Hydrometallurgical recovery of copper and cobalt from reduction-roasted copper converter slag

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ABSTRACT

The paper is concerned with a simple hydrometallurgical method for selective recovery of copper and cobalt from industrial copper converter slag. The following consecutive stages are proposed: roasting of the slag in reduction conditions to produce Cu–Co–Fe–Pb alloy, electrolytic dissolution of the alloy in an ammonia–ammonium chloride solution, ammoniacal leaching of the slime, selective copper and cobalt electrowinning. Cu27–Co6–Fe64–Pb1.5 alloy was a five-phase system and did not dissolve uniformly during electrolysis. This resulted in the separation of the metals, wherein iron remained in the slime, while copper and cobalt were components of slime, electrolyte and cathodic deposit. A mechanism of the alloy dissolution was developed. A series of secondary processes took place in the system: precipitation of iron compounds, copper cementation with cobalt and iron; adsorption of copper and cobalt ions on the iron precipitates. Final products were metals of high purity (99.9% Cu, 92% Co).

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1. Introduction

At the present time economical and environmental requirements impose the development of effective and inexpensive methods for the recovery of valuable metals from secondary sources. Significant amounts of copper and cobalt are present in low-grade metallurgical wastes, which are produced in the thousands of tons per year in copper smelters. Various methods were used to extract the metals from the copper converter slags. Hydrometallurgical treatment of the slag, including direct leaching in sulphuric acid (Anand et al., 1983) or ferric chloride (Anand et al., 1980) was proposed. Roasting of the slag with sulphuric acid (Arslan and Arslan, 2002; Sukla et al., 1986), ammonium sulphate (Sukla et al., 1986), ferric sulphate (Altundogan and Tümen, 1997) or in reduction conditions (Anand et al., 1981) followed by acidic leaching was also reported in the literature. However, very limited data can be found on the application of ammoniacal solutions to the dissolution of the polymetallic waste materials.

To develop a new method for the recovery of copper and cobalt from the copper converter slags, cooperation between the Faculty of Non-Ferrous Metals of the AGH University of Science and Technology in Cracow and the Institute of Non-Ferrous Metals in Gliwice (Poland) was established. The following method for the processing was proposed. In the first stage, the copper converter slag was subjected to roasting in an electric furnace. The pyrometallurgical tests were performed at the Institute of Non-Ferrous

Metals. Products of the reduction roasting were Cu–Co–Fe–Pb alloys with various chemical and phase compositions, which were dependent on temperature, reduction time and amounts of reducing additives. The second stage of the processing was the hydrometallurgical treatment of the reduced material in ammoniacal solutions. This research was realized at the AGH University of Science and Technology. Preliminary studies with synthetic Cu–Co–Fe alloys (Burzyńska et al., 2004) showed that anodic dissolution in the ammoniacal solution could be a suitable method for the separation of the metals. The high-copper (90 wt%) alloy dissolved spontaneously in a Cu^{2+}–ammonia–ammonium sulphate solution, while low-copper (5% Cu) alloys were unaffected by chemical leaching, but did dissolve during electrolysis in an ammonia–ammonium chloride solution.

The Cu–Co–Fe–Pb alloys obtained from the industrial slag were multiphase materials. It affected the mechanism of their electrolytic dissolution in the ammoniacal solution. The results of that research are described elsewhere (Burzyńska et al., 2008, in press). The present paper reports the anodic dissolution of Cu27–Co6–Fe64–Pb1.5 alloy in the ammonia–ammonium chloride solution. A mechanism of the process was proposed. The recovery of copper and cobalt from anodic slime and solutions is also presented.

2. Experimental

2.1. Materials

The copper converter slag used in this experimental study was taken from the copper smelter in Legnica (Poland). The chemical

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composition of the slag was (in wt%): Cu (1.70–5.60); Co (0.90–1.45); Pb (3.42–7.61); Fe (30.40–38.00); As (0.05–0.12); Zn (3.10–6.40); Ag (0.005–0.014); S (0.17–0.78); Ni (0.045–0.095); SiO_2 (25.50–32.84); CaO (0.43–2.49); MgO (0.23–1.94). Batches of the slag (900 kg) were reduced in an industrial electric furnace at voltages of 80–90 V and the current intensities of 900–950 A. The process was carried out in the presence of fluxing agents (limestone 8.6%, dolomite 8.6%) and reducing agents (coke breeze 2.7%, pig iron 2.0%). A temperature of 1425–1570 °C was applied. The thermal treatment of the slag was performed at various dwell times in the furnace (112–142 min) and with a constant reduction time (90 min). The sample described in the present paper was obtained at the dwell time in the furnace of 138 min. The product of the reduction was a Cu27–Co6–Fe64–Pb1.5 alloy. The alloy was examined by means of scanning and optical microscopes. Wet chemical analysis (AAS method) and a scanning microscope (Hitachi) with an EDS analyzer (Noran) were used for determination of the chemical composition of the sample. Volume fractions of the phases were determined by image analysis using the Aphelion software. Calculations were done on gray or color levels images of polished deposit surfaces observed with the use of the scanning (areas of 400 μm × 300 μm) and optical (areas of 600 μm × 600 μm) microscopes.

2.2. Electrolytic dissolution

A cuboid alloy anode (with a total area of 30 cm^2) was hung vertically between two rectangular platinum cathodes (each with an area of 90 cm^2) in 1 dm^3 of an ammonia–ammonium chloride electrolyte. The chemical composition of the solution was 2.5 M ($NH_3 + NH_4^+$) and 1.0 M Cl$^-$ (pH 10.1). The electrolyte was agitated with a peristaltic pump with a circulation rate of 15 dm^3/h. The bath temperature was maintained at 50 ± 0.2 °C. The anodic dissolution was carried out under galvanostatic conditions at the anodic current density of 350 A/m^2. During the electrolysis the cathode potential was monitored using a saturated calomel electrode as the reference. The voltage of the electrolysis was controlled as well. Four experimental runs were performed in order to obtain reliable results. The electrodes were weighed before and after electrochemical measurement. After the electrolysis, the cathodic deposits, the anodic slime and the suspension in the electrolyte were obtained. The suspension was filtered. The cathodic deposits, the anodic slime and the filtration sediment were thoroughly washed with water and then dissolved in hot 2.5 M HCl with H_2O_2 addition. The concentrations of the metals in the solutions were determined by the AAS method (Perkin Elmer Atomic Absorption Spectrometer 3110). Two 8 h electrolyses were also performed to produce large amounts of the slime. Dry slime was studied by an X-ray diffractometry (X-ray Philips diffractometer, CuK$_\alpha$ radiation).

2.3. Recovery of copper and cobalt

Copper and cobalt were recovered from the slimes and ammoniacal electrolytes. The slime (obtained in 8 h measurements) was leached threefold with the ammonia–ammonium chloride solution to deplete it in copper and cobalt. Solid residues were dissolved in 2.5 M HCl to determine their chemical composition. Acidic solutions from the slime dissolution in HCl (4-h electrolyses) were purified from Fe^{3+} ions by iron oxide precipitation with concentrated ammonia. The ammoniacal-chloride filtrate was used then for copper and cobalt recovery. Ammoniacal electrolytes from all stages (electrolytic dissolution of the alloy, ammoniacal leaching of the slime, filtrate after Fe^{3+} removal) were blended and then evaporated to reduce the volume. However, the latter was accompanied by precipitation of crystalline salts. The precipitates were dissolved in water acidified to pH 0 with HCl. In spite of that, pur-

ple powder remained in the solution. After filtration, the filtrate (1 dm^3) was subjected to copper electrowinning. The electrowinning was conducted at room temperature with 500 cm^3 of the electrolyte. After copper recovery, pH of the solution was raised to pH 6 with NaOH and cobalt electrowinning was carried out. The electrolyses were carried out with platinum plate electrodes at the cathodic current density of 100 A/m^2. The electrolyte was agitated with a magnetic stirrer with a rotation rate of 180 rpm. During the process, the samples of the solution were taken and concentrations of Cu^{2+} and Co^{2+} ions were determined by AAS. The cathodic deposits were stripped from the substrate with HNO$_3$ solution to determine their chemical composition.

3. Results and discussion

3.1. Phase composition of the alloy

The product of the reduction roasting was the iron base alloy with a general composition of Cu27–Co6–Fe64–Pb1.5 (in wt%). Since the slag was an industrial material, the alloy contained a few other elements (e.g. S, Ni, Si, Sn). Microstructures of the alloy are shown in Fig. 1.

The alloy was a five-phase system. The alloy matrix (phase I) was a copper rich (90%) solid solution with iron (6%). Some amounts of tin (2%) were also detected. Main components in irregular gray precipitates of phase II were iron (80%), copper (10.5%) and cobalt (8%). Microscopic observations showed the presence of fine precipitates (phase IIa) within the area of the phase II, however, their composition was not analyzed in details. Light gray oval precipitates represented phase III, which was a iron–copper solid solution (87% Fe, 12.5% Cu). Large black precipitates of phase IV were iron rich (75%) with addition of cobalt (10%), copper (6.5%) and nickel (3.5%). Some amounts of sulphur (3.8%) and oxygen (detected, but not analyzed) were also present. It seems that the phase IV represented a mixture of chemical compounds, i.e. sulphides and oxides of copper and iron as the residues of the copper converter slag from the pyrometallurgical treatment of copper matte. White precipitates of phase V were visible only in SEM images. They were rich in lead (91%) with some amounts of iron (5%) and copper (2%) as well as cobalt and sulphur (1%). Detailed compositions of the alloy and the individual phases are present in Table 1. It was noticed that results of the chemical analyses of the alloy dependent in some extent on the method used (AAS, SEM-EDS). It seems obvious, since AAS method allows to determine an average composition of the bulk of the sample, while SEM-EDS examination is a surface analysis of a relatively small area.

The volume fractions of the phases in the alloy were determined with the image analysis. These are: I – 21%, II – 25.5%, III – 24%, IV – 28% and V – 1.5%. Molar masses and densities of the main components in the alloy are similar, hence, it was assumed that the volume fractions of the phases corresponded to their mass fractions.

It worth also to note, that the total contents of Cu, Co, Fe and Pb in the alloy calculated according the percentage fractions and compositions of the alloy phases were in very good accordance with the results of AAS analysis.

3.2. Electrolytic dissolution of the alloy

The Cu27–Co6–Fe64–Pb1.5 alloy was dissolved during electrolysis in the ammonia–ammonium chloride solution. Anodic current efficiencies were 84–100%. The dissolution of the alloy resulted in the transfer of the metals into the electrolyte, the slime and the cathodic deposit. The distribution of elements at the end of the process is given in Table 2. It was found that the alloy dissolution was accompanied by accumulation of the elements mainly in the slime, however, about 13% of copper and cobalt codeposited as