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STUDY OF COPPER BEARING ALLOYS CORROSION CHARACTERISTICS

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ABSTRACT

This paper addresses investigation of the corrosion behavior of copper bearing anodes with high nickel content. Anodes are produced from different solid wastes formed during the copper or nickel row materials treatment. Nickel content in anode samples had values up to 10 mas %. The content of tin, lead and antimony was up to 1 % for each of elements. Sulphuric acid solution, concentration of 172 g/l was used as electrolyte for corrosion behavior investigation. The corrosion behavior of anode samples was defined by using the anode linear potential sweep method. Obtained results showed that the pasivation of anode in sulphuric acid solution is not registered during the process with current density up to 200 mA cm^2.

Keywords: anode, Cu, Ni, Sn, Pb, row material

1. INTRODUCTION

Large amounts of solid and liquid waste materials appeared during the copper and nickel row materials treatment. These wastes are suitable materials for further recycling aim to valorisation of useful components. The main problem is to find appropriate technology for treatment of these wastes based on various materials characterictics.

The electrorefining process of copper anodes which purity is up to 99,5 % Cu, obtained during the mining and metalurgical treatment of copper bearing ore, is using in many plants for cathode copper production, according to standard BS: 6017.

Copper ions dissolve at the anode, enter the electrolyte and then selectively deposit onto the cathode under the force of an applied direct current. Impurities in the anode either dissolve into the electrolyte and circulate with it or remain at the anode and become part of the anode slime (1).

For the copper bearing anodes obtained by treatment of solid wastes based on copper and nickel, it is known that that nickel in concentration up to 3% dissolves virtually 100 % into the electrolyte. The content in excess of that amount result in the formation of some NiO upon the anode solidification (2,3).

Aim to define the corrosion behavior of the recycled anodes in sulphate solution, the different electrochemical measuring were done, (4).

2. EXPERIMENTAL PROCEDURE

The waste solid materials on the copper and nickel base are used for the preparation of copper bearing anode material with nickel content up to 10 %. These anode samples are used for the electro refinement process aim to cathode copper valorisation as the cathode copper. On the other side, nickel from anode is dissolved into electrolyte with possibility for valorisation in a form of salts.

According to this request, it was done multiphase experiment according to the industrial parameters.

Material which was used as anode samples for the tests were prepared from pure metals: copper, nickel, tin, antimony and lead. Copper was main component, nickel was added in content up to 10 % and other components in content up to 1 %.

An induction furnace with melting power of 10 - 15 kW is used for casting. The crucible made of graphite; with volume of 1.8 l. Smelting and casting process does not carry out by the use of pressure or vacuum. When temperature of 1300°C is reached, alloying elements are added. Graphite sticks are utilized for oxygen reduction in melt. Oxygen content was measured before casting. Glass pipettes were used for sampling and determination of oxygen content. Reduction process is stopped when the oxygen content was achievement the value of under the 200 ppm. and melt is cast at approx. 1300°C. After the self-adsorption cooling, anodes are preparing for the electrolytic treatment by mechanical removal of 2 mm surface area.

Chemical analyses were performed using an optical emission spectrometry (OES) on apparatus OES ARL 4460.

Electrochemical measurements were conducted in a three electrode arrangement cell where the working anode was from:

1. Cathode copper – Pure copper
2. Technical nickel - Pure nickel
3. Copper bearing alloys with Ni content up to 10 %. The content of alloying elements was max 1 % for each of elements.

The saturated Calomel electrode (SCE) was used as reference electrode and Pt with the same area as so as counter electrode. Electrochemical measurements by anodic liner sweep voltammetry (ALSV) method are done on potentiostat PAR 273 A, on voltage scan rate of 2 mV s^{-1}. Electrolyte concentration of 172 g/dm^3 was prepared by using the 98 % sulphuric acid p.a quality and bidestilated water.

3. RESULT AND DISCUSSION

From the diagram on Figure 1, the values of corrosion potential as so as the values of corrosion current for nickel anode, copper anode and Cu-Ni alloys anode sample, could be readout. It could be seen that the corrosion current value of Ni anode is lower than corrosion current value of cathode copper. Also, the corrosion current value for pure Ni is lower than values for Cu-Ni alloys. The value for corrosion potential for pure Ni is 200 mV more negative regard to corrosion potential for pure Cu and Cu-Ni alloys.

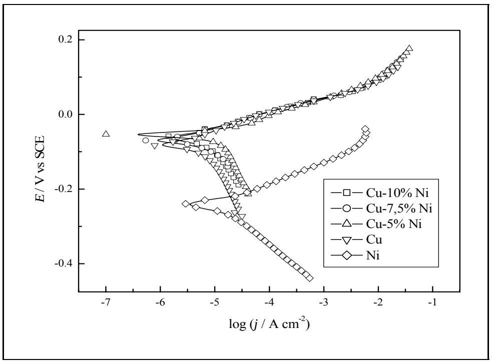

Fig.1. Corrosion behavior of different anode samples in sulphuric acid solution

The corrosion current values, as so as the anode and cathode Tafel slope was determinate aim to define this recycling anode stability in sulphuric acid solution. The values for Tafel slope for anode reaction on pure Cu and alloys were about 0.040 V dec^{-1} . Those values are enough stabile. In a case of pure Ni, the obtained value was 0.060 V dec^{-1}. The values for Tafel slope for cathode reaction were in range from 0.080 to 0.260 dec^{-1}. It was explanation by high potential of hydrogen evolution reaction on pure copper and cop per alloys. This value is decreased with nickel content increasing. For the pure nickel, this value is 0.120 V dec^{-1}. All alloys have got the very low corrosion current values, up to 10 μA cm^{-2}.
The values for standard Ni potential is $E^{\ominus}(Ni^{2+}| Ni)$ = - 0,250 V, and the values for standard potential of nickel oxide formatting is $E^{\ominus}(NiO | Ni)$ = +0,110 V. It is explanation for the fast appearance of passivation area and short time of E - log j_a linear dependence in confined range of current density.
In the acid sulphate solution, the values of Tafel slope for nickel anode dissolution is $dE / d(\log j_a)$ = 40 mV dec^{-1} and reaction array relative to H^+ ions is:
$p(H^+) = d(\log j_a) / d(\log c(H^+)) = -1$ or about 60 mV dec^{-1} under the unstationar measurements.

The obtained parameters are accordant with the next mechanism:

$$Ni + H_2O \rightleftarrows NiOH_{ads} + H^+ + e^- \quad (1)$$

$$NiOH_{ads} \rightarrow NiOH^+_{ads} + e^- \quad (2)$$

$$NiOH^+_{ads} + H^+ \rightleftarrows Ni^{2+} + H_2O \quad (3)$$

and summary

$$Ni \rightleftarrows Ni^{2+} + 2\,e^- \quad (4)$$

The stationary anodic current is presented by the following equation:

$$j_a = k\, a\left(\mathrm{H}^+\right)^{-1} \exp\left[\frac{3FE}{2RT}\right] \quad (5)$$

4. CONCLUSION

Based on literature data, it is known that copper alloys with nickel content higher than 3 % become passivity in sulphuric acid solution.
The results of experimental investigation are indicated that copper bearing alloys with nickel content up to 10 % Ni and other alloying elements up to 1 % were not passivated in sulphuric acid solution. The results of the investigations also indicated that the values of electrolytic dissolution could be up to 200 mA cm^{-2}.

5. REFERENCES

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