Hydrometallurgy 159 (2016) 110–119

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Electrochemical dissolution of smelted low-grade electronic scraps in acid sulfate-chloride solutions

Ewa Rudnik *, Erdenetsogt Bayaraa

AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals, Al. Mickiewicza 30, 30-059 Cracow, Poland

ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form 8 November 2015
Accepted 16 November 2015
Available online 17 November 2015

Keywords:
Acid
Alloy
Copper
Electrolysis
E-waste
Recovery
Tin

ABSTRACT

The paper reports hydrometallurgical method for recovery of bronze (80–92% Cu) from smelted low-grade waste electronic parts. Detailed analysis of five phases in Cu–Zn–Sn–Ag–Pb alloy was presented. Anodic dissolution of the alloy in acid sulfate and sulfate-chloride solutions resulted in distinct metal separation with copper and tin codeposited on the cathode, lead and silver accumulation in the slimes, while zinc, iron and nickel were transferred to the electrolyte. Phase and chemical analyses of slimes and cathodic deposits were performed. The most favorable conditions for the alloy dissolution were obtained in 2 M H_2SO_4 with 0.1 M NaCl at the temperature of 60 °C, where the highest anodic current efficiency and the lowest energy consumption were found. At lower temperatures periodical inhibition of the alloy dissolution was observed in sulfate-chloride solutions.

1. Introduction

Discarded and obsolete electric and electronic equipment is one of the fastest growing waste streams in the world (Baldé et al., 2015a,b). It was estimated that annual consumption of new electrical and electronic goods reaches about 58 Mt (in 2012), while solely last year (2014) almost 42 Mt of e-waste were generated globally (Baldé et al., 2015a). The latter is seriously affected by launching innovative and miniaturized products, mainly for communication and information branches. Many companies practice also the so-called "planned obsolescence" of the products resulting in their shortened lifespan (Keeble, 2013; Victor and Kumar, 2012) thus forcing consumers to buy new models of cell phones, laptops, printers, wash machines etc. Producers would rather pay a fee for collection and recycling of spent products than remanufacture and reduce waste generation (Bartl, 2014; Victor and Kumar, 2012; King et al., 2006).

E-waste represents currently a serious resource of valuable materials (Baldé et al., 2015a; Cui and Zhang, 2008), but also a source of toxins, health and environmental problems (Perkins et al., 2014; Ongondo et al., 2011; Robinson, 2009). Every year about 16.5 Mt of iron and steel, 2–4.5 Mt of copper, 90 kt of tin, 1–6 kt of silver, 0.3 kt of gold are "hibernated" in the worldwide WEEE as potential metal supply (Baldé et al., 2015b; Ongondo et al., 2011) leading to the development of novel trend called "urban mining". For comparison, annual global production of the particular materials reaches 2.75 Gt of iron pig and raw steel, 17.9 Mt of copper, 230 kt of tin, 26 kt of silver, 2.7 kt of gold (US Geological Survey, 2014). Simultaneously, it was estimated that only 25% of used electronic and electric products are treated in formal recycling centers with adequate worker protection (Perkins et al., 2014). Majority of WEEE are recycled in the unregulated sector, mainly in developing countries in Africa and Asia, where rich countries of European Union, US, Australia, Japan export own e-wastes (Perkins et al., 2014; EEA, 2012; Ongondo et al., 2011). Primitive techniques used for metals recovery (e.g. burning of plastics from cables, PCB etc. at low temperatures, manual dismantling, using of open-pit acid baths) expose the people to hazardous substances like heavy metals, toxic fumes of inorganic and organic compounds (Perkins et al., 2014; Robinson, 2009; Puckett and Smith, 2002). Although some destination regions banned importation of e-waste, this illegal trade is still continued due to a lack of control by local governments (EEA, 2012; Ongondo et al., 2011; Puckett and Smith, 2002).

Consciousness of the world public on WEEE as a potential source of profits and law regulations gradually increases development of the professional recycling business. Currently, most of the waste is recycled pyrometallurgically in the copper smelters (Khalig et al., 2014; Cui and Zhang, 2008; Hagelüken, 2005), where scraps are a part of copper concentrate batch. Hydrometallurgical treatment of waste materials is proposed as an alternative low-cost and more environmental friendly technology (Khalig et al., 2014; Tuncuk et al., 2012; Cui and Zhang, 2008). Biological leaching of metals using bacteria or fungi as a cost effective method was also studied recently in a laboratory scale (Pant et al., 2012).

* Corresponding author.
E-mail address: erudnik@agh.edu.pl (E. Rudnik).

http://dx.doi.org/10.1016/j.hydromet.2015.11.008
0304-386X/

Independently on the method used, the main problem in the recovery of metals is a treatment of plastics rich e-waste stream. A variety of polymers (e.g. PVC, PE, ABS, PS, PP, PU, PA, POM) is intermingled and embedded with metals, hence separation methods are necessary to implement into the recovery route. A few techniques are used for plastics removal from the metals. Mechanical treatment is applied usually, but pyrolysis (Moltó et al., 2009; de Marco et al., 2008) or combustion (Moltó et al., 2009) were also implemented. However, thermal decomposition of the plastics is accompanied by emission of more than one hundred toxic organic substances, mainly brominated and aromatic compounds.

This paper is focused on the investigation of copper and tin recovery from smelted low-grade electronic waste, containing no precious metals like gold, platinum or palladium. It should be noted that “low-grade” (or “low-value”) e-scrap is generally defined by gold content below 100 ppm (Hagelüken, 2005). A combined treatment route of the scraps was examined: mechanical separation of the metallic elements from a part of plastics, melting of the metallic phase and anodic dissolution of the obtained alloy with simultaneous deposition of high copper bronze on the cathode. In the previous papers (Rudnik et al., 2014, 2015), alloyed scraps were leached in ammoniacal solutions of various composition to dissolve copper via autocatalytic reaction or anodic oxidation. In the current work acid sulfate-chloride baths were used for electrochemical treatment of the material.

Acidic sulfate-chloride system (H_2SO_4–$CuSO_4$–NaCl-air/oxygen) was used earlier by Yazici and Deveci (2013) for metals leaching (Cu, Ni, Fe, Ag, Pd, Au) from waste printed circuit boards (PCB). It was found that complete extraction of copper, 58% Pd and over 90% of Fe, Ni and Ag dissolution were obtained at the Cl^-/Cu^{2+} concentration ratio of 21 at the temperature of 80 °C and 1 wt.% PCB content in the leaching bath. Leaching of Cu, Zn, Pb and Sn using electro-generated chlorine in HCl solution was proposed by Kim et al. (2011) resulting in 78% Cu, 98% Zn and 98% Sn and Pb dissolution from the waste PCB. Havlik et al. (2010) found that increased temperature of thermal treatment (burning, pyrolysis) of the PCBs enhanced extraction of copper and tin in HCl solution at 80 °C. However, authors of the above reports did not show any further separation methods of metals from the final loaded solutions. Recently, Lister et al. (2014) proposed a combined method of electrorecycling, where leaching of the electronic scraps was followed by electrodeposition of dissolved metals. H_2SO_4–Fe^{3+} solution was used for dissolution of Cu, Sn and Ag, while Pd and Au were leached in HCl–Cl_2 system. In both cases oxidizing agents (Fe^{3+}, Cl_2) were generated at the anode simultaneously with deposition of metals on the cathode.

Anodic oxidation is also used for hydrometallurgical treatment of multicomponent materials originated from industrial processes (Feng et al., 2014; Rudnik et al., 2009). Electrochemical treatment of smelted PCB in H_2SO_4 and HCl solutions was reported by Groot and van der Linde (2009a). They found that behavior of dissolved alloy in the individual baths was seriously affected by phase composition of the anode, mainly the presence of lead phase as well as α and δ bronzes.

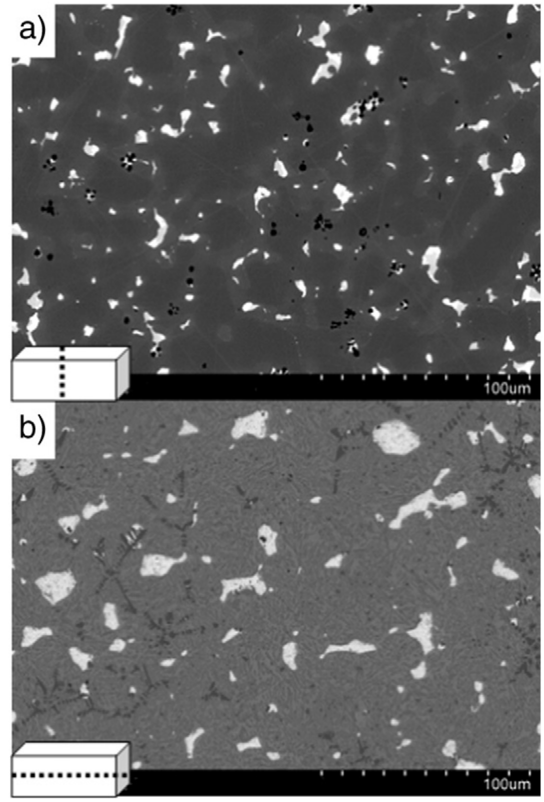

Fig. 1. Morphology of cross-sections of the alloy ingot: a) vertical plane, b) horizontal plane.

The aim of the present work was to recover copper and tin and verify behavior of the metals dissolving from the alloy during electrolysis. The influence of bath composition and temperature on the slime, electrolyte and cathode deposit composition, process efficiency and energy consumption was determined.

2. Experimental

A mixture of waste computer boards and printed circuit boards of mobile phones from an urban scrap heap was collected, then mechanically separated and final granulate was pyrometallurgically treated (without any additives or any special atmosphere) for about 2 h in an industrial chamber furnace (9 kW) to remove remaining non-metallic elements and organic compounds. Obtained ingot was cut into rectangular

Table 1
Composition of the alloy and individual phases.

Area	Average content, wt.%									
	Al	Si	P	Fe	Ni	Cu	Zn	Ag	Sn	Pb	Cr
Alloy	1.49	0.06	0.08	2.34	0.75	68.96	10.67	3.98	9.17	2.50	
Std dev. (alloy)	1.40	0.06	0.04	1.33	0.73	5.26	6.69	2.97	8.77	2.46	
I phase — matrix Dark gray areas	0.24			0.72	0.12	78.37	16.85	3.08	0.64		
II phase — matrix Light gray areas	0.37			0.28	0.11	71.38	17.30	7.11	3.48		
III phase White areas	0.67					6.65	1.01	2.15	2.50	89.14	
IV phase Gray areas in III						6.82	3.85	80.49	8.76	0.09	
V phase Black areas		6.20	0.44	86.03	0.78	4.70	0.87	0.22			0.89