Hydrometallurgical Reclamation of Cu, Ag and Sn from Waste Pb-free Solder Using Nitric Acid

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Abstract

The development of a hydrometallurgical process based on nitric acid leaching of the waste Pb-free solder is reported to recover copper, silver and tin. The nitric acid dissolved copper and silver from the waste material while converting tin to stannic acid (H_2SnO_3) which is very sparingly soluble in this acid. The parameters such as nitric acid concentration, leaching temperature and time, and pulp density were investigated to optimize the conditions for complete extraction of copper and silver from the waste solder, with simultaneous precipitation of high purity stannic acid. The progress of leaching reaction was monitored by XRD phase identification of the residue generated during the process. Almost complete recovery of silver was achieved from the leach liquor by cementation using copper powder as a reductant and copper was electro-won from the solution as cathode. The stannic acid of 99.9 % purity obtained from the leaching was characterized in terms of particle size and shape for its possible utilization as advanced materials.

Key words: Pb-free tin solder, recycling, silver, copper, stannic acid

1. Introduction

Tin/lead (Sn-Pb) solder has been famous for its outstanding solderability and reliability, and has therefore, been predominantly used as the interconnecting material in electronic packaging (Ma and Suhling, 2009; Pan et al., 2005). However, lead is a toxic material which can cause kinds of negative impacts to both the environment and the human body. EU's directives, WEEE (the waste of electrical and electronic equipment) and RoHS (the restriction of the use of certain hazardous substances), regulate the use of lead in electric and electronic equipments. The Sn-Pb solder has been substituted by various Pb-free solders such as Sn-Ag-Cu series, Sn-Ag-Cu-Bi series, Sn-Ag-Cu-Sb series, Sn-Ag series, Sn-Ag-Bi series, Sn-Cu series and Sn-Zn-Bi series (Ma and Suhling, 2009). The market share of Sn-Ag-Cu series reaches to approximately 70% for reflowing lead-free solders (Ma and Suhling,

2009; Pan et al., 2005; Turbini et al., 2001).

Spent Sn-Pb solder was recycled using lead refining process which consists of melting and re-powdering processes (Takahashi et al., 2009). Similarly, the majority of Pb-free solder has been reused as solders by simple melting processes. RICOH Microelectronics Co. Ltd and Tottori University of Environmental Studies jointly developed a recycling process for waste Pb-free cream solder, where the solder is melted at 220-230 °C, and then organic flux and metal components are separated by specific gravity difference. However, these pyrometallurgical processes have disadvantages such as the consumption of high energy and the emission of carbon dioxide, besides the generation of harmful gas from combustion of the organic flux (Takahashi et al., 2009).

Therefore, hydrometallurgical routes were developed for waste solder recycling as alternatives, which included the studies for recycling of Sn-Pb solder using inorganic leaching reagents. Rhee and co-workers (1994) investigated the feasibility of tin recovery from lead frame scrap using sodium hydroxide with sodium persulfate as an oxidant. Mecucci and Scott (2002) reported the recovery of Sn, Pb and Cu from scrap printed circuit boards (PCBs) using nitric acid, where the contents of Sn and Pb are about 0.4 mass % and 0.3 mass % in PCB as minor components. Although, Takahashi and co-workers (2009) developed the recycling process of solder paste using organic solvents such as toluene, there have been a very few reports on recycling processes for Pb-free tin solder using inorganic leaching reagents.

Therefore, an attempt was made to develop a recycling process for waste Sn-Ag-Cu series solder, which consists of nitric acid leaching followed by subsequent recovery of metal components such as Sn, Ag, and Cu. The present study is aimed to examine the behaviors of Sn, Ag, and Cu during nitric acid leaching while optimizing the parameters such as nitric acid concentration, leaching temperature, pulp density, and agitation speed on the dissolution of metals. In addition, the residue from the nitric acid leaching was investigated with XRD.

2. Experimental

2.1. Materials

Waste Pb-free solder was obtained from a recycling company in Korea which was generated from manufacturing processes of electronic appliances. The chemical composition and the particle size distribution of the solder are given in Tables 1 and 2. It contained 87.7 % Sn, 3.09 % Ag, and 0.85 % Cu as main components. The X-ray diffraction (XRD) pattern (see Fig. 1) of the solder shows that it is composed of Sn and Ag_3Sn. All reagents used in this study are of reagent-grade.

Table1. Chemical composition of the waste Pb-free solder

Elements	Sn	Ag	Cu	Bi	Pb
Weight (%)	87.8	3.09	0.85	0.022	0.021

Table 2. Particle size distribution of the waste Pb-free solder

Sieve size (μm)	>1000	1000-710	710-500	500-250	250-125	<125
Weight (%)	2.6	18.5	21.5	31.2	18.2	8.0

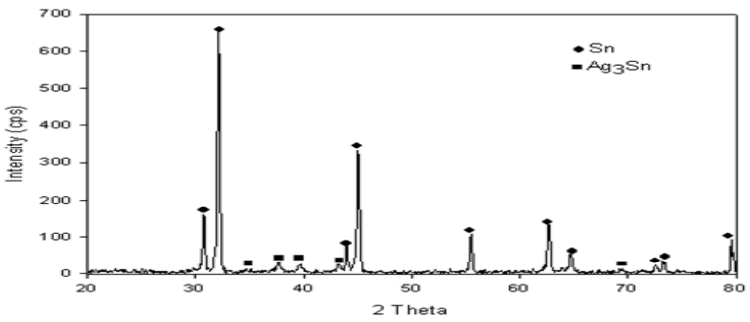

Fig. 1 XRD pattern of the waste Pb-free solder used in this study.

2.2. Leaching procedures

The leaching tests of the waste Pb-free solder in HNO_3 solution were carried out in a 500 dm^3 three necked Pyrex reactor in a heating mantle. The reactor was fitted with an agitator and a reflux condenser. The reflux condenser was inserted in one port to avoid solution loss at high temperatures. In a typical run, 200 dm^3 of acid solution (1–6 kmol m^{-3} HNO_3) was poured into the reactor and allowed to reach thermal equilibrium (30–90 °C). A 2 g solder sample (mixed size) was then added to the reactor in the experiments except the test of pulp density, and the agitator was set to run at 100-600 rpm. During the experiment 3 cm^3 of the solution sample was withdrawn periodically at a desired time interval (10–360 min) with a syringe. The sample was filtered and then the filtrate was diluted with 5 % HNO_3 solution for Cu and Ag analyses and 15% HCl solution for Sn analysis, respectively. At the end of the leaching test, the entire slurry was filtered, and then dried overnight at 105 °C for metal and XRD analysis.

2.3. Analytical methods

The sample solutions were analyzed by an atomic absorption spectrometry (AA, SpectrAA400, Varian Inc.) and an inductively coupled plasma-atomic emission spectrometry (IC-AES, JY-38 plus, Jobin Yvon Ltd.). The residue containing tin precipitates was also characterized by X-Ray Diffraction (D-max-2500PC, Rigaku Co.).

3. Results and discussion

The nitric leaching of the spent Pb-free solder at agitation speeds in the range 100–600 rpm was tested to investigate the effect of liquid film boundary diffusion surrounding solid particles on the

leaching efficiency of metals in 1 kmol m^{-3} HNO_3 at 50 °C. As can be seen from Fig. 2 and 3, the results indicate that the leaching rates of Ag and Cu are independent of the agitation rate at speeds of higher than 200 rpm. Therefore, in all subsequent leaching tests, a working agitation speed of 400 rpm was selected to ensure effective particle suspension in the solution while minimizing the effect of liqu

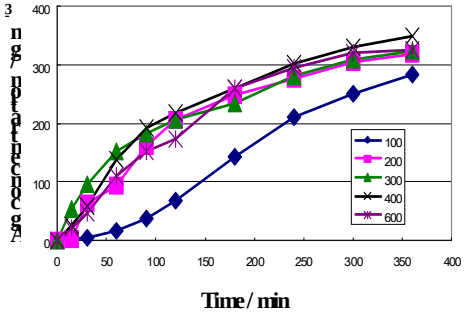

Fig. 2 Effect of agitation speed on Ag dissolution from waste solder in 1 kmol m^{-3} HNO_3 at 50° C.

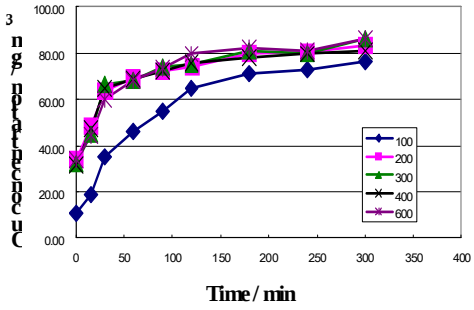

Fig. 3 Effect of agitation speed on Cu dissolution from waste solder in 1 kmol m^{-3} HNO_3 at 50° C.

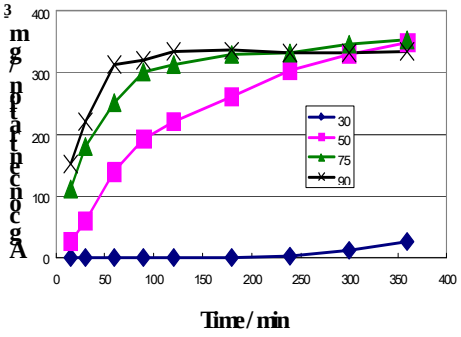

Fig. 4 Effect of temperature on Ag dissolution from waste solder in 1 kmol m^{-3} HNO_3, 400 rpm.

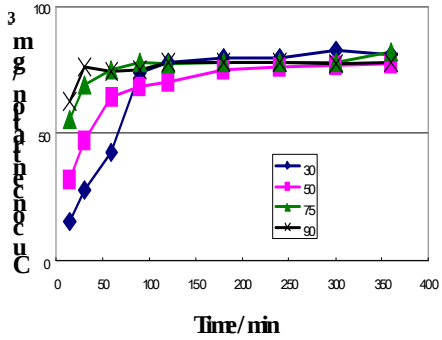

Fig. 5 Effect of temperature on Cu dissolution from waste solder in 1 kmol m^{-3} HNO_3, 400 rpm.

Figs. 4 and 5 show the effect of temperature on the dissolution of Ag and Cu from the solder in 1 kmol m^{-3} HNO_3 solution. The dissolution temperature was varied in the range 30–90 °C, while all other parameters were kept constant. It can be seen from Figs. 4 and 5 that higher temperatures yielded higher dissolution rates of silver and copper from the solder. At 50 °C the silver concentration was 302.2 g m^{-3} at 240 min, while the concentration reached to 313.7 g m^{-3} at 60 min when the dissolution temperature was increased to 90 °C.

The dissolution of silver and copper from the solder was investigated at HNO_3 concentrations of 1–6 M at 50 °C. Figs. 6 and 7 show the effect of nitric acid concentration on the dissolution of silver and copper. The concentrations of both metals increased with increase in leaching time at 1 kmol m^{-3}

HNO_3, whereas the concentrations became almost constant at more than 2 kmol m^{-3} HNO_3. The dissolution of Ag and Cu in nitric acid could be represented as the following equations;

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O \quad (1)$$

$$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O \quad (2)$$

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O \quad (3)$$

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O \quad (4)$$

where the stoichiometry varies according to nitric acid concentration and the equations (2) and (4) are predominant at higher HNO_3 concentration (Sadrnezhaad et al., 2006; Stairs, 1990), while tin precipitates as stannic acid during nitric acid leaching.

$$3Sn + 4HNO_3 + H_2O = 3SnO_2 \cdot H_2O + 4NO \quad (5)$$

$$Sn + 4HNO_3 = SnO_2 \cdot H_2O + 4NO_2 + H_2O \quad (6)$$

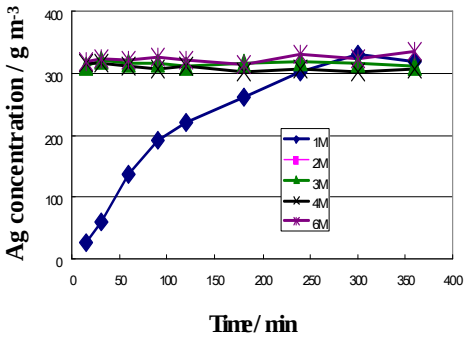

Fig. 6 Effect of HNO_3 concentration on Ag dissolution from waste solder at 50°C and 400 rpm.

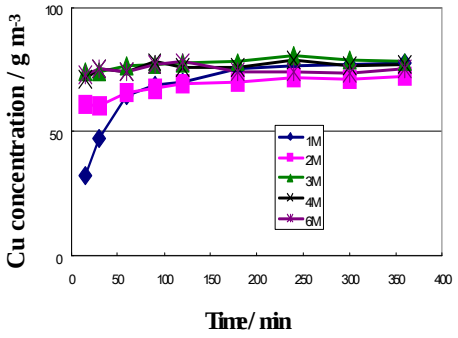

Fig. 7 Effect of HNO_3 concentration on Cu dissolution from waste solder at 50°C and 400 rpm.

In the nitric leaching tests, tin concentrations were found to be extremely low. Fig. 8 shows the XRD patterns of the precipitate obtained from the nitric acid leaching of the solder sample at 50 °C and 400 rpm in the 1 kmol m^{-3} HNO_3; the phase identified is found to be stannic oxide. This result suggests that tin component can be successfully separated from silver and copper components during the leaching stage.

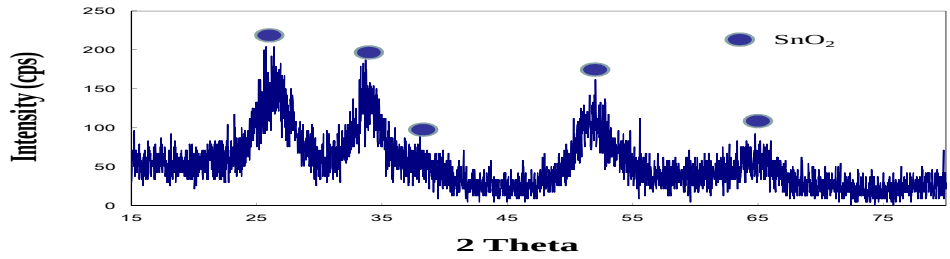

Fig. 8 XRD pattern of the precipitate obtained in the leaching at 50 °C and 400 rpm in 1 kmol m^{-3} HNO_3.

The effect of pulp density from 40 kg m^{-3} to 100 kg m^{-3} was investigated under the leaching condition: 2 kmol m^{-3} HNO_3, 400 rpm, and 75 °C. As shown in Figs. 9 and 10, the concentrations of silver and copper reached to plateau within 15 min at the pulp density of 40 kg m^{-3} and 50 kg m^{-3}, while at 100 kg m^{-3}, the concentrations increased gradually in 120 min, and then became constant. The leach liquor containing silver and copper was neutralized with sodium hydroxide to remove free acid and to bring the pH to above 2.0. From this solution silver could be cemented out with copper powder. The resulting solution containing copper could be processed to produce metal cathode. The purity of the stannic oxide obtained from the leaching was determined by chemical analysis and was found to be 99.9%.

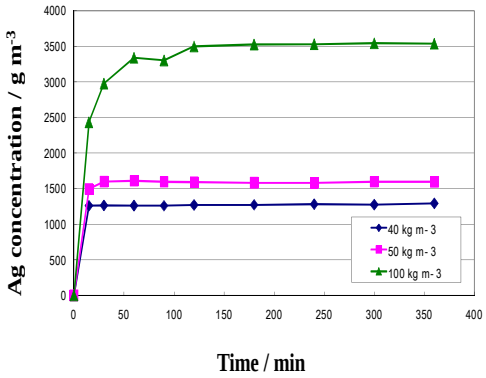

Fig. 9 Effect of pulp density on Ag dissolution from waste solder at 75 °C and 400 rpm in 2kmol m^{-3} HNO_3.

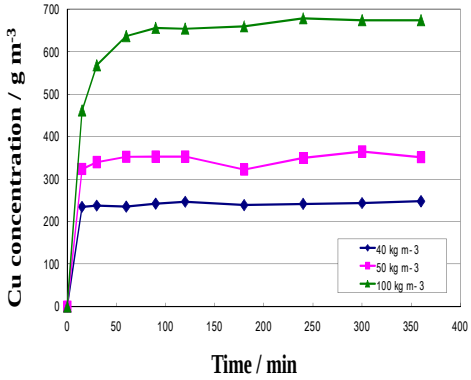

Fig. 10 Effect of pulp density on Cu dissolution from waste solder at 75 °C and 400 rpm in 2 kmol m^{-3} HNO_3.

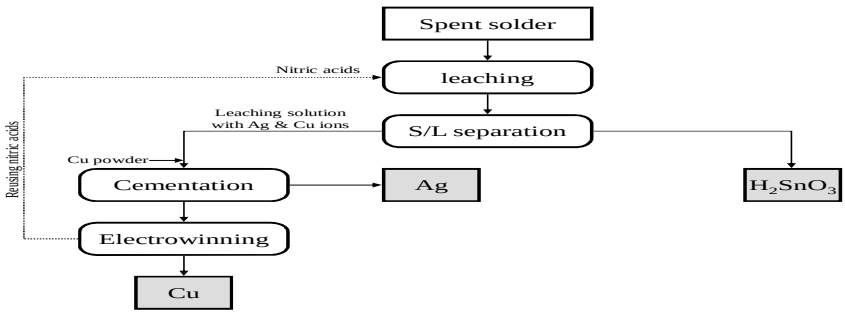

Fig. 11 Proposed schematic diagram for recycling waste Pb-free solder.

Based on the aforementioned results, a recycling process of the waste Pb-free solder is proposed (Fig. 11). Silver and copper are dissolved by nitric acid and then recovered in the cementation process with copper powder addition and subsequent electrowinning process, respectively. Further studies will

be required to recover metals from the leach solution and the precipitates in the process shown in Fig. 11.

4. Conclusions

The nitric acid leaching of waste Pb-free solder was performed to establish a recycling process, while investigating the behaviors of tin, silver and copper. During nitric acid leaching, silver and copper were dissolved while tin precipitated as stannic acid. The concentrations of silver and copper increased with increasing dissolution temperature, nitric acid concentration, and agitation speed. Silver and copper were leached out from the waste Pb-free solder under the leaching condition: 75 ℃ and 400 rpm in 2 kmol m^{-3} with a pulp density of 100 kg m^{-3}. This result indicates that tin component can be separated successfully from the silver and copper components in the waste Pb-free solder. Thus, a recycling process is proposed based on nitric acid leaching to treat the waste Pb-free solder followed by subsequent metal recovery processes.

Acknowledgement

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