Journal of Hazardous Materials 304 (2016) 409–416

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

A new membrane electro-deposition based process for tin recovery from waste printed circuit boards

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HIGHLIGHTS

- A process for tin recovery based on membrane electro-deposition is proposed.
- Tin can be recovered as the form of high purity cathode tin.
- Anolyte can be reused as leaching agent for leaching tin again after electrowinning.
- The optimum parameters for electro-deposition are introduced.

ARTICLE INFO

Article history:
Received 30 August 2015
Received in revised form 3 November 2015
Accepted 5 November 2015
Available online 10 November 2015

Keywords:
WPCBs
Tin recovery
Chloride leaching
Membrane electrodeposition

ABSTRACT

The current research investigated a process combining leaching, purification and membrane electrodeposition to recover tin from the metal components of WPCBs. Experimental results showed that with a solid liquid ratio of 1:4, applying 1.1 times of stoichiometric $SnCl_4$ dosage and HCl concentration of 3.5–4.0 mol/L at a temperature of 60–90 °C, 99% of tin can be leached from the metal components of WPCBs. The suitable purification conditions were obtained in the temperature range of 30–45 °C with the addition of 1.3–1.4 times of the stoichiometric quantity of tin metal and stirring for a period of 1–2 h; followed by adding 1.3 times of the stoichiometric quantity of Na_2S for sulfide precipitation about 20–30 min at room temperature. The purified solution was subjected to membrane electrowinning for tin electrodeposition. Under the condition of catholyte Sn^{2+} 60 g/L, HCl 3 mol/L and NaCl 20 g/L, current density 200 A/m^2 and temperature 35 °C, a compact and smooth cathode tin layer can be obtained. The obtained cathode tin purity exceeded 99% and the electric consumption was less than 1200 kW h/t. The resultant $SnCl_4$ solution generated in anode compartment can be reused as leaching agent for leaching tin again.

1. Introduction

Printed circuit boards (PCBs) are typical and fundamental components of almost all electric and electronic equipment (EEE). With the rapid development of technology and the society, high-performance requirements and great demands in EEE make replacement of PCBs more frequent, resulting in large quantities of WPCBs that need to be disposed. Mechanical and pyrometallurgical methods are the current ways of recycling WPCBs, and pyrolysis process also attracts more and more attention nowadays [1,2].

Almost all waste EEE recycling enterprises in China use various mechanical methods to separate metals and non-metals from WPCBs. As a result, approximately 30 wt.% of the original mass, enriched multi-metal fraction (Cu, Sn, Pb, Fe, Zn, Sb, and so on) is separated from the non-metal components. At present the enriched multi-metal fraction is mainly sold to copper smeltery as copper smelting raw material, and the tin contained in multi-metal fraction is not only failed to get effective recovery, but also cause serious interference to the copper recovery. In addition, the existing pyrometallurgical and hydrometallurgical recovery processes generate pollution because of the release of dioxins and furans or high volume of effluents [3–6].

Hydrometallurgical treatments have more flexibility during the upscaling and control processes. Sulfuric, hydrochloric and nitric acid solutions are often used as leaching agents in hydrometallurgical technologies [7–9]. Bin et al., proposed a hydrometallurgical recovery process to recover copper and tin by constant-current and constant-voltage electrolysis from the leaching solution of tinned copper wastes [10]. Fogarasi et al., introduced two new cop-

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http://dx.doi.org/10.1016/j.jhazmat.2015.11.007
0304-3894/

Table 1
Chemical composition of the enriched multi-metal fraction (wt.%).

Elements	Content/%	Elements	Content/%
Sn	8.8	Al	0.70
Cu	56.04	Ca	1.41
Pb	5.85	Ni	0.37
Zn	0.71	Ag	0.07
Fe	1.51	Others	24.54

Table 2
Tin occurrence analysis of the enriched multi-metal fraction/%.

Tin occurrence	Sn	SnO	Other
Content/%	8.63	0.09	<0.1
Proportion/%	98.1	1.02	<1.0

per recovery processes from waste printed circuit boards [11,12], and Kim et al., investigated the leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution [13]. The experimental results show that the elements could be deposited on the cathode in turns by different deposition potentials. García-Gabaldón et al., studied the performance of a two-compartment batch electrochemical reactor separated by a ceramic diaphragm for tin removal from the activating solutions [14,15]. However, even under optimized conditions, the tin leaching efficiency was proven to be incapable of reaching more than 90%, whereas the current efficiency cannot exceed 85%. The low tin recovery are the obvious disadvantages that limit the application.

In our previous study [16,17], a process and related fundamental principle was proposed for the separation and recovery of antimony, bismuth from a concentrate using a membrane electrodeposition process. Further, a new process based on membrane electrodeposition for tin recovery from the metallic fraction of WPCBs is proposed. Thus leaching, purification and membrane electrodeposition to recover tin was investigated. This process has been applied for patent in China recently [18]. The current paper demonstrates that not only tin can be efficiently recovered from WPCBs, but also $SnCl_4$ can be regenerated from the anode compartment and to be used as leaching agent again.

2. Experimental

2.1. Materials

The metal components of WPCBs, obtained from Lv-yan Resource Recycle Co., China, were characterized for chemical composition and phase analysis. The dry screen used for the analysis was about 10 mesh (2 mm), and all samples were leached without further grinding. Chemical analysis of the enriched multi-metal fraction was conducted by atomic absorption spectroscopy, except for the copper, tin, lead and zinc contents were analyzed by chemical titration, and the results are given in Table 1. Tin occurrence analysis showed that tin was present mainly as metallic tin (>98%) and as stannous oxide (SnO) (<1%) in small quantity (Table 2). The other chemicals used were of reagent grade. The hydrochloric acid, stannic chloride, etc., were purchased from Changsha Shenghua, Inc., China, with no further purification introduced.

2.2. Method

The WPCBs were first treated by using mechanical methods, such as multi-crushing, grinding, electrostatic separation, gravity separation, and magnetic separation to separate metals and non-metals from WPCBs. The schematic of the electrodepositon apparatus and procedure for leaching, purification and electrodeposition tin from the enriched multi-metal fraction is shown in Fig. 1.

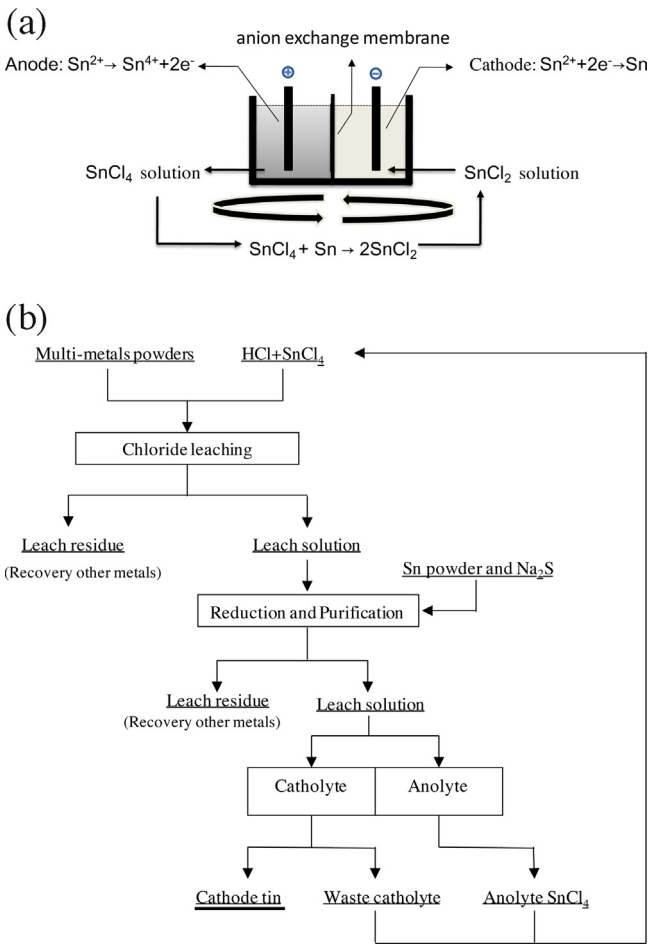

Fig. 1. Schematic representation of the experimental apparatus for electrodepositon and experimental procedure.

Leaching was carried out in 500 mL glass flasks by adding a weighed amount of multi-metals powder, sodium chloride and stannic chloride to diluted HCl solution at the desired temperature with magnetic stirring at 250 r/min. The temperature of the system was controlled within 2 °C on a hot plate. A condenser was attached to the flask to prevent vaporization losses. At the end of each experiment, the insoluble leach residue was filtered and washed with 1 mol/L HCl and then distilled water. The recovery of tin was calculated by mass balance using the analysis of the multi-metals powder and the leach residue.

In the purification procedure, a weighed amount of tin powder and Na_2S was added to the stirred solution to remove Cu^{2+} and Pb^{2+}. After filtration, the degree of purification was calculated from analysis of Cu^{2+} and Pb^{2+} concentrations by and atomic absorption spectroscopy.

In the electrowinning experiment, a two-compartment acrylic cell ($90 \times 120 \times 150$ mm) was used, where the anode and cathode compartments were separated by a widely used commercial quaternary-ammonium-hydroxy-type anion exchange membrane (HF-201, Beijing Enling Technology Co., Ltd., China). The applied HF-201 type anion exchange membrane has the anion selective permeability. The membrane only allows the chloride ion and water molecules to penetrate, while other ions are difficult to penetrate. The cathode plate was made of titanium and the anode was a graphite plate with the same surface area. The catholyte and anolyte contained Sn^{2+} (stannous chloride) and HCl. Both electrolytes are