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 Na₂SO₄ 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 30 mm, and a bulk weight of 1.0–1.1 g cm⁻³.
The powders obtained were subjected to an X-ray phase analysis on a DRON-3M diffractometer (Cu Kα, radiation, 0–20 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

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-.$$ (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

$$\text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O},$$ (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 $i_{a \text{r}}$ ($i_{a \text{r}} = I/S$, 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 $i_{a \text{r}}$ 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, $i_{a \text{r}}$ 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$_2$SO$_4$), and (3) temperature.