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The use of anodic linear sweep voltammetery analysis (ALSV) for characterization the copper anodes used for sulphur acidic waste solution treatment

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ABSTRACT

This paper addresses on investigation the possibility of electrolytic treatment the sulphur acidic waste solution, obtained in the conventional electrolytic copper refining process. The copper anodes with non-standard nickel, lead, tin and antimony content were specially prepared for the refining process. Nickel content of all anodes was approximately 7.5 mass %, and the content of lead, tin and antimony was varied. Results, obtained using the standard electrochemical techniques, have indicated that the anodes could be used under the same conditions as well as in the conventional copper refining process.

Key words: *copper anodes, non-standard chemical composition, electrorefining, sulphur acidic waste solution, alloying elements*

1. Introduction

The commercial anodes with copper content from 98.0 to 99.5 mass %, obtained in the flame refining process and the base working solution with Cu^{2+} ion concentrations ranging from 35 to 50 g dm^{-3} and sulphuric acid concentrations ranging from 150 to 250 g dm^{-3}, are used in the conventional copper electrolytic refining process [1]. The process is developed under the force of an applied direct current such as Cu ion dissolves at the anode, enter the electrolyte and then selectively deposit onto the cathode. The ingredients have impact on the structure of anode material. Thus, by changing its properties, they could be dissolved at the anode, remain dissolved into the base electrolyte, remain at the anode and become part of anode slime, forming the "floating slime" and possible deposit onto a cathode.

2. Experimental

Copper anodes, used for the investigation in the electrorefining process, were prepared from the next pure metal components: anode copper, nickel, lead, tin and antimony. In all anodes, nickel content was approximately 7.5 mass %, while lead, tin and antimony content was variable, where total maximum content of these elements was up to 3 mass %. Induction furnace (Balzers), power of 15 kW and a graphite crucible, were used for preparation the suitable mixture. Upon reaching the melt temperature of 1300 °C, the alloying elements were added. Graphite rods were used for oxygen reduction, and oxygen quantity in the melt was checked using device for determination the oxygen content (LECO Corp. RO-II6). Melt was casted into

the suitable steel moulds at temperature of 1300 ^{o}C, only when the oxygen content was under 200 ppm.

Cyclic voltammograms were recorded using potentiostat PAR 273A at ambient temperature of 25 $\pm$ 1 ^{o}C in aqueous sulphuric acid solution. The experiments were carried out in a standard three electrode arrangement cell. The working electrode (analyzed samples of pure metals Cu and Ni as well as copper bearing anodes) had surface area of 1 cm^2. The saturated calomel electrode was used as the reference electrode, while the counter electrode was platinum foil with the same characteristics as working electrode. Before the start of experiments, the samples were held in the solution at open circuit potential during 10 min in order to establish the stable corrosion potential. The samples were analyzed starting from the cathode potential of -1 V towards the anode potential of 1 V, at the potential change rate of 2 mV s^{-1}.

2. Results and Discussion

2.1. Chemical composition of anodes

The average values of Ni, Pb, Sn, Sb and Cu content, obtained by analyzing the composite samples preparing from the material from bottom, middle and top of the anode, are presented in Tab. 1.

Tab. 1 Chemical composition of anodes

Anode	Elements				
	Ni	Pb	Sn	Sb	Cu
	Chemical composition, mass %				
A1	7.49	0.123	0.873	0.902	90.47
A2	7.52	0.367	0.815	0.889	90.30
A3	7.49	0.728	0.825	0.893	89.91
A4	7.35	0.129	0.432	0.429	91.51

The samples of pure Cu and Ni metals as well as the samples of anodes, with chemical composition, presented in Tab. 1, were analyzed using the ALSV method [2], at room temperature in 2 mol dm^{-3} H$_2$SO4. Based on dissolution voltammograms, it is evident from Fig. 1, that the all examined materials were passivated in the analyzed working electrolyte, but at various potential values and current density.

Fig. 1 shows that Ni first starts to dissolve through two peaks, after the region of active metal dissolution occurred. Also, Ni at the lowest potential values first enters into the passivation region. The amount of electrical charge witch accompanied the dissolution, was the lowest. Thereupon, Cu starts to dissolve with the peak maximum, of about 220 mA cm^{-2}, what is suitable to the current density range of 200 - 270 mA cm^{-2}, at which the most conventional copper refining plants operate.

Also, Fig. 1 shows that dissolution currents density of anodes, as well as suitable electrical charge, are higher than in the case of pure Cu and Ni metals and that the recorded current density values, at the dissolution peak maximum, are higher than 250 mA cm^{-2} even at room temperature. Fig. 1 also shows that there is only one dissolution peak on the voltammograms of copper anodes dissolution that points out that Cu and Ni formed a solid

solution. At scan rate of 2 mV s^{-1}, there are no peaks that could correspond to dissolution of Pb, Sn and Sb impurities.
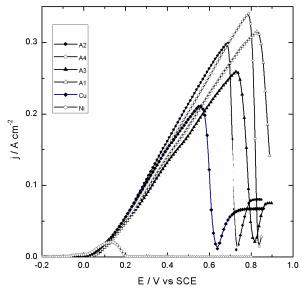

Fig. 1. Voltammograms of pure metals Ni, Cu and copper anodes dissolution in 2 mol dm^{-3} H$_2$SO$_4$, at scan rate of 2 mV s^{-1}.

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Considering that Ni content is approximately 7.5 mass %, the observations could be made regarding the influence of other alloying elements (Pb, Sn and Sb) on electrochemical characteristics of copper. Anode (A3) with the highest Pb content, is the last one that starts to dissolve and the voltammogram shows that this dissolution is associated with the least amount of electrical charge as well as the value of current density that corresponds to a dissolution peak maximum has the lowest value, slightly higher value than 250 mA cm^{-2}. By comparison the dissolution voltammograms of A1 and A4 anodes with the same Pb content, and A4 has double less content of Sn and Sb, and total the least content of ingredients, it was observed that the dissolution value of current density, corresponding to the maximal dissolution peak of A4 anode, has higher value than 350 mA cm^{-2}.

With decrease of Pb content, active dissolution of copper anodes started earlier. The lowering of Pb content in anode lead to larger amount of dissolved anode material. All voltammograms show that active dissolution of anodes was developed continuously at current density of 250 mA cm^{-2}, and that they are able to be used even at significantly higher values of current density. Based on measured values of copper anodes current density dissolution and compared to the values of current density dissolution in the sulphur acidic electrolyte in conventional production, it was found that the obtained values for the copper anodes are higher. Also, it was found that the copper anodes were in the region of active dissolution all the time at the current density used in conventional production.

Based on the obtained results shown in Fig. 1, it could be concluded that copper anodes with non-standard content of ingredients could be used in the electrolytic refining process, with the same technological parameters used in conventional production of cathode copper.

Acknowledgment

References

[1]. A. K. Biswas and W. G. Davenport, *Extractive Metallurgy of Copper,* 1980, 2ndedition, Pergamon Press, London, pp. 230-238.

[2]. V.D.Jović, R.M.Zejnilović, A.R.Despić, J.S.Stevanović, "Characterization of Electrochemically Formed Thin Layers of Binary Alloys by Anodic Linear Sweep Voltammetry", J.Appl.Electrochem. 18 (1988) 511-517.

3. R. Marković, B. Friedrich, J. Stajiić Trošić, B. Jordović, B. Jugović, M. Gvozdenović, J. Stevanović, "Behaviour of non-standard composition copper bearing anodes from the copper refining process", Journal of Hazardous Materials 182 (2010) 55–63