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Synthesis of Dispersed System (CuO, ZnO) from Lump Braze with a Vertical Flow-through Electrolyzer

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Abstract—The electrochemical synthesis of a mixture of dispersed oxides (CuO and ZnO) from secondary lump braze was studied. The influence exerted by electrolysis parameters on the intensity of synthesis of the oxide mixture was investigated. The design of the electrolyzer and the flow diagram for synthesis of a mixture of oxides (CuO and ZnO) from lump braze was suggested.

The electrochemical synthesis of inorganic compounds of nonferrous metals: oxides [1, 2], hydroxides [3, 4], and salts [5, 6], is one of the areas of preparative chemistry that have been rapidly developing in the last decade. Use of electrolysis makes it possible to obtain not only pure target products, but also substances with certain physicochemical characteristics. For example, electrochemically obtained vanadium(V) oxide is distinguished by good performance as a cathode material for lithium batteries [7], and copper(II) oxide, by high dispersity and purity [8].

In this study, we continued a comprehensive study of the electrochemical synthesis of hydroxides, oxides [2], and salts [6] of nonferrous metals from secondary raw materials.

EXPERIMENTAL

Anodic polarization curves were measured in a standard thermostated electrochemical cell at a potential sweep rate of 5.0 mV s^{-1} with a PI-50-1.1 potentiostat. Platinum was used as the auxiliary electrode, and silver chloride, as reference. Zinc, copper, and braze (L63 brand, 63 wt % copper and 37 wt % zinc) in the form of rods 2-mm in diameter pressed into a fluoroplastic cartridge served as working electrodes. The samples were trimmed with a fine emery paper and washed with ethanol prior to each experiment. A 0.5 M solution of Na_2SO_4 was used as a working electrolyte.

The mixture of oxides CuO and ZnO was synthesized from lump braze in an electrolyzer schematically shown in Fig. 1.

The steel vessel of the electrolyzer is coated with nickel by means of electroless plating. The inner walls are lined with a dielectric film. Current is conveyed to the bulk anode through the bottom. The cross-sectional diameter of the bulk anode is 100 mm. As the cathode serves a copper disc 60 mm in diameter, closed from above and on sides with a polypropylene cap, so that only its lower part is working. The spacing between the cathode and bulk anode can be adjusted by moving the cathode. In the experiments, braze cuttings with a conventional diameter of 2–3 mm, length of 3–30 mm, and a bulk weight of 1.0–1.1 g cm^{-3}

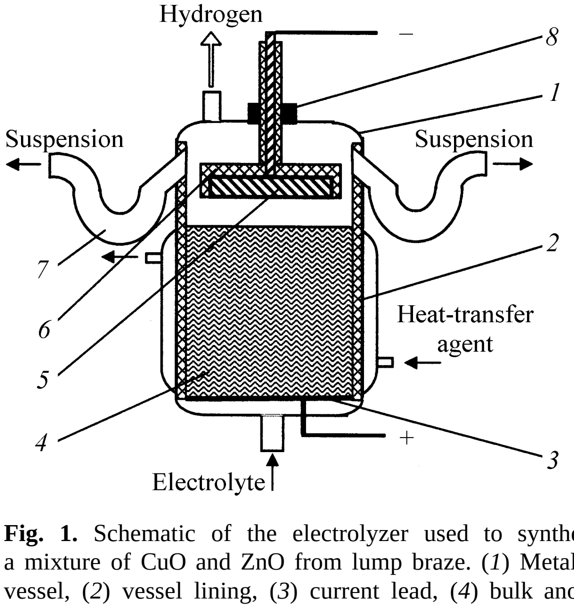


Fig. 1. Schematic of the electrolyzer used to synthese a mixture of CuO and ZnO from lump braze. (*1*) Metallic vessel, (*2*) vessel lining, (*3*) current lead, (*4*) bulk anode (cuttings), (*5*) copper cathode, (*6*) insulating cap, (*7*) hydraulic lock, and (*8*) seal.

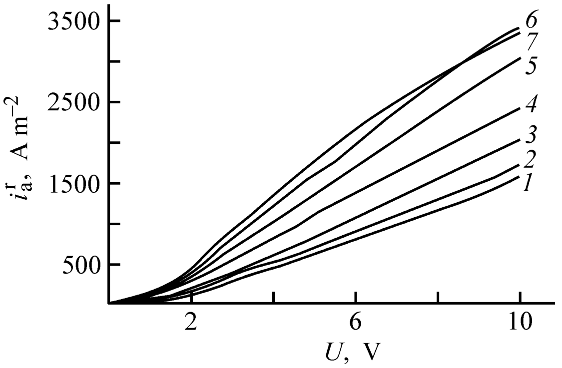


Fig. 2. Current–voltage curves measured in anodic dissolution of L63 braze in a 0.5 M Na_2SO_4 solution. (i^r_a) Current density and (U) voltage. Temperature (°C): (*1*) 20, (*2*) 30, (*3*) 40, (*4*) 50, (*5*) 60, (*6*) 70, and (*7*) 80.

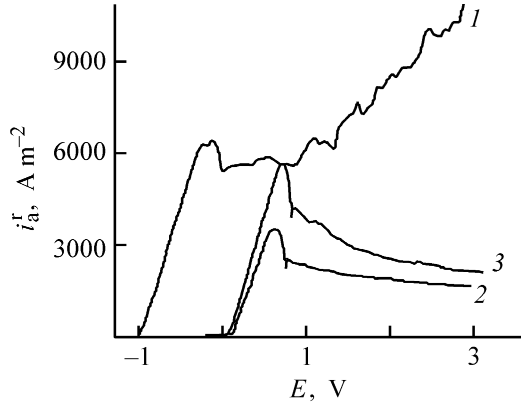


Fig. 3. Anodic polarization curves obtained under hydrostatic conditions for (*1*) zinc, (*2*) copper and (*3*) braze in a 0.5 M Na_2SO_4 solution at 60°C. (i^r_a) Current density and (E) voltage.

(copper 1.3–1.4 g cm^{-3}) were charged, after being degreased, into the electrolyzer to a height of 150 mm. The electrolysis was performed in the flow-through mode using a preheated 0.5 M solution of Na_2SO_4. The working temperature of the electrolyte was maintained by thermostating the electrolyzer. Current–voltage characteristics were recorded in the range 20–80°C, with voltage sweeping from 0 to 10 V in steps of 0.5 V and the system kept for 30 s at each point. The electrochemical synthesis was performed at U = const. The suspension passed through the electrolyzer was filtered immediately after that or upon being heated to the boiling point. Then it was allowed to settle, washed with water, and dried at 50°C in air. The pH value of the filtrate was adjusted when necessary and again fed into the electrolyzer. The CuO + ZnO content was determined by calcination of predried powders at 600°C.

The powders obtained were subjected to an X-ray phase analysis on a DRON-3M diffractometer (Cu_{K_α} radiation, θ–2θ scan angle, Bragg–Brentano technique), with a stepwise recording of diffraction patterns.

In a flow-through electrolyzer (Fig. 1), Zn^{2+} and Cu^{2+} ions formed in the near-anode space through anodic dissolution of braze are carried by the electrolyte into the interelectrode space and the near-cathode layer, where pH > 7 is established because of the occurrence of a cathodic reaction

$$2H_2O + 2e \rightarrow H_2 + 2OH^-. \qquad (1)$$

Therefore, insoluble complexes $Zn(OH)_2$ and $Cu(OH)_2$ are formed in the interelectrode space and, in part, in the near-cathode space, which predetermines electrodeposition of copper and zinc onto the cathode.

As temperature increases (≥50°C), $Cu(OH)_2$ starts to decompose by the reaction

$$Cu(OH)_2 \rightarrow CuO + H_2O, \qquad (2)$$

which is indicated by the fact that the deposit turns dark, to become virtually black at above 90°C, and by the results of the X-ray phase analysis.

The results of the study show that the reduced anodic current density i^r_a ($i^r_a = I/S$, where I is current strength, and S, surface area of the bulk anode) is proportional to the voltage across the electrolyzer and grows with increasing temperature (Fig. 2). Above 70°C, a decrease in the rate at which the i^r_a increases is observed.

The anodic currents of dissolution of lump braze are considerably higher than those of lump copper under the analogous conditions of electrolysis.

For example, at voltages of 5, 7, and 9 V and a temperature of 70°C, i^r_a is 1605, 2445, and 3159 A m^{-2}, respectively, for lump braze and 1120, 1745, and 2370 A m^{-2} for lump copper. This is due to the fact that the anodic dissolution currents of the main component of braze, zinc, are higher than those of copper (Fig. 3). In addition, the dissolution of braze is a selective process: first dissolves zinc, as a more electronegative metal, and only after that, copper [9]. The surface of braze becomes porous after the removal of zinc, which also facilitates the anodic dissolution.

The intensity of electrochemical synthesis of the oxide mixture may be governed by (1) electrolysis voltage, (2) concentration of a supporting electrolyte (Na_2SO_4), and (3) temperature.

As the voltage increases, the current density at the electrodes grows; however, the limiting anodic current density [10, 11], which increases for a bulk anode owing to the electrochemical inhomogeneity of the surface, is not reached even at 10 V.

The concentration of the supporting electrolyte is not the limiting factor, because, as shown in our study, the dissolution currents of braze in a 0.2–0.5 M Na_2SO_4 solution are virtually equal even at a voltage of 15 V.

With temperature raised by 10°C, the rate of electrochemical synthesis increases by 15–25% (table, Fig. 2). Apparently, this result can be accounted for by a decrease in the electrical resistance of the electrolyte and by the diffusion factor.

In addition, raising the temperature accelerates the coagulation of the deposit and leads to changes in its composition. For example, according to the results of an X-ray phase analysis, the deposit obtained below 50°C contains only the hydroxide $Cu(OH)_2$, and that formed at 60°C, also the oxide phase CuO. The content of the oxide phase grows with increasing temperature and, after the boiling temperature is reached, the suspension is virtually composed of a single phase, CuO. An X-ray phase analysis of powders obtained from the suspensions below 100°C revealed intermediate compounds of basic salts. For example, the powders synthesized below 50°C contain $6Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$.

The rate of removal of the products formed in the dissolution of the anode (braze) is determined by the flow rate of the electrolyte. Calculations show that, at a flow rate of the electrolyte in the electrolyzer equal to 1 $dm^3\ min^{-1}$, its flow velocity near the anode surface is about 1 $cm\ s^{-1}$. It was experimentally established that higher flow rates of the electrolyte (≥2–3 $dm^3\ min^{-1}$) lead to removal of fine metallic particles from the surface layer and to contamination of the oxides synthesized with these particles. In addition, these values are lower by one or two orders of magnitude than those in fast anodic dissolution of metals in electrochemical anodic sizing (EAS) [12]. Consequently, the electrolyte flow velocity is not an essential parameter in control over the rate of electrochemical synthesis of the oxides CuO and ZnO.

Main parameters of electrochemical synthesis of a CuO and ZnO mixture from lump braze in a 0.5 M Na_2SO_4 solution at an electrolyte flow rate of 1 $dm^3\ min^{-1}$

T, °C	U, V	Synthesis intensity CuO, ZnO,* kg m^{-2} h^{-1}
50	5	1.68
	7	2.50
	9	3.29
60	5	2.05
	7	3.07
	9	4.15
70	5	2.41
	7	3.67
	9	4.74
80	5	2.67
	7	3.82
	9	4.78

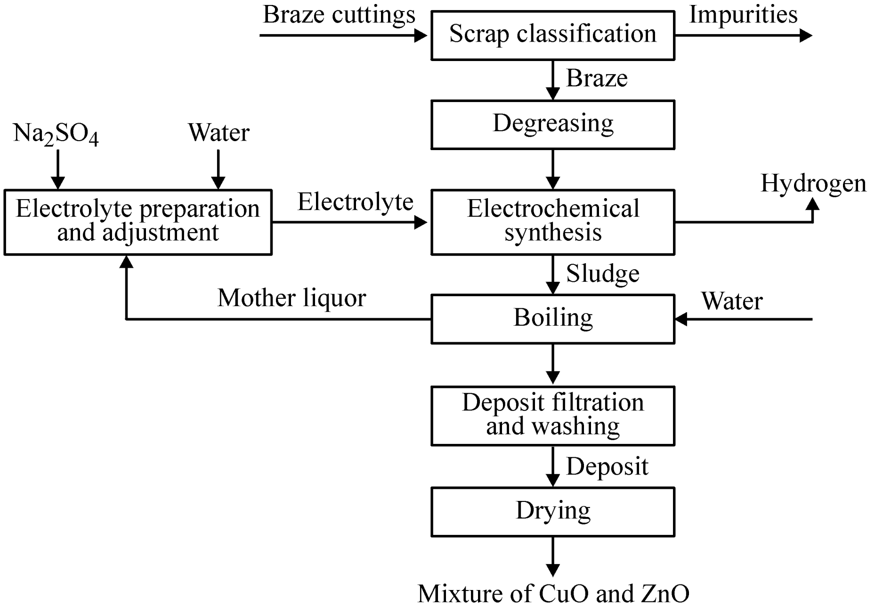
* In terms of anhydrous metal oxides CuO and ZnO.

Thus, the main factors responsible for the intensification of the electrochemical synthesis of a mixture of oxides CuO and ZnO from lump braze in a vertical flow-through electrolyzer are the electrolyzer voltage and temperature. However, as the electrolyzer voltage increases, the specific electric power consumption W_{sp} ($W_{sp} = U/1.5\,CE_a$, where CE_a is anodic current efficiency) becomes higher. By assuming that CE_a is approximately 100% (electrochemical equivalent of the CuO and ZnO mixture is 1.5 g A^{-1} h^{-1}), a value of 3.33 kW h kg^{-1} is obtained for the specific power consumption W_{sp} (CuO, ZnO) at 5 V, which increases by 0.67 kW h kg^{-1} as the voltage is raised by 1 V.

Our study demonstrated that the interelectrode spacing is predetermined by the electrolysis rate. The higher i_a^r, the more vigorous is the gas evolution at the cathode. When interelectrode spacing is small, the resulting gaseous foam can reach the bulk anode, which results in the formation of hydroxides (oxides) and their adherence in the zone of the lump metal. It was found that, at an electrolyte flow velocity of 1 $cm\ s^{-1}$ and more and a reduced anodic current density of 2000, 3000, and 4000 A m^{-2}, the optimal interelectrode spacing is 15, 20, and 25 mm, respectively.

It was found that raising the electrolyte temperature to above 70°C is ineffective as regards the electrolysis intensification. However, with account of the necessity for boiling of the sludge of copper and zinc hydroxides in order to enhance the coagulation and, accordingly, the filterability of the deposit obtained, to prevent formation of basic salts, and to ensure complete transformation of oxides into hydroxides, the optimal temperature of the electrolysis should be 70–80°C.

Based on the results obtained, we suggested the following flow diagram of the electrochemical synthesis of a mixture of oxides CuO and ZnO from lump braze.



Flow diagram of synthesis of dispersed oxides.

In the stage of classification of the scrap, the impurities are removed from braze cuttings by a method dependent on the type and content of impurities. After that, the cuttings are degreased, if necessary.

The thus prepared cuttings are charged into the electrolyzer as a bulk anode. The electrolyte (Na_2SO_4 solution) is fed into the electrolyzer continuously, thus ensuring removal of the electrolysis products in the form of a sludge. The sludge is boiled to improve its filterability, separated from the electrolyte by filtration, and washed. The mother liquor is recycled into the stage of electrolyte preparation. The deposit obtained is dried at 150–200°C.

CONCLUSIONS

(1) It is suggested to perform the electrochemical synthesis of a mixture of oxides CuO and ZnO by anodic dissolution of lump braze in a flow-through vertical electrolyzer in a Na_2SO_4 solution.

(2) It is shown that the main factors important for raising the electrolysis rate are the temperature of the electrolyte and the electrolysis voltage. The intensity of electrochemical synthesis of oxides CuO and ZnO may be as high as 4.8 kg m^{-2} h^{-1} and more when the temperature and voltage have the optimal values.

(3) The flow diagram of electrochemical synthesis of a mixture of oxides CuO and ZnO from lump braze is suggested and tested in laboratory conditions.

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