operations. Thus, it is essential to study the effects of such impurities on the process parameters of copper electrodeposition and the quality of the deposits.

Several researchers have studied the effects of various metal impurities such as iron, manganese, cobalt, etc., on the electrodeposition of copper from sulfate solutions (Cheng et al., 2000; Das and Gopala Krishna, 1996; Hui et al., 2010; Loutfy and Bharucha, 1978; Panda et al., 2009). It has been reported in the literature (Andersen et al., 1983; Safizadeh et al., 2012) that the presence of selenium is detrimental to copper cathodes in many respects. Andersen et al. (1983) have reported that the presence of selenium results in nodular copper cathodes

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and that of Cu_2Se results in nodule free deposits. It has also been reported that the presence of selenium even at ppm levels affects the conductivity and softening temperature of copper. Recently, Safizadeh et al. (2012) have investigated the influence of selenium during electrorefining of copper. They observed that the presence of selenium affects the quality of electrorefined copper and the preferred crystal orientation. They also observed that selenium polarized the cathode during electrorefining. However, the information with regard to the influence of selenium on the electrodeposition of copper from sulfate baths is lacking in the literature.

Keeping this in view, an attempt has been made in the present study to investigate the effects of selenium on the cathodic current efficiency, energy consumption, polarization behavior of the cathode, crystal orientations, deposit surface morphology and purity of the deposits during the electrodeposition of copper from sulfate baths.

2. Experimental

All the electrodeposition experiments were carried out in an electrolytic cell made of glass containing aqueous solution of copper sulfate (Cu, 40 g dm^{-3}) and free sulfuric acid of 150 g dm^{-3} at an ambient temperature (31 °C) for 3 h at a current density of 200 Am^{-2}. The electrolytic solutions were prepared taking the required amount of copper sulfate and sulfuric acid in doubly distilled water. In order to examine the effects of selenium, freshly prepared stock solutions of sodium selenite (Na_2SeO_3) at a concentration of 2 g dm^{-3} was prepared by dissolving calculated amounts of sodium selenite in doubly distilled water. All the chemicals used were of AnalaR grade (MercK Chem. Ltd., India). Some experiments were carried out at 60 °C to observe the effect of selenium in particular on copper electrodeposition.

Before conducting electrodeposition and polarization studies, the surface of the cathodes was polished with 400 and 1200 grade silicon carbide paper and then rinsed with 1 M HCl and washed with distilled water. SS 304 and Pb–Sb (7%) sheets were used as cathode and anode, respectively, for electrodeposition studies. The distance between the electrodes was kept at 2.5 cm. The constant DC source was provided through a regulated power supply system [0–10 V, 2 A, Aplab Ltd., India]. Cell voltage was recorded using a multimeter connected across the anode and cathode. The cathodic current efficiency was determined from the weight gained by the cathode at the end of electrolysis.

The cathodic current efficiency (CE) and the energy consumption (EC) during the electrolysis of copper were calculated as per the following equations:

$$CE = {W_E}/{W_T} \times 100 \qquad (1)$$

where

CE	current efficiency (%)
W_E	experimental weight gain by the cathode (g)
W_T	theoretical weight gain to be expected if there is no side reaction (g).

$$EC = {V \times I \times T}/{W_E} \qquad (2)$$

where

EC	energy consumption (kWh/kg)
V	cell voltage (V)
I	current supplied to the cathode (A)
T	time (h)
W_E	experimental weight gain by the cathode (g)

Sections of the deposits were dissolved in nitric acid and aliquots were analyzed by atomic absorption spectrophotometer (AAS) to find out the extent of selenium contamination in the copper deposits.

Polarization studies were carried out in a three-electrode glass cell using Metrohm potentiostat/galvanostat model 128A. A platinum sheet was used as the working electrode, and a platinum wire was used as the counter electrode. Standard calomel electrode (SCE) was used as the reference electrode, and the potentials have been reported as such. Voltammetric scans were performed in the potential range of 0.5 to −0.1 V vs SCE at a scan rate of 10 mV s^{-1} to examine the effects of selenium on the current–voltage profile during the electrodeposition of copper. The electrolytic solutions were deoxygenated by purging high purity nitrogen gas before 15 min and during each voltammetric scan to ensure the system free from aerial or any dissolved oxygen which may affect the redox reactions.

The crystal orientations have been detected from the X-ray diffractograms generated from an X-ray diffractometer (PAN ANALYTICAL PW 1830) using Cu-K$_\alpha$ radiation having $\lambda = 1.5404$ Å. The changes in surface morphology have been examined using field emission scanning electron microscope (FESEM, Jeol:JSM 6510).

3. Results and discussion

3.1. Cathodic current efficiency and energy consumption

The variations in current efficiency (CE) and energy consumption (EC) for copper electrodeposition with the increase in the concentration of selenium in the electrolytic solution are shown in Fig. 1. For the electrodeposition of copper from pure solution, the CE was found to be about 100%. With the increase in selenium content in the solution, the change in the CE was insignificant till a concentration of 50 mg dm^{-3} beyond which it started decreasing gradually and reached 77.5% at 1000 mg dm^{-3} of selenium. It is also clear from the figure that the increase in selenium concentration in the system raised the EC of the cell. The EC was 1.6 kWh kg^{-1} while depositing copper from pure solution; however, it rose to ~2.114 kWh kg^{-1} in the presence of 1000 mg dm^{-3} of selenium in the solution. Thus, it is vital to mention here that the presence of selenium in the copper electrolytic bath affects adversely the electrodeposition of copper from sulfate system. From the AAS analysis report, it was observed that the contamination level of the deposits increased with increase in selenium concentrations in the bath (Table 1). It was also observed that the effect of selenium worsen at 60 °C, which caused decrease in current efficiency values significantly.
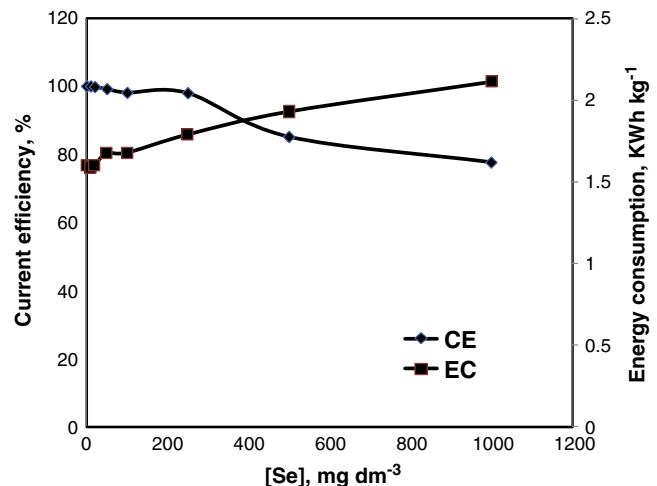

Fig. 1. Effect of selenium concentration on current efficiency and energy consumption during electrodeposition of copper.