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DEVELOPMENT OF A METHOD OF ELECTRODEPOSITION OF NON-FERROUS METALS ON A ROTATING CATHODE COVERED WITH GALLIUM

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Preliminary Note – Prethodno priopćenje

Electrodeposition of copper and nickel from acidic solutions using a rotating cathode coated with liquid and solid gallium has been studied. Methods of nonferrous metals separation from the gallium coating of the cathode were determined. Electrodeposition on the liquid gallium coating was carried out at a temperature of 50 °C. Separation of metals from gallium was performed by alkaline treatment. On the solid gallium cathode coating, electrodeposition was performed at 25 °C. The metal precipitates were separated from the cathode after it was heated. When using cathode with hard gallium coating the reduction of electric power consumption for copper by 85 % and for nickel by 15 % was obtained.

Keywords: non-ferrous metals, electrodeposition, gallium, copper, nickel, X-ray research

INTRODUCTION

Non-ferrous metals can be extracted from a variety of industrial products, scrap, sewage and waste products [1-3]. Electrochemical methods of extraction of non-ferrous metals from solutions are widely used [4,5]. The possibility of using the method of non-ferrous metals electrodeposition from acid solutions on a rotating cathode coated with liquid and solid gallium has been studied. Electrolyzer with this cathode have been successfully used for recovery of gallium from alkaline solutions [6-8]. The principle of the electrolyzer operation is based on the use of a cathode partially immersed in liquid gallium. During rotation an intensive stirring of the electrolyte near-cathode layer takes place, the concentration polarization of metal electrodeposition is removed and the gallium coating of the cathode is renewed.

The initial raw material of non-ferrous metals for solution production was neutralization sludge separated as a result of stage cleaning of commercial copper electrolyte of scrap copper smelting plant of

“Casting” LLP of the Republic of Kazakhstan. During purification of the electrolyte from the stage neutralization sludge, copper and nickel oxides were isolated, which were processed to produce metals by electrolysis using a rotating cathode coated with liquid or solid gallium. The use of gallium for cathode coating eliminates the need for cathode matrices and the complicated operation of precipitated metal removal.

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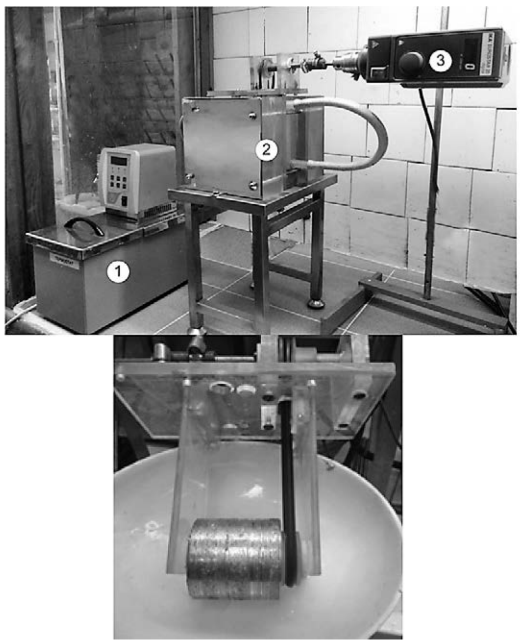
MATERIALS AND METHODS

X-ray fluorescence analysis of the chemical composition was performed on a Venus 200 wave dispersion spectrometer (PANalytical B.V., Holland).

Chemical analysis was performed on an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, Perkin Elmer).

Semi-quantitative X-ray phase analysis was carried out on a D8 Advance diffractometer (BRUKER) using Cu-Kα radiation at an accelerating voltage of 36 kV, current of 25 mA.



a

b

Figure 1 Electrolyzer installation. a) 1-liquid thermostat; 2-electrolyzer; 3-drive rotation; b) cathode block

Table 1 **Electrodeposition of copper and nickel from hydrochloric acid solutions on a rotating cathode coated with liquid gallium**

Product name	HCl concentration / g/dm^3	pH / (initial solution)	pH / (final solution)	Electrodeposition parameters		
				Final concentration of HCl / g/dm^3	Extraction rate / %	Electricity consumption / kWh/t
Copper	10	0,96	0,82	0,015	85,4	1710,0
	30	0,39	0,31	0,009	99,0	1680,0
	50	0,13	0,1	0,012	91,3	1850,0
Nickel	10	0,96	0,83	0,015	90,1	3890,0
	30	0,39	0,32	0,005	85,3	3620,0
	50	0,13	0,11	0,006	85,0	3640,0

An electrolyzer with a rotating cathode coated with liquid or solid gallium was used for electrodeposition of non-ferrous metals (Figure 1).

The unit consists of: an electrolyzer with a bath volume of 2 dm^3 with a rotating cathode coated with gallium, diameter 6,0 cm, surface area 75 cm^2; a rotation drive brand IKA EUROSTAR 20 with adjustable rotation speed; a liquid thermostat brand LT-205. Lead plates served as anode.

A block with a rotating cathode in the form of a cylinder coated with gallium was installed in the electrolyzer bath made of Plexiglas. The bottom of the cathode chamber has a recess whose shape follows the shape of the cathode cylinder. The bath has a water jacket.

When operating the electrolyzer with liquid gallium coating of cathode, liquid gallium was poured into the recess of the electrolyzer bottom, to which the current lead was connected. When the solid gallium electrolyzer was operated, the electric power was supplied through a copper brush at the bottom of the electrolyzer.

Before electrolysis, the cathode surface was heated with hot water at 80 - 90 ^{0}C and the gallium layer was melted. Then the cathode was treated with 20 % HCl solution and a passive film was removed from the gallium coating. The fresh gallium layer was applied to the cathode by rubbing. During electrolysis on the hard gallium coating the cathode was treated with cold water until curing.

RESULTS AND DISCUSSION

Initial products for the study were copper and nickel-containing sludge obtained as a result of stage-by-stage purification by the method of neutralization of copper electrorefining solution during recycling of scrap non-ferrous metals of the copper smelter “Casting” LLP Republic of Kazakhstan.

Chemical composition of copper-containing sludge / mas. %: Fe_2O_3 0,4; NiO 1,4; CuO 80,14; other 18,06. After calcination of the precipitate at temperature 200 ^{o}C and duration of 30 minutes a copper oxide precipitate with CuO content of 98,18 % was obtained.

Chemical composition of the nickel-containing precipitate / mas. %: NiO 65,93; Fe_2O_3 5,09; CuO 0,63; other 28,35. After calcination of the precipitate at temperature 350 ^{o}C and duration of 30 minutes a nickel oxide precipitate with NiO content of 94,28 % was obtained.

Electrochemical extraction of copper and nickel metals on the cathode coated with liquid gallium is possible to carry out only in case of using as an acidic electrolyte hydrochloric acid solution, this is due to the property of liquid gallium surface, which in solutions of other acids has no smooth surface, which causes intensive evolution of hydrogen and sludge formation.

The melting point of gallium is 29 ^{0}C, so the electrolysis using liquid gallium coating was carried out at 50 ^{0}C at which the gallium is in the molten form. The cathodic current density was maintained at 250 A/m^2, with a bath voltage of 3,0 V. Duration of electrolysis was 3 hours.

The choice of optimum conditions of non-ferrous metals electrodeposition depending on concentration of hydrochloric acid electrolyte was researched. The content of copper and nickel in all hydrochloric acid solutions was 50 g/dm^3.It follows from the obtained results that the optimum solution containing 30 g / dm^3 of hydrochloric acid for copper and nickel electrodeposition under the chosen conditions.

The possibility of electrodeposition of metals Cu and Ni on a hard gallium-coated cathode at 25 ^{0}C, i.e. below the melting point of gallium, was studied table 1).

When the solid gallium coating of cathode is used, electrodeposition can be carried out from any acidic solution.

For copper electrodeposition an electrolyte of the composition, g/dm^3 50,0 Cu^{2+}, g/dm^3 50 H_2SO_4 was used. Electrolysis was carried out for 1 hour at a cathodic current density of 2,5 A/dm^2 and a bath voltage of 2,7 V. As a result of electrolysis copper layer was obtained on the cathodic surface covered with solid gallium. Current yield was 94 % at electricity consumption of 258 kWh/t Cu.

After heating the cathode in hot water to a temperature of 40 ^{o}C, copper was separated in the form of thin plates (Figure 2).

Nickel electrodeposition was carried out from the solution with pH 4,6 used for nickel plating composition, g/dm^3 140,0 $NiSO_4$; 50,0 Na_2SO_4; 30,0 $MgSO_4$; 5,0 NaCl; 20,0 H_3BO_3. Electrolysis was carried out for 1 hour, at a cathodic current density of 1 A/dm^2 and a bath

Figure 2 Copper cathode removed from a galvanized surface

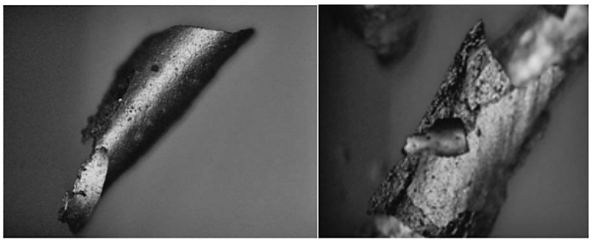


Figure 3 Cathode nickel x 100

voltage of 4.3 V. As a result of electrolysis a gallium-coated nickel layer was obtained on the cathodic surface. Current yield was 95 %, power consumption was 3200 kWh/t Ni.

The cathode nickel was removed by treatment with hot water at 80 - 90 ^{0}C . The obtained nickel is small coiled plates 1 - 2 mm in size, the surface of which is characterized by porosity (Figure 3).

Thus, as a result of electrodeposition on the solid rotating gallium surface of the cathode at 25 °C, Cu and Ni were isolated in the form of porous plates, which are easily separated from the cathode after its warming up. The obtained cathode metals can be considered as primary and used for recycling into alloys or casting. The method facilitates the operation of removing metals from the surface of cathode matrices and replaces the need to produce matrices. In contrast to electrodeposition on a liquid gallium-coated cathode, using a solid gallium-coated cathode results in an ~ 85 % reduction in energy consumption for copper and ~ 15 % reduction for nickel.

CONCLUSION

Studies of non-ferrous metals electrodeposition from acidic solutions using neutralization precipitation from purification of commercial copper electrolyte as a raw material have been carried out.

The use of a gallium-coated cathode eliminates the need for cathode matrices and the complicated operation of the precipitated metal removal.

Power consumption when using solid gallium coating is significantly lower.

Optimal conditions for electrodeposition of copper and nickel on a cathode coated with liquid gallium from hydrochloric acid solution have been determined.

On the cathode surface coated with solid gallium:

- from a solution containing 50,0 g/dm Cu^{2+}, and 50 g/dm^3 H_2SO_4, a copper precipitate was obtained. The current yield was 94 % at an electricity consumption of 258 kWh/t;
- from a solution containing / g/dm^3: 140,0 $NiSO_4$; 50,0 Na_2SO_4; 30,0 $MgSO_4$; 5,0 NaCl; 20,0 H_3BO_3 obtained nickel precipitate. The current yield was 95 %, power consumption was 3200 kWh/t.

Methods of nonferrous metals separation from liquid and solid gallium cathode coating were determined.

Obtained cathode metals can be considered as primary and used for recycling into alloys or castings.

Acknowledgments

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Note: The responsible for englich language, lector from Satbayev University.