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Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 25(2015) 2763–2771

Comparative studies on hydrometallurgical treatment of smelted low-grade electronic scraps for selective copper recovery

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Received 28 October 2014; accepted 12 March 2015

Abstract: A comparison of three hydrometallurgical methods for selective recovery of copper from low-grade electric and electronic wastes was reported. Scraps were smelted to produce Cu–Zn–Sn–Ag alloy. Multiphase material was analyzed by SEM–EDS and XRD. The alloy was dissolved anodically with simultaneous metal electrodeposition using ammoniacal and sulfuric acid solutions or leached in ammonia–ammonium sulfate solution and then copper electrowinning was carried out. This resulted in the separation of metals, where lead, silver and tin accumulated mainly in the slimes, while copper was transferred to the electrolyte and then recovered on the cathode. The best conditions of the alloy treatment were obtained in the sulfuric acid, where the final product was metal of high purity (99% Cu) at the current efficiency of 90%. Ammoniacal leaching of the alloy led to the accumulation of copper ions in the electrolyte and further metal electrowinning, but the rate of the spontaneous dissolution was low. Anodic dissolution of the alloy in the ammonia–ammonium sulfate solution led to the unfavorable distribution of metals among the slime, electrolyte and cathodic deposit.

Key words: copper alloy; leaching; electrolysis; recovery; waste electric and electronic equipment

1 Introduction

The recovery of metals from waste electric and electronic equipment (WEEE) is a necessary operation nowadays. It is mainly driven by fast growing amounts of obsolete devices displaced by saving energy innovative products, which are more attractive for users. It corresponds to the increased e-waste quantities collected in the individual countries. For example, based on the Eurostat data [1] solely, collection of used IT and telecommunications equipment (computers, laptops, mobile phones, smartphones, etc.) in the European Union increased from approximately 61.400 t in 2005 to approximately 714.700 t in 2010, while total recycling and reuse reached approximately 48.400 t in 2005 and 402.600 t in 2010. It not only showed better assortment ranges, but also declined effectiveness of such electronic waste treatment from 79% to 56%, caused mainly by various advances in the development of the recycling technologies in particular member countries. A large volume of used WEEEs are also shipped out of the European Union as well as United States, Canada, Japan and Australia to West Africa or South Asia [2,3]. Most of them are falsely classified as used goods though they are non-functional, in fact. General estimations of this illegal trade shows that at least 250.000 t of WEEEs were sent annually from the EU [2], while 50%–80% of e-wastes collected for recycling in US can be exported to the developing countries [3]. Although some African or Asian destination regions banned importation of second-hand electronic and electric equipment, it is still continued in practice due to a lack of control by local governments [4].

WEEEs are classified in several categories, among them large household appliances (49%), consumer (21%), IT and telecommunications (16%) equipment represent dominating fractions [4]. These multicomponent materials are a mixture of metals, ceramics and plastics. Electronic waste containing precious metals is the most economically attractive [5,6], but a low-value scrap (i.e., below 1×10^{-4} Au [6]) with low content or no gold,

Foundation item: Project (NNOTECH-2/IN2/18/181960/NCBR) supported by the National Centre for Research and Development, Poland Corresponding author: Ewa RUDNIK; Tel: +48-12-6177124; Email: erudnik@agh.edu.pl DOI: 10.1016/S1003-6326(15)63901-2

palladium or platinum still remains useful for recycling due to the presence of other elements like copper or tin.

Metals are recovered mainly by hydrometallurgical or pyrometallurgical routes [5-8] and the latter is currently the dominating way of e-waste recycling in the industry [8]. Bioleaching of the metals is also introduced, although only on a laboratory scale [9]. Hydrometallurgical treatment of the electronic scraps offers a variety of advantages over thermal processes, including relatively low capital costs, profitability of a small scale plants, high metal recovery and reduced environment pollution. Extraction of precious metals directly from the scraps is usually carried out using aqua regia, alkaline cvanide or thiosulfate solutions, resulting over 90% recovery of gold and silver [7–9]. Low grade wastes are leached mainly in hydrochloric and sulfuric acids or ammoniacal solutions to recover tin and copper, respectively [7,10].

A combination of thermal (e.g., smelting, pyrolysis) and hydrometallurgical procedures gives a new practice for the recovery of metals. It allows removing polymers, plastics and non-metallic elements from the origin material with simultaneous concentration of metals during pyrometallurgical stage (Table 1). The obtained alloys [11] are then dissolved in acidic or ammoniacal solutions [12-14]. GROOT and LINDE [12] reported results of cyclic voltammetry applied for the identification of the most soluble phases from the alloy immersed in HCl and H₂SO₄ solutions. LIM et al [13] presented comparative research on the behavior of some metals (Cu, Zn, Ni, Pb, Sn, Au, Ag) dissolved from pure powders and an alloy obtained from smelting reduction process of mobile phone and printed circuit boards, using sulfate and chloride ammoniacal baths. Enhanced extraction of copper from thermally pretreated (burning, pyrolysis) printed circuit boards in HCl solution was also studied and 98% efficiency instead of 6% for non-burned scrap was obtained [14].

The aim of the current work was to investigate the dissolution of an alloy obtained after pyrometallurgical treatment of low grade electronic scraps. Three methods were used: anodic dissolution in sulfuric acid or ammoniacal–sulfate solutions and spontaneous leaching in ammoniacal solution with addition of cupric ions. A comparison of the results allowed determining the behavior of the individual metals in various baths and selection of the most suitable system for the recovery of copper from smelted e-waste.

2 Experimental

Low-grade mixed electronic waste (mainly computer boards and printed circuit boards from mobile phones) from an urban scrap heap was collected, then crushed and directly thermally treated (without any additives or any special atmosphere) for a few hours in an industrial chamber furnace to remove non-metallic elements and organic compounds. Obtained alloy ingot was cut into rectangular samples ($\sim 17 \text{ cm}^2$). Structure of the alloy was observed under scanning electron microscope (Hitachi), while the analysis of the chemical composition was performed by energy dispersive spectroscopy (EDS).

Samples of the alloy were dissolved anodically $(J_A = 3 \text{ A/dm}^2)$ in acid (1 mol/L H₂SO₄) and ammoniacal (0.5 mol/L NH_{3aq} with 1 mol/L (NH₄)₂SO₄) solutions or leached in ammoniacal electrolyte with Cu(II) ions addition (50 mmol/L, added as sulfate). Platinum plate (50 cm²) was used as a cathode ($J_C = 1 \text{ A/dm}^2$). Solution (400 mL) was agitated with a magnetic stirrer at a rotation rate of 300 r/min. Process was carried out for 24 h.

Solution after ammoniacal leaching was used for further recovery of copper. It was diluted to 1 L and then portions of 400 mL were used for the electrolysis. The process was carried out at the current density of 1 A/dm^2 using two platinum electrodes (each 50 cm²) and magnetic stirring (300 r/min).

All measurements were performed at ambient temperature (~ 20 °C). Before and after measurement, all samples were weighed. Slimes produced on the alloy surface as well as cathodic deposits were collected, washed, dried at the temperature of 60 °C for 4 h and then weighed.

Samples (2.5 mL) of the solutions were taken during the alloy dissolution and electrowinning, then diluted with 2 mol/L H_2SO_4 and analyzed by atomic absorption spectrometry (AAS Solaar M5, Thermo Elemental) to determine concentrations of metal ions. Weighted portions of the slimes and cathodic deposits were dissolved in hot 2 mol/L H_2SO_4 with H_2O_2 addition and then analyzed by means of AAS. X-ray diffractometry (Rikagu) was used for identification of the phase composition of the alloy and obtained solids.

Stationary potential of the dissolved samples was monitored every 5 min using saturated calomel electrode as a reference. Obtained results were subsequently converted versus standard hydrogen electrode (SHE).

3 Results and discussion

3.1 Alloy composition

The alloy obtained from low-grade electronic scraps was a polymetallic and multiphase material with a general composition shown in Table 1. It contained 72.6% Cu, 16.4% Zn and 6.4% Ag, comparable amounts of Fe and Sn (\sim 1.6%) as well as some other metals (each below 1%). Comparison of the data with the results of

Refs. [11,13] shows that similar contents of copper may be expected in the thermally treated e-wastes, while percentages of remaining metals are dependent on the origin material composition.

Table 1 Composition of alloys obtained from electronic scraps(mass fraction, %)

Element	Smelting, mixed electronic scraps	Smelting reduction, PCB [13]	Induction furnace, PC boards [11]	Range in electronic scraps [5,7]
Al	0.2	_	No data	1-14
Ag	6.4	2.6	No data	(6-3300)×10 ⁻⁶
Au	_	0.8	No data	(3-1000)×10 ⁻⁶
Cu	72.6	68.0	70	3-27
Fe	1.5	12.9	No data	4-62
Ni	0.2	1.9	4	0.03-2
Pb	0.8	0.2	9	0.2-3
Sn	1.7	3.2	13	0.5-2.9
Si	0.2	-	No data	No data
Zn	16.4	_	4	No data

Figure 1 shows morphology of the polished crosssection of the ingot. Micrograph was taken using back scattered electrons detector. Five phases were found in the alloy: three of them appeared as small inclusions within two-phase brass-based alloy matrix. The latter was able to be detected only by the analysis in the BSE mode. The brass matrix consisted of two phases of various Sn and Ag concentrations: phase I–78.4% Cu, 16.7% Zn, 3.2% Ag, 0.6% Sn and 0.7% Fe; phase II–71.0% Cu, 17.5% Zn, 7.2% Ag and 3.5% Sn. Lead-rich (phase III; white areas) and silver-rich (phase IV; gray areas) inclusions were distributed along the centers of the bands formed by phase II. Main components of phase III were 92.0% Pb, 6.4% Cu and 1.6% Zn, while the phase IV included 74.8% Ag, 8.6%



Fig. 1 Morphology of polished alloy surface

Cu, 8.5% Sn and 4.3% Zn. Iron-rich precipitates (phase V, black areas) were randomly dispersed within the matrix and they consisted of 86.5% Fe, 5.5% Si, 4.6% Cu and 1.0% Cr. Other elements (Al, Ni, P, Si) were not present in the individual phases or their fractions were below 0.4%.

Figure 2 shows XRD pattern of the alloy. Cubic α -CuZn dominated in the sample, but two separate brass phases were not distinguishable due to relatively small difference in their chemical compositions. Position of the brass peaks corresponded also to the tetragonal Cu_{5.6}Sn intermetallic compound. No ε -Cu₃Sn was detected despite that it is the most thermodynamically stable Cu–Sn phase at room temperature according to the Cu–Sn–Ag and Sn–Zn–Cu equilibrium diagrams [15,16]. Ag₃Sn intermetallic compound may be found in the silver-enriched phase IV. The occurrence of lead-rich inclusions as well as stainless steel residues was also confirmed.



Fig. 2 XRD pattern of alloy

Phase composition of the alloy used in this work was somewhat different from that reported earlier by GROOT and LINDE [11], although three main phases were found. By analyzing phase diagrams for appropriate binary systems, two bronze phases were identified: low (74.6% Cu, 13.0% Sn, 7.8% Zn, 1.1% Ni) and high (62.8% Cu, 32.0% Sn, 2.8% Zn, 1.6% Ni, 0.5% Ag) tin areas (i.e., α and δ bronzes). Cu₃Sn phase was not found. It is supposed that it could not form at appreciable rate due to its low transformation temperature (~350 °C). Lead precipitates in that alloy contained 87.9% Pb, 6.2% Cu, 3.5% Bi and 0.8% Ag. Iron and aluminum were eliminated selectively from the material by the smelting process carried out at 1200 °C under argon atmosphere.

Comparison of the data shows that it can be assumed that pyrometallurgical treatment of the used PC and PCB boards results mainly in the production of high copper alloys (~70% Cu) consisting of two Cu–Zn–Sn–(Ag) phases with lead-rich inclusions.

3.2 Alloy dissolution

The Cu–Zn–Ag alloy was electrochemically dissolved in the acid or ammonia–ammonium sulfate solutions as well as leached in ammoniacal sulfate system with Cu(II) ion addition (3 g/L). The latter was introduced to the bath to force autocatalytic dissolution of copper from the alloy, and thus to achieve better separation from co-extracted metals.

$$Cu(NH_{3})_{4}^{2+}+Cu \rightarrow 2Cu(NH_{3})_{2}^{+}$$
(1)
$$2Cu(NH_{3})_{2}^{+}+4NH_{4}^{+}+2OH^{-}+\frac{1}{2}O_{2} \rightarrow 2Cu(NH_{3})_{4}^{2+}+$$

$$3H_{2}O$$
(2)

Other elements (i.e., zinc, silver, nickel) occurring in the metallic phase may be also transferred into electrolyte as soluble ammine complexes, but the rates of their dissolution are determined by the oxygen diffusion to the metal surface [17]:

$$M+4NH_{3}+\frac{1}{2}O_{2}+H_{2}O \rightarrow M(NH_{3})_{4}^{2+}+2OH^{-}$$
(3)

where M is a divalent metal (Zn,Ni), or

$$2Ag+4NH_3+\frac{1}{2}O_2+H_2O \rightarrow 2Ag(NG_3)_2^++2OH^-$$
 (4)

The alloy was dissolved in various conditions and after 24 h, mass decrements of the samples were (0.926 ± 0.003) g/cm² and (0.166 ± 0.006) g/cm² for both electrochemical and chemical processes, respectively. Figure 3 shows changes of the alloy potential with time. Dissolution in the ammoniacal solutions was accompanied by the rising of the potential caused by the gradual formation of the slime on the alloy surface, but it was much more emphasized for the electrolysis due to higher dissolution rate achieved. Totally different courses were registered in the acidic bath, where periodical potential changes were registered. It seems that active dissolution of the sample was disturbed by the gradual changes in the composition of the electrode surface caused by the selective dissolution of less and more



Fig. 3 Changes of alloy potential during dissolution

noble phases. It is worth noting that some interruption of the anode oxidation occurred after 7–8 h of the electrolysis in both electrolytes. No total passivation of the anode was observed for 24 h, indicating that slimes form porous layers, enabling dissolution of the underlying metal.

Figure 4 shows changes of the metal ions concentrations with time. As it was expected, behavior of the individual metals was different and dependent on the dissolution conditions. Copper was extracted from the alloy in all cases. It accumulated in the electrolyte during leaching, while some amounts were recovered on the cathode during electrolysis. Initially, anodic dissolution run similarly in both solutions, but after a few hours, Cu(II) concentration decreased in the acid electrolyte, while stabilized at almost constant level in the ammoniacal bath. It corresponded to the enhanced cathodic metal recovery in H_2SO_4 (~0.13 g/cm²) than in the alkaline solution (~0.06 g/cm²).

Electrochemical process in sulfuric acid favored dissolution of zinc, iron and nickel, which accumulated in the aqueous phase. In the ammoniacal solution, only zinc concentration was quite significant (2 g/L) due to its higher content in the alloy. Iron does not form stable ammonia complexes and could precipitate as solid particles [18]:

$$Fe+4NH_3 \rightarrow Fe(NH_3)_4^{2+} + 2e$$
 (5)

$$\operatorname{Fe}(\mathrm{NH}_{3})_{4}^{2+}+2\mathrm{H}_{2}\mathrm{O} \rightarrow \operatorname{Fe}(\mathrm{OH})_{2}\downarrow+2\mathrm{NH}_{4}^{+}+2\mathrm{NH}_{3}\uparrow \qquad (6)$$

(7)

$$Fe(OH)_2 \rightarrow FeO+H_2O$$

and/or

$$2Fe(NH_3)_4^{2+} + \frac{1}{2}O_2 + 2H_2O \rightarrow 2Fe(OH)_3 \downarrow + 4NH_4^+ + 4NH_3^{\dagger}$$
(8)

$$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O \tag{9}$$

Anodic dissolution of silver was observed and similar results were obtained in both systems, while spontaneous process was seriously hindered. It shows that stable $Ag(NH_3)_2^+$ complexes may be present in the alkaline electrolyte. Dissolution of silver in sulfuric acid is also accepted due to rather appreciable Ag_2SO_4 solubility in aqueous solutions (~ 8 g/L).

Behavior of lead was clear only in ammoniacal solutions; it did not dissolve spontaneously with a noticeable rate, but only under current. OISHI et al [19] reported that metallic lead can be easily oxidized by Cu(II) ions to Pb(II) species in ammoniacal solutions with the formation of lead ammine complexes, e.g., $Pb(NH_3)_2^{2+}$ [20]. It was confirmed by LIM et al [13], who found some solubility of lead in ammoniacal systems, but then concentration of Pb(II) ions decreased rapidly in relatively short time. In sulfuric acid, serious scatter of the results was found, but it may be attributed

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Fig. 4 Changes of metal ion concentrations in sulfate solutions with time: (a) Cu; (b) Zn; (c) Ni; (d) Fe; (e) Pb; (f) Ag; (g) Sn

to the secondary processes occurring in the system, and precipitation of the compounds as the slime flows in the bulk of the electrolyte.

$$Pb^{2+} + SO_4^{2-} \to PbSO_4 \downarrow \tag{10}$$

$$Pb^{2+}+2H_2O \rightarrow PbO_2\downarrow +4H^++2e \tag{11}$$

Similar tendencies for silver and lead during electrolysis in the ammoniacal solution correspond to the increase in the alloy potential. Hence, it seems that after 7 h, lead-rich and silver-rich precipitates were released from the brass matrix.

Tin was resistant for the action of the ammonia solution, since it cannot exist as soluble ammonia complexes. However, some amounts of tin ions were found in the electrolyte in the early stages of the electrolysis, probably as randomly taken particles of the slime:

$$\operatorname{Sn}^{2+}+2\operatorname{NH}_{3}\cdot\operatorname{H}_{2}O \longrightarrow \operatorname{Sn}(OH)_{2}\downarrow+2\operatorname{NH}_{4}^{+}$$
(12)

An opposite effect was observed in sulfuric acid, where the metal was oxidized anodically and transferred to the solution as sulfate. However, during late hours of the electrolysis, concentration of tin ions decreased due to codeposition with copper on the cathode or precipitation on the anode surface:

$$\mathrm{Sn}^{2+}+2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{Sn}\mathrm{O}_{2}\downarrow +\mathrm{H}^{+}+2\mathrm{e} \tag{13}$$

$$\mathrm{Sn}^{2+} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{SnO} \downarrow + 2\mathrm{H}^+ \tag{14}$$

Table 2 shows percentages of the metals in the cathodic deposits and the slimes, while Figs. 5 and 6 show corresponding diffraction patterns. It was found that the main component of the cathodic deposits was copper, but the purity of the metal was higher in the acid system. Some amounts of copper oxide were detected (Fig. 5) as a result of the powdery metal drying. It is not excluded that Cu₃Sn phase can deposit on the cathode in the acid solution.

Slimes produced on the alloy surface were complex system in their phase composition. The presence of some compounds may be debatable due to covering of

Table 2 Compositions of cathodic deposits and slimes

characteristic peaks for various phases. Application of sulfuric acid allows cumulating silver, lead and tin in the anodic slime mainly as metals, sulfates, oxides or intermetallic phases released from the alloy during brass matrix dissolution (Fig. 6). GROOT and LINDE [12] reported earlier that high tin bronze was more resistant on the leaching in H_2SO_4 than low tin phase, resulting in the passivating layer of SnO on the alloy surface. They also found that lead phase was not dissolved or at very low rate, but this was dependent on the applied anode potential.

Dissolution in the ammoniacal solution led to the formation of rich-copper slimes, but it was unfavorable in relation to the effectiveness of the metal recovery. However, this can be overcome by additional leaching stage, since main oxides or basic copper salts were formed. Remaining stainless steel was also found in the slimes. Intermetallic compounds present in the alloy (Ag₃Sn and Cu_{5.6}Sn) were resistant to the anodic oxidation and were transferred directly to the slimes. Similar behavior may be expected during alloy leaching in the ammoniacal solution, but in the current study, these were difficult to detect due to low rate of the alloy dissolution.

Table 3 summarizes distribution of the individual metals among the slime, electrolyte and cathodic deposit. Anodic dissolution in acidic solution enhanced separation of lead, silver and partially tin from other metals since these accumulated in the slime, while iron, zinc and nickel were transferred into the electrolyte. Copper deposited on the cathode. Electrolysis carried out in the ammoniacal system is not as selective as in the former case and metals were present in large fractions in all parts of the system. The best conditions were obtained during leaching of the alloy in the ammoniacal solutions and almost 100% of silver, iron lead and tin were gathered in the slime. However, the rate of the spontaneous alloy dissolution was not enough. This can be improved by development of the alloy surface by crushing, but such operation can be unremunerative.

Process	Bath	Sample	w(Ag)/%	w(Cu)/%	w(Fe)/%	w(Ni)/%	w(Pb)/%	w(Zn)/%	w(Sn)/%
Anodic oxidation	H_2SO_4	Cathode	0.2	99.0	l.w.	0.1	l.w.	l.w.	0.7
		Slime	43.0	3.1	0.0	0.0	50.5	1.1	5.1
	(NH ₄) ₂ SO ₄ +NH ₃ (aq)	Cathode	0.3	95.7	1.7	0.1	1.6	0.6	0.7
		Slime	1.0	95.4	0.7	l.w.	1.6	1.2	1.7
Leaching	$(NH_4)_2SO_4+NH_3(aq)+Cu^{2+}$	Slime	26.0	37.1	0.2	0.5	13.3	12.3	10.6
Electrowinning	$(NH_4)_2SO_4+NH_3(aq)+Cu^{2+}$	Cathode	Trace	98.3	0.0	Trace	0.0	1.6	0.0

l.w. = low value, i.e., below 0.02%; Trace=below 0.005%



Fig. 5 Diffraction patterns of cathodic deposits during anodic oxidation of alloy in acid and ammoniacal baths: (a) Acid bath (bottom); (b) Ammoniacal bath (top)

Anodic and cathodic current efficiencies were calculated according to the mass change of the alloy or cathode substrates Δm :

$$\eta = \frac{\Delta m}{m} \times 100\% \tag{15}$$

For simplicity, it was assumed that all metals can be transferred from the alloy according their total mass fraction w in the anode. Therefore, theoretical mass of the dissolved alloy was determined according the following formula:

$$m = (Jt) / [F(\frac{2w_{Cu}}{M_{Cu}} + \frac{2w_{Zn}}{M_{Zn}} + \frac{2w_{Fe}}{M_{Fe}} + \frac{2w_{Pb}}{M_{Pb}} + \frac{w_{Ag}}{M_{Ag}} + \frac{2w_{Ni}}{M_{Ni}} + \frac{2w_{Sn}}{M_{Sn}})]$$
(16)

where *M* are mole masses of the individual metals, respectively, *J* is the current intensity, *t* is the electrolysis time and *F* is the Faraday constant. It was found that anodic current efficiencies were 101% and 102% for acid and ammoniacal solution, respectively. It means that alloy can be attacked chemically by the solution. However, it has to be noted that secondary reactions occurring during the process as well as mechanical dropping of the insoluble inclusions out from the alloy matrix can mislead the real results of such calculations. Cathodic current efficiencies were much lower and reached 89% in H₂SO₄ and 46% in (NH₄)₂SO₄+NH₃ electrolytes.



Fig. 6 Diffraction patterns of slimes: (a) Anodic oxidation in acid; (b) Anodic oxidation in ammoniacal bath; (c) Leaching in ammoniacal bath

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Process	Bath	Sample	Mass fraction/%						
			Ag	Cu	Fe	Ni	Pb	Zn	Sn
Anodic oxidation	$\rm H_2SO_4$	Cathode	0.5	97.1	1.0	20.9	Trace	0.1	13.2
		Slime	98.2	2.5	1.7	0	100	4.9	79.8
		Electrolyte	1.3	0.4	94.6	79.1	0	95.0	7.0
	$(NH_4)_2SO_4 + NH_3(aq)$	Cathode	18.5	44.3	55.4	83.9	21.3	3.2	30.4
		Slime	49.4	55.1	33.6	14.7	43.8	9.5	61.8
		Electrolyte	32.1	0.5	11.0	1.4	34.9	87.2	7.8
Leaching	(NH ₄) ₂ SO ₄ +NH ₃ (aq)	Slime	100	4.5	100	20.2	100	12.0	99.9
		Electrolyte	0	95.5	0	79.8	0	88.0	0.1
Electrowinning I stage	(NH ₄) ₂ SO ₄ +NH ₃ (aq)	Cathode	-	98.6	_	84.1	-	71.7	-
		Electrolyte	-	0.4	_	15.1	_	28.3	-
Electrowinning II stage	e (NH ₄) ₂ SO ₄ +NH ₃ (aq)	Cathode	_	100	_	99.5	_	99.8	_
		Electrolyte	-	0	-	0.5	_	0.2	-

Table 3 Distribution of metals among slime, electrolyte and cathodic deposit

Alkaline solution obtained after leaching stage was used for the copper electrowinning. Figure 7 shows changes of the metal ions amounts in the electrolyte with time. Copper, zinc and nickel ion were mainly present in the bath. It was observed that after 6 h electrolysis, almost all copper (~99%) was recovered, but other metals were codeposited simultaneously. Obtained deposit contained 98.3% Cu (Table 2) at the current efficiency of 40%. After second stage of the electrowinning, zinc of 86% purity was deposited, but at very low current efficiency (3%).



Fig. 7 Recovery of metals during two stages of electrowinning from ammoniacal solution (initial ion concentrations of Cu, Zn and Ni are 3.15, 0.48, and 8.7 g/L, respectively)

4 Conclusions

1) Smelting of low grade electric and electronic wastes produces polymetallic and multiphase alloys. The high-copper alloy (\sim 70% Cu) consists mainly of two Cu–Zn–Sn–(Ag) phases with lead-rich precipitations.

2) The most favorable conditions for the electrochemical alloy dissolution can be achieved in the sulfuric acid. It allows separation of copper from other metals, resulting in the cathodic deposit of high purity (99% Cu) at high current efficiency (~90%).

3) Ammoniacal leaching of the alloy enables accumulation of copper ions in the electrolyte and further metal electrowinning, but the rate of the spontaneous dissolution is insufficient for practical purposes.

4) Anodic dissolution of the alloy in the ammonia–ammonium sulfate solution led to the unfavorable distribution of metals among the slime, electrolyte and cathodic deposit.

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熔炼低品位电子废料中铜的湿法冶金选择性回收

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摘 要:比较从低品位电工电子废料中选择性回收铜的 3 种湿法冶金方法。首先将废料熔炼成 Cu-Zn-Sn-Ag 合金,并采用 SEM-EDS 和 XRD 进行表征。对合金进行阳极溶解,首先采用氨溶液和硫酸溶液对合金进行电沉积 或在氨-硫酸铵溶液中浸出,然后进行电沉积铜。实现了各种金属分离,Pb、Ag 和 Sn 等沉积在阳极泥中,而铜 则转移至电解液中并在阴极上还原析出。最佳的处理条件为在硫酸溶液中浸出,获得的最终产品为高纯 Cu(99%),电流效率为 90%。采用氨浸出可使 Cu 离子富集在电解液中,利于后续的电沉积,但是自发溶解的速率较低。在 氨-硫酸铵溶液中进行阳极溶解不利于各种金属在阳极泥、电解液和阴极沉积物进行分离。 关键词:铜合金;浸出;电解;回收;电工电子废料

(Edited by Yun-bin HE)