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Analyzing the corrosion characteristics of anodes used for the sulphur acidic waste water treatment

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ABSTRACT

This paper addresses an investigation of the possibility of electrolytic treatment of 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. It was observed, that anodes with O₂ content lower than 200 ppm, were not passivated. Results, obtained using the standard electrochemical techniques, have indicated that the anodes with non-standard chemical composition could be used under the same conditions as well as in the conventional copper refining process.

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

1. Introduction

Presence of Ni content up to 0.3 mass %, has no effect on solubility of copper anodes, whereas in excess of that amount, resulted into formation of NiO. Nickel oxide is not soluble in the sulphur acidic electrolyte, remains in the anode slime and may cause the effect known as anode passivation [1-3]. The quantity of NiO in anodes and anode slime is also the function of oxygen content such as the quantity of NiO in anode and anode slime increases with the oxygen content increase. Sb content less than 0.01 mass %, has no significant effect on electrochemical behaviour of anodes, but it could cause Cu₂O spheroidization in the eutectic region [4, 5], until Sb content higher than 0.05 mass % at presence of Ni of 0.25 mass %, leads to the formation of thin laminated inclusions at the copper grain boundaries. High concentration of Ni and Sb in anodes resulted in formation of insoluble phase in the form of 3Cu₂O-4NiO-Sb₂O₅ [4-7]. Formation of "Kupferglimmer" is undesirable, since it leads to passivation of the anode and formation of floating slime.

2. Experimental

The copper anodes, used in the process of electrorefining, 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 %. Copper content in the anodes is a difference up to 100 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 °C, only when the oxygen content was under 200 ppm.

Polarization curves were recorded using potentiostat PAR 273A at ambient temperature of 25 ± 1 °C in aqueous sulphuric acid solution. The experiments were carried out in a standard three electrode arrangement cell (200 cm³). The working electrode (analyzed samples of pure metals Cu and Ni as well as copper bearing anodes) had surface area of 1 cm². The saturated calomel electrode was used as the reference electrode, while the counter electrode was platinum foil with the same characteristics as working electrode. 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.

3. Results and Discussion

3.1. Chemical composition of anodes

Chemical analysis of all anodes showed that oxygen content was up to 200 ppm. 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 copper bearing 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

3.2. Analyzing the corrosion characteristics of pure nickel, copper and copper anodes

For the purpose of analyzing the corrosion stability of Ni, Cu and copper anodes, the corrosion current density as well as anode and cathode Tafel slopes was determined in sulphuric acid solution.

Fig. 1 shows the values of corrosion potentials as well as corrosion current density of Ni, Cu and anodes. Corrosion potentials of Cu and anodes are not stable in contrast to Ni, because the section of anode and cathode Tafel lines is not at corrosion potential. Value of Ni corrosion current density is higher than the appropriate values for Cu and anodes and corrosion potential of Ni is more than 150 mV negative than corrosion potential of Cu and anodes.

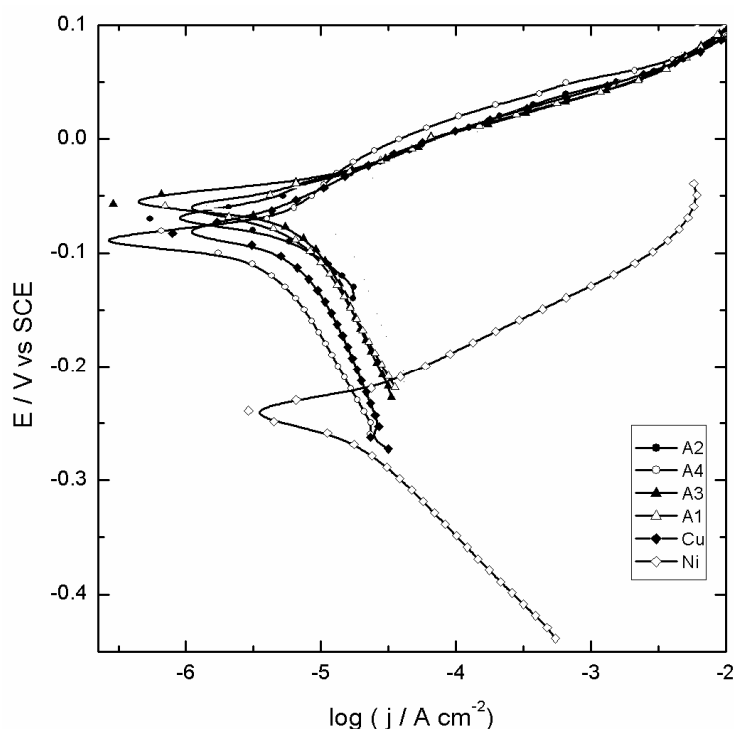


Fig. 1. Corrosion characteristics of pure metals Ni, Cu and copper anodes in $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, at scan rate of 2 mV s^{-1} .

Fig. 1 shows that corrosion current density of Cu as well as the appropriate values for copper anodes has very low values of about 6 mA cm^{-2} , while Ni corrosion current density value is about 12.5 mA cm^{-2} .

Values of the anode Tafel slopes of all analyzed materials, are quite stable. For pure copper and copper anodes, the obtained values are about 40 mV dec^{-1} . Value of the anode Tafel slope, measured using Ni is 60 mV dec^{-1} . Although the value of standard Ni potential is at $E^\ominus(\text{Ni}^{2+}|\text{Ni}) = -0,250 \text{ V}$, the standard potential of oxide formation is at $E^\ominus(\text{NiO}|\text{Ni}) = +0,110 \text{ V}$. Therefore, Ni passes rapidly into the pre-passivation region during determination the anode polarization curves in acid solutions, consequently, the linear dependence $E - \log j_a$ is obtained only in a narrow region of current densities (Fig. 2). Kinetics of anode dissolution of Ni can be explained by several dissolution mechanisms. The Tafel slope of anode dissolution of nickel in acid solutions, at stationary measurements, is $b = dE / d(\log j_a) = 40 \text{ mV dec}^{-1}$ and, in this paper at non-stationary measurements, the obtained value is $dE / d(\log j_a) = 60 \text{ mV dec}^{-1}$.

Values of the cathode Tafel slopes of Cu and copper anodes are very disseminated, ranged from 90 to 260 mV dec^{-1} , what is the result of high overstrain of hydrogen escape. Value of the cathode Tafel slope, measured on Ni is 120 mV dec^{-1} .

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