



## ELECTROCHEMICAL BEHAVIOR OF COPPER WITH NON-STANDARD IMPURITIES CONTENT

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### Abstract

This paper presents the results of electrochemical behavior of copper recycling anode with non-standard impurities content in sulphuric acid solution. The anodes were obtained by casting the waste material formed in Cu refining processes and contained the next alloying elements: Ni in concentration up to 10 % and Sn and Pb in concentration of some percentage. The present impurities remain the various problems on electrochemical behavior of anode material.

The obtained results showed that the passivation of recycling anode during the electrolytic process in sulphuric acid solution is not registered. Copper is dissolved from the anode and deposited on cathode by using the direct current. In the same time, nickel is dissolved from anode and retained in electrolyte. The possibility of nickel separation and production from this solution in a form of salts using chemical method or pure metal form of electrochemical deposition is feasible according to concentration increasing.

For better understanding the electrochemical behavior of recycled anodes, the corrosive behavior of anodes was studied in a three arrangement cell. Sulphuric acid solution was used as electrolyte, and the method of linear potential change was used in defining the phase content.

### Key words:

recycling anode, Cu, Ni, Sn, Pb, electrochemical process

## 1. INTRODUCTION

Large amounts of waste materials from the copper smelting process are used for recycling. Selection of recycling methods depends on material type for recycling.

The most often used method for Cu, Ni, Sn and Pb production from various types of waste materials is the electrolytic refining process. It is known that Ni presence in anode material, higher than about 3 %, results into anode passivation in the sulphuric acid solution.(1,2). For better understanding the electrochemical behavior of recycled anodes, the various electrochemical measuring were done.

## 2. EXPERIMENTAL PROCEDURE

The copper and nickel bearing waste materials obtained in copper refinement processes are used for the production of materials which could be use in electrolytic process for copper cathode production in the one side and on the other side, for the nickel transferring in solution form aim to further valorization.

According to this request, it was done multiphase experiment in a three electrode arrangement cell, according to the industrial parameters:

- ✚ Material which was used as anode material was prepared from pure metals: copper, nickel, tin and lead. Copper was main component, nickel was added in content up to 10 % and tin and lead in content up to 1 %.

An induction furnace (Balzers) 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 by the use of Electro- Niter oxygen measuring system. 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. an melt is cast at approx. 1300°C. After the self-adsorbtion 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 3 electrode arrangement cell where the working anode was pure Cu, pure Ni or some copper bearing alloys. The saturated Callomel electrode (SCE) was used as reference electrode and Pt with the same area as so as working anode. Polarization curves and measurements by anodic liner sweep voltammetry (ALSV) method are done on potentiostat PAR 273 A, on voltage scan rate of 2 mV/s. Electrolyte of concentration of 172 g/dm<sup>3</sup> was prepared by using the 98 % sulphuric acid p.a quality and bidestilated water.

### 3. RESULT AND DISCUSSION

The results of chemical analyses:

1<sup>st</sup> sample: Cu - purity of 99.95 %

2<sup>nd</sup> sample: Ni - purity of 99.9 %

3<sup>rd</sup> sample: Alloy Cu-Ni with 5 % Ni and up to 1 % of Sn and Pb

4<sup>th</sup> sample: Alloy Cu-Ni with 7.5 % Ni and up to 1 % of Sn and Pb

5<sup>th</sup> sample: Alloy Cu-Ni with 10 % Ni and up to 1 % of Sn and Pb

The corrosion property of different samples is presented on Figure 1.

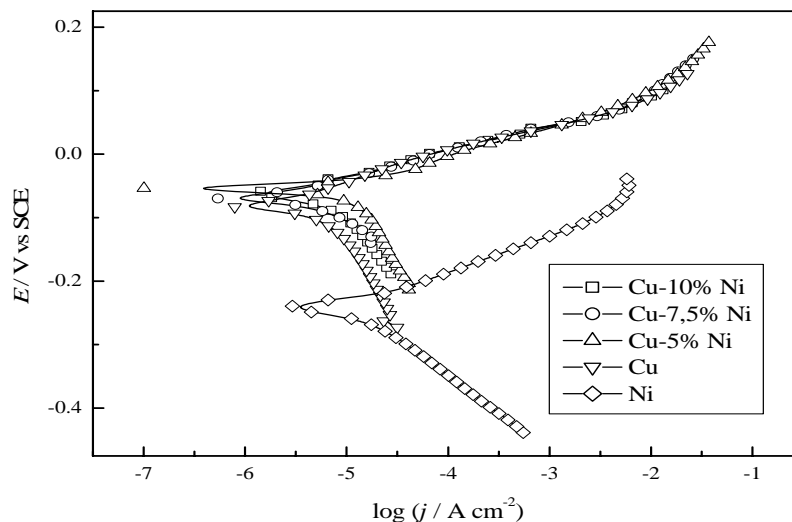


Figure 1. Corrosion behavior of pure Ni, pure copper and Cu-Ni alloys with 5 % Ni, 7.5% Ni and 10% Ni in sulphuric acid solution.

From the diagram on Figure 1, the values of corrosion potential as so as the values of corrosion current for pure Ni, pure Cu and Cu-Ni alloys could be readout. It could be seen that the corrosion current value of pure Ni is lower than corrosion current value of pure Cu. 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.

The corrosion current values, as so as the anode and cathode Taffel inclinations was determinate aim to define this recycling anode stability in sulphuric acid solution. The results are presented in Table 1.

Table 1. Corrosion current and Tafel inclinations

Description	$b_{\text{cath.}}$ (V dec <sup>-1</sup> )	$b_{\text{anod.}}$ (V dec <sup>-1</sup> )	Corrosion ( $\mu\text{A cm}^{-2}$ )
Cu-Ni, 10 % Ni	0.080	0.050	6.0
Cu-Ni, 7.5% Ni	0.090	0.040	3.0
Cu-Ni, 5% Ni	0.200	0.040	6.0
Pure Cu	0.260	0.045	5.0
Pure Ni	0.120	0.060	12.5

The next values are obtained:

1. The values for Tafel inclination for anode reaction on pure Cu and alloys were about 0.040 V dec<sup>-1</sup> and. Those values are enough stabile. In a case of pure Ni, the obtained value was 0.060 V dec<sup>-1</sup>.
2. The values for Tafel inclination for cathode reaction were in range from 0.080 to 0.260 V dec<sup>-1</sup>. It was explanation by high potential of hydrogen evolution reaction on pure copper and copper alloys. This value is decreased with nickel content increasing. For the pure nickel this value is 0.120 V dec<sup>-1</sup>.
3. All alloys have got the very low corrosion current values, up to 10  $\mu\text{A cm}^{-2}$ .

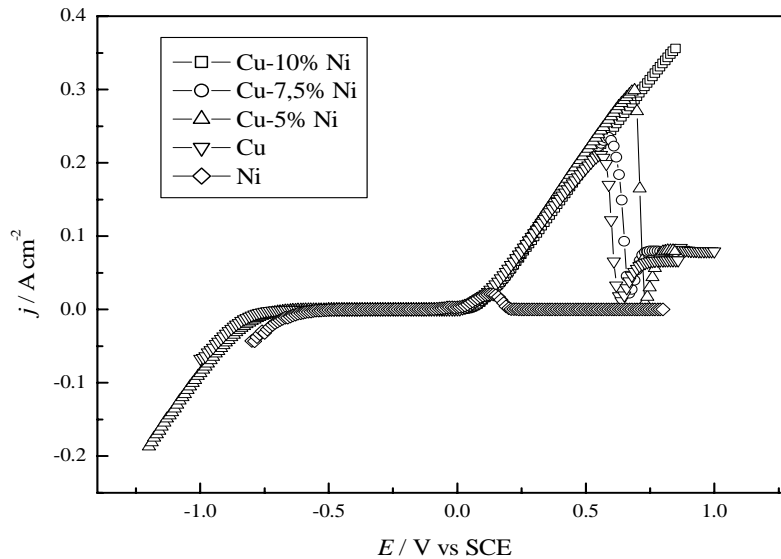


Figure 2. Current density versus voltage curve at a voltage scan rate of 2 mV/s

From the diagrams on Figure 2, could be seen that dissolution of pure Ni started before all other materials. For dissolution of pure is characteristic that the electric arc charge is the minimal and the area of active dissolution is terminated on potential of 0,2 vs SCE. The dissolution of pure copper started on more positive potential regarding to value of pure nickel potential. The quantity of electric arc charge is higher than for pure nickel. The electrolytic dissolution process of alloys: first started alloy with 5 % Ni, than alloy with 7.5 % Ni and than alloy with 10 % Ni. The characteristic of Cu-Ni alloy where the Ni content was 10 % is the highest quantity of electric arc charge and the value for potential on which started passivation is the most positive regarding to other materials.

#### 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 (Figure 2) are indicated that copper bearing alloys with nickel content from 5 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<sup>2</sup>.

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## REFERENCE

- [1] G.Jarjoura and G.J.Kipouros, "Electrochemical Studies on the Effect of Nickel on Copper Sulphate Solutin" Canadian Metallurgical Quarterly, Vol 45, No 3, pp 283-294, 2006
- [2] G.Jarjoura and G.J.Kipouros, "Effect of nickel on copper anode passivation in a copper sulfate solution by impedance spectroscopy", Journal of Applied Electrochemistry, Vol 36, pp 691-701 (2006).
- [3] V. Jović, R. Zejnilović, A. Despić, J. Stevanović, Characterization of electrochemically formed thin layers of binary alloys by linear sweep voltammetry, Journal of Applied Electrochemistry, Vol. 18, No. 4. (1988), pp. 511-520