Journal of International Scientific Publication:
Materials, Methods & Technologies, Volume 3

INFLUENCE OF ZINC IONS ON COPPER ELECTRODEPOSITION FROM SULPHURIC ACID ELECTROLYTES

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Abstract

By means of potentiodynamic and galvanostatic methods the influence of H_2SO_4, Zn^{2+} and hydroxyethylated-2-butyne-l, 4-diol (Ferasine) on the electroextraction of copper from sulphate electrolytes was studied. It was established that Zn^{2+} - ions and organic additive Ferasine decreases the cathodic currents and quantities of deposited copper during scanning to different vertex potentials only in electrolytes containing sulphuric acid. Thus they inhibit the process of copper deposition. Dense and smooth copper coatings on with current efficiency higher than 95% are deposited when Cu^{2+} concentration is higher than 5.0 g.dm^{-3} and current density is in the range 0.5 ÷ 2.0 A.dm^{-2}. More fine-grained coatings are obtained in the presence of H_2SO_4 and organic additive hydroxyethylated-2-butyne-l, 4-diol (Ferasine).

Key words: *copper, cyclic voltammogram, deposition, electroextraction, zinc*

1. INTRODUCTION

After a number of pyro- or hydrometallurgical ores treating, large amount of wastes with high metal content remains. For example, the waste product known as “blue powder” that results by condensing furnace gases during the thermometallurgical processing of non-ferrous ores contains: Zn (25-41%), Pb (20-25%), Fe (3-5%), Cu (0.5-1%), Cd (0.5-1%), etc. (Muresan et al. 1999, 2000). The purification of the electrolytes for Zn electrowinning by cementation is another process that produces wastes containing large amount of different metals such as: copper cake, containing Cu (36-54%), Zn (5-10%) and Cd (0.08-0.16%); copper-cadmium cake, containing Cu (10%), Zn (30%), Cd (12%); collective cake, containing Cu (5.8%), Zn (35.9%), Cd (7.2%); cobalt-nickel cake, containing Cu (25%), Zn (20%), Cd (3%), Co (0.75%), Ni (0.05%) (Karoleva, 1986). Cementates obtained during the hydrometallurgical zinc winning process, where the sulphate leach liquor is treated with arsenic trioxide and zinc powder for the removal of Cu, Ni, Co, Cd and other impurities contain: Cu (28.6%), Zn (22.4%), Cd (6.7%), Co (1.32) and Ni (0.16%) (Melzner et al., 1984). Flue dusts at a secondary copper smelter treated in the electrowinning zinc plant contain: Zn (40-65%), Cu (1-6%), Pb (6-20%), Cd (0.5-0.8%), Ni (0.1-1%), Sn (1-2%), etc. (Kammel et al., 1987)

These industrial wastes are a source of different valuable metals like copper, zinc, cobalt, nickel, cadmium, etc.

Muresan et al. studied the process of Cu electrowinning from sulphate acidic electrolytes and observed that the addition of small amounts of Zn^{2+} had no effect on the composition of the Cu deposits, but it increased their microscopic roughness (Muresan et al. 1999). The effect of horse-chestnut extract (HCE) and IT-85, representing a mixture of triethyl-benzyl-ammonium chloride (TEBA) and hydroxyethylated-2-butyne-l, 4-diol (Ferasine) upon the morphology and structure of Cu deposits, as

well as upon the cathodic polarization was investigated and compared to the effect exerted by thiourea and animal glue (Muresan et al., 2000). The additive IT-85 was found to be an efficient inhibitor of the Cu electrocrystallization process, leading to levelled and fine grained cathodic deposits. The effect of HCE was similar to the effect exerted by animal glue, leading to deposits consisting of rounded nodules, reflecting a smaller levelling effect. Varvara et al. studied the influence of TEBA, Ferasine and IT-85 on the kinetics of Cu electrodeposition from such electrolytes and on the morphology and structure of Cu deposits (Varvara et al. 2001, 2004, 2005). TEBA acts as an inhibitor of electrodeposition process only as a blocking agent competing for adsorption active sites of the cathodic surface with cuprous ions. Due to its adsorption on the electrode surface, Ferasine inhibits the charge transfer and thus affects the electrocrystallization step, impeding the crystal growth process and promoting the nucleation of Cu. In spite of their different chemical nature both additives were found to be efficient as levelling agents, leading to fine-grained cathodic deposits. Comparison of the inhibiting effects exerted by IT-85 and its components on the electrodeposition process pointed to the existence of a beneficial complementarity of TEBA and Ferasine when they are used in mixture. The aim of this paper is to study the influence of H_2SO_4, Zn^{2+} ions, hydroxyethylated-butyne-2-diol-1, 4 (Ferasine) and some experimental conditions on the process of Cu electroextraction from sulphuric acid electrolytes.

2. EXPERIMENTAL

The experiments were carried out in a thermostated (37 ± 1ºC), three-electrode glass cell without stirring of the electrolyte. The cathode (2,0 cm^2) and both anodes (4,0 cm^2 total area) were Pt plates. The reference electrode was a mercury/mercurous sulphate electrode in 0,5 M H_2SO_4 (SSE), its potential vs. NHE being +0,720 V. The studies were carried out using a cyclic potentiodynamic technique. Potential scannings at a rate of 30 mV sec^{-1} in the potential range from +1,000 to -1,800 V vs. SSE were performed by means of a computerized PAR 263A potentiostat/galvanostat using Soft Corr II software. The quantity of deposited copper was obtained by integration of the anodic peaks on the cyclic voltammograms. Galvanostatic deposition was carried out on copper cathodes (4,0 cm^2) at current densities in the range 0,5 ÷ 2,0 A.dm^{-2} using two Pb anodes containing 1% Ag. Pt and Cu electrodes were degreased in ultrasound bath and than only Cu cathode was etched in HNO_3 (1:1). Cu^{2+} ions (1.0, 5.0 or 10.0 g.dm^{-3}) were added to the base electrolytes: BE-1, containing 220 g.dm^{-3} $ZnSO_4.7H_2O$ and BE-2, containing 220 g.dm^{-3} $ZnSO_4.7H_2O$ and 130 g.dm^{-3} H_2SO_4. The organic additive in both electrolytes was 30% solution of hydroxyethylated-butyne-2-diol-1, 4 (Ferasine).

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic studies

3.1.1 Influence of Zn^{2+} and H_2SO_4 on copper deposition

Figure 1 shows CV curves obtained in electrolytes containing 10 g dm^{-3} Cu^{2+} (curve 1), 10 g dm^{-3} Cu^{2+} and 50 g.dm^{-3} Zn^{2+} (curve 2), 10 g.dm^{-3} Cu^{2+} and 130 g.dm^{-3} H_2SO_4 (curve 3) and 10 g.dm^{-3} Cu^{2+}, 50 g.dm^{-3} Zn^{2+} and 130 g.dm^{-3} H_2SO_4 (curve 4). The scan direction is changed at cathodic potential (vertex potential) -0.8 V. It is observed that in the presence of H_2SO_4 in the electrolyte (curves 3 and 4) both cathodic current and anodic peaks of Cu dissolution are higher than that's obtained in the absence of H_2SO_4 (curves 1 and 2). In Figure 2 are shown the current densities reached at different vertex potentials. It is observed that during scanning in electrolytes without H_2SO_4 (curves 1 and 2) they are not dependent on the presence of Zn^{2+} and are much lower than those obtained in electrolytes containing H_2SO_4 (curves 3 and 4). In electrolytes containing H_2SO_4 the current values reached during

scanning in electrolytes containing Zn^{2+} (curve 4) are lower than the values reached during scanning in electrolytes without Zn^{2+} (curve 3). The influence of Zn^{2+} is stronger pronounced at potentials higher than -1.0 V.

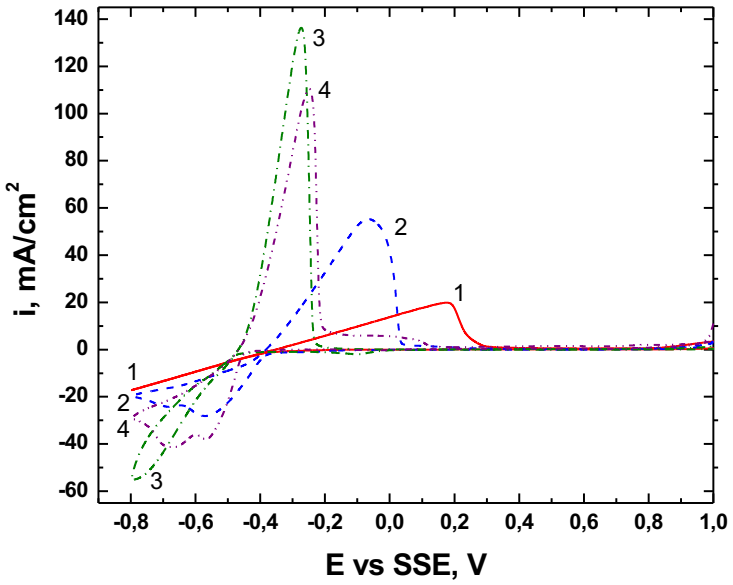


Figure 1. Cyclic voltammograms obtained on Pt cathode in electrolytes containing: 1) Cu^{2+} - 10 g.dm^{-3}, 2) Cu^{2+} - 10 g.dm^{-3} and Zn^{2+} - 50 g.dm^{-3}, 3) Cu^{2+} - 10 g.dm^{-3} and H_2SO_4 - 130 g.dm^{-3}, 4) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3} and H_2SO_4 - 130 g.dm^{-3}. E_{vertex} = -0.8 V vs. SSE

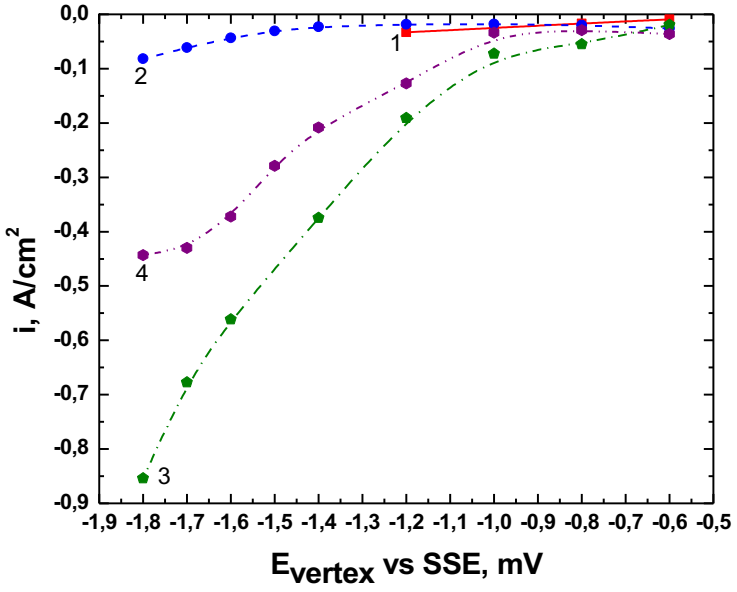


Figure 2. Current densities reached at different vertex potentials on Pt cathode in electrolytes, containing: 1) Cu^{2+} - 10 g.dm^{-3}, 2) Cu^{2+} - 10 g.dm^{-3} + Zn^{2+} - 50 g.dm^{-3}, 3) Cu^{2+} - 10 g.dm^{-3} + H_2SO_4 - 130 g.dm^{-3}, 4) Cu^{2+} - 10 g.dm^{-3} + Zn^{2+} - 50 g.dm^{-3} + H_2SO_4 - 130 g.dm^{-3}

In Figure 3 are presented the amounts of deposited Cu as a function of vertex potentials. It is observed that the quantities of deposited Cu in the electrolytes without H_2SO_4 (curves 1 and 2) are much smaller than those obtained in the presence of H_2SO_4 (curves 3 and 4). Zn^{2+} ions lead to decrease in the amounts of deposited Cu only in the presence of H_2SO_4 and at vertex potentials higher than -1.2V (curves 3 and 4).

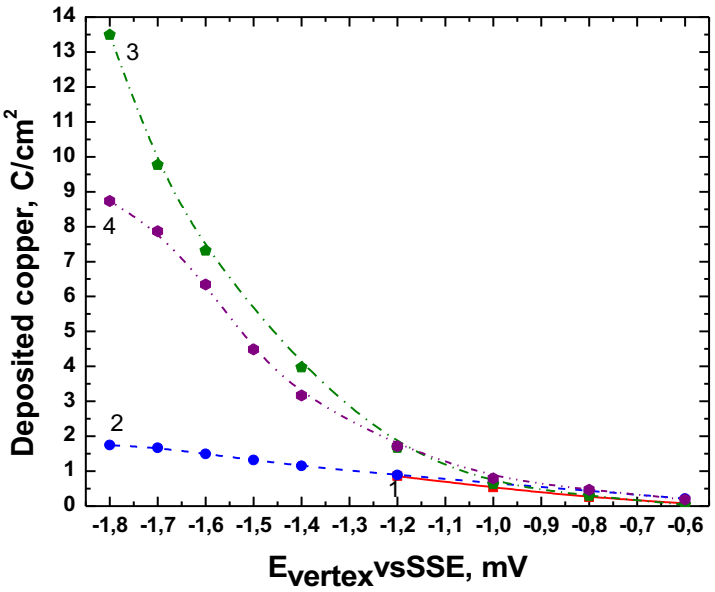


Figure 3. Deposited copper as a function of vertex potentials obtained on Pt cathode in electrolytes containing: 1) Cu^{2+} - 10 g.dm^{-3}; 2) Cu^{2+} - 10 g.dm^{-3} + Zn^{2+} - 50 g.dm^{-3}; 3) Cu^{2+} - 10 g.dm^{-3} + H_2SO_4 - 130 g.dm^{-3}, 4) Cu^{2+} - 10 g.dm^{-3} + Zn^{2+} - 50 g.dm^{-3} + H_2SO_4 - 130 g.dm^{-3}

The results presented in Figures 2 and 3 show that H_2SO_4 rising the conductivity of electrolytes has beneficial influence on Cu deposition. At the same time Zn^{2+} ions taking part in the electricity transport and eventually adsorbing on the cathode surface impede the process of Cu deposition and thus decrease the amount of deposited metal.

3.1.2. Influence of hydroxyethylated-butyne-2-diol-1, 4 (Ferasine) on copper deposition

Figure 4 shows CV curves obtained in electrolytes, containing 10 g.dm^{-3} Cu^{2+} and 50 g.dm^{-3} Zn^{2+} (curve 1), 10 g.dm^{-3} Cu^{2+}, 50 g.dm^{-3} Zn^{2+} and 1.0 cm^3.dm^{-3} Ferasine (curve 2), 10 g.dm^{-3} Cu^{2+}, 50 g.dm^{-3} Zn^{2+} and 130 g.dm^{-3} H_2SO_4 (curve 3) and 10 g.dm^{-3} Cu^{2+}, 50 g.dm^{-3} Zn^{2+}, 130 g.dm^{-3} H_2SO_4 and 1.0 cm^3.dm^{-3} Ferasine (curve 4). The scan direction is changed at cathodic potential (vertex potential) -0.8 V. It is observed that only in the electrolytes containing H_2SO_4 both cathodic current and anodic peaks of Cu dissolution obtained in the presence of Ferasine (curve 4) are lower than those obtained in its absence (curve 3). In Figure 5 is shown the influence of Ferasine on the dependence of the cathodic currents versus the vertex potentials. It is seen that Ferasine decreases significantly the current values only in electrolytes containing H_2SO_4 (curves 3 and 4). The Ferasine polarizing effect expressed by the relative decrease in currents rises from 23.7 % (at Evertex = -0.8 V) to 40.4% (at Evertex = -1.6 V)

showing that the eventually Ferasine adsorption on the cathodic surface rises with the vertex potential increase.

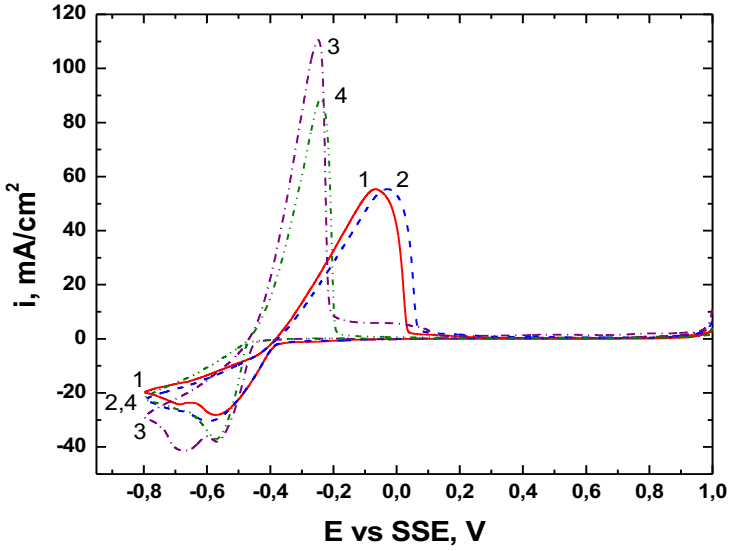


Figure 4. Cyclic voltammograms obtained on Pt cathode in electrolytes containing: 1) Cu^{2+} - 10 g.dm^{-3} and Zn^{2+} - 50 g.dm^{-3}, 2) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3} and Ferasine 1.0 cm^3.dm^{-3}, 3) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3} and H_2SO_4 - 130 g.dm^{-3}, 4) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3}, H_2SO_4 – 130 g dm^{-3} and Ferasine 1 cm^3 dm^{-3}. E_{vertex} = -0.8 V vs. SSE

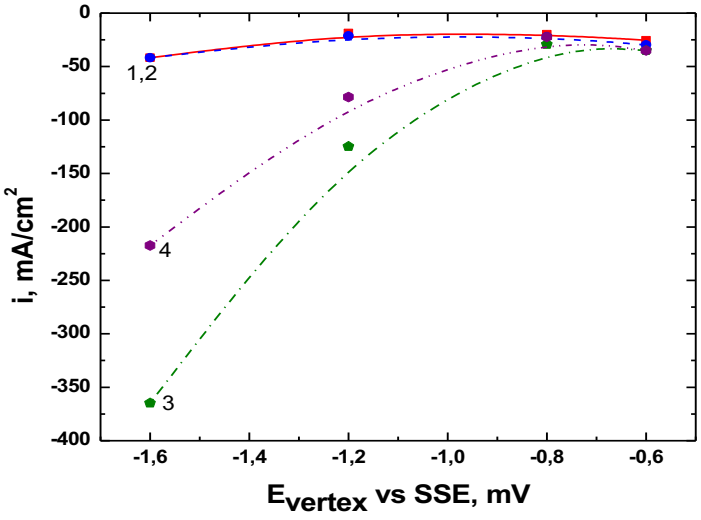


Figure 5. Current densities reached at different vertex potentials on Pt cathode in electrolytes containing: 1) Cu^{2+} - 10 g.dm^{-3} and Zn^{2+} - 50 g.dm^{-3}, 2) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3} and Ferasine 1.0 cm^3.dm^{-3}, 3) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g/L and H_2SO_4 - 130 g.dm^{-3}, 4) Cu^{2+} - 10 g dm^{-3}, Zn^{2+} - 50 g.dm^{-3}, H_2SO_4 - 130 g.dm^{-3} and Ferasine - 1.0 cm^3 dm^{-3}

In Figure 6 is shown the influence of Ferasine on the amoumt of deposited Cu as a function of vertex potentials. It is seen that addition of Ferasine decreases slightly (about 10%) the quantity of deposited Cu only in the case of deposition in electrolytes, containing H_2SO_4 (curves 3 and 4). The results presented in Figures 5 and 6 show that Ferasine polarizes predominantly the hydrogen evolution reaction than the electrodeposition of Cu.

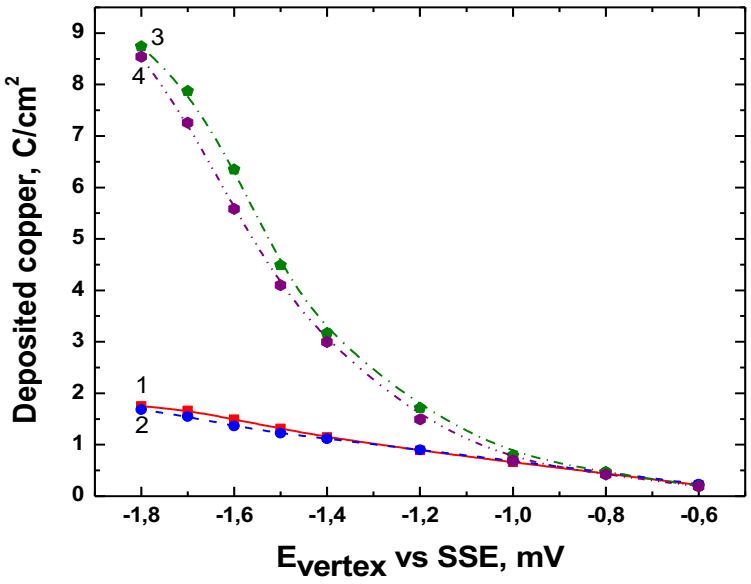
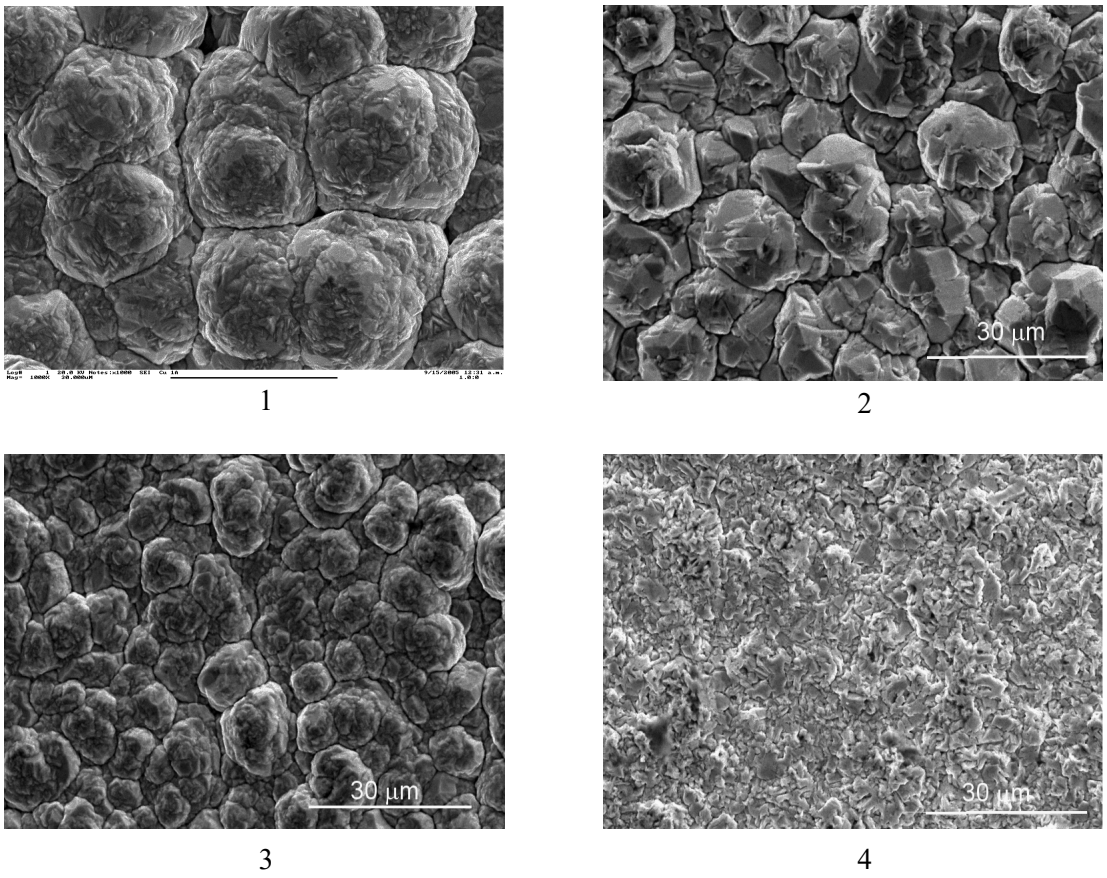


Figure 6. Deposited copper versus vertex potentials obtained on Pt cathode in electrolytes containing: 1) Cu^{2+} - 10 g.dm^{-3} and Zn^{2+} - 50 g.dm^{-3}, 2) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3} and Ferasine 1.0 cm^3.dm^{-3}, 3) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3} and H_2SO_4 - 130 g.dm^{-3}, 4) Cu^{2+} - 10 g.dm^{-3}, Zn^{2+} - 50 g.dm^{-3}, H_2SO_4 -130 g.dm^{-3} and Ferasine - 1.0 cm^3.dm^{-3}

3.2. Galvanostatic studies

The effect of current density and electrolyte composition on the surface morphology and composition of galvanostatically deposited coatings on Cu substrates was also studied. In all cases only copper is detected by microprobe analysis. It has been established that dense and smooth Cu coatings are deposited when the Cu^{2+} concentration is higher than 5.0 g dm^{-3} and the current density is in the range of 0.5 ÷ 2.0 A.dm^{-2}. At 1.0 A.dm^{-2} the deposition potential is -0.500 ÷ -0.600 V. In all cases the current efficiency of Cu deposition is higher than 95%. Figure 7 shows SEM micrographs of Cu coatings obtained after 3 h deposition at 1 A dm^{-2} in an electrolyte, containing 50 g dm^{-3} Zn^{2+} and 10 g dm^{-3} Cu^{2+} in the absence (Figure 7.1) and in the presence of 130 g dm^{-3} H_2SO_4 (Figure 7.2). In the presence of H_2SO_4 the morphology of Cu coatings is more fine-grained. In both cases the coatings are light red, smooth and semi bright. The addition of Ferasine (1.0 cm^3.dm^{-3}) leads to more fine-grained surface morphology of the coatings both in the presence (Figure 7.3) and in the absence of H_2SO_4. The additive effect is more strongly expressed at Ferasine concentration 5.0 cm^3.dm^{-3} (Figure 7.4). In all cases the coatings are light red, smooth and bright. The SEM micrographs confirm the results obtained by potentiodynamic investigations.



1 2

3 4

Figure7. SEM micrograph of Cu coatings obtained at different experimental conditions: 1) after 3 h deposition at 1 A dm-2 in an electrolyte, containing 50 g.dm^{-3} Zn^{2+} and 10 g.dm^{-3} Cu^{2+}; 2) after 3 h deposition at 1 A.dm^{-2} in an electrolyte, containing 50 g.dm^{-3} Zn^{2+}, 10 g.dm^{-3} Cu^{2+} and 130 g.dm^{-3} H_2SO_4; 3) after 2 h deposition at 1 A.dm^{-2} in an electrolyte, containing 50 g.dm^{-3} Zn^{2+},10 g.dm^{-3} Cu^{2+}, 130 g.dm^{-3} H_2SO_4 and 1 cm^3.dm^{-3} Ferasine; 4) after 2 h deposition at 1 A.dm^{-2} in an electrolyte, containing 50 g.dm^{-3} Zn^{2+}, 10 g.dm^{-3} Cu^{2+}, 130 g.dm^{-3} H_2SO_4 and 5 cm^3.dm^{-3} Ferasine. The magnification of pictures is x1000

The grain size of all coatings is presented in Table 1.

Table1: Grain size (µm) of Cu coatings obtained in different electrolytes.

Electrolyte	Grain size (µm)
50 g.dm^{-3} Zn^{2+} + 10 g.dm^{-3} Cu^{2+}	25-30
50 g.dm^{-3} Zn^{2+} + 10 g.dm^{-3} Cu^{2+} + 130 g.dm^{-3} H_2SO_4	12-18
50 g.dm^{-3} Zn^{2+} + 10 g.dm^{-3} Cu^{2+} + 130 g.dm^{-3} H_2SO_4 + 1 cm^3.dm^{-3} Ferasine	10-12
50 g.dm^{-3} Zn^{2+} + 10 g.dm^{-3} Cu^{2+} +130 g.dm^{-3} H_2SO_4 + 5.0 cm^3.dm^{-3} Ferasine	< 3

4. CONCLUSIONS

Sulphuric acid increases the cathodic currents and quantities of deposited copper. Zn^{2+} ions decrease the cathodic currents and quantities of deposited copper only in the electrolytes containing sulphuric acid. Thus Zn^{2+} ions impede the process of copper deposition. In both cases the effect of acid or Zn^{2+} ions is more clearly pronounced at vertex potentials higher than - 1.0 V vs. SSE. Ferasine decreases the cathodic currents and quantities of deposited copper only in the electrolytes, containing sulphuric acid which shows that it inhibits the reaction of copper deposition. Dense and smooth copper coatings on Cu cathode with current efficiency higher than 95% are deposited when Cu^{2+} concentration is higher than 5.0 $g.dm^{-3}$ and current densities are in the range 0.5 ÷ 2.0 $A.dm^{-2}$. More fine-grained coatings are obtained in the presence of H_2SO_4 and organic additive hydroxyethylated-2-butyne-l, 4-diol (Ferasine).

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