

Recovery of Sn, Ag and Cu from Waste Pb-Free Solder Using Nitric Acid Leaching

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The development of a hydrometallurgical process for the recycling of waste Pb-free solder based on nitric acid leaching, followed by the separation of Ag and Cu through AgCl precipitation or cementation, was investigated. Nitric acid dissolved Cu and Ag from the waste material while converting tin to stannic oxide (SnO₂), which is very sparingly soluble in the HNO₃ solution. More than 99% of the Ag and Cu in the waste Pb-free solder were dissolved in 2 kmol·m⁻³ HNO₃ under the leaching conditions of 75°C, 100 kg·m⁻³ pulp density and stirring at 400 rpm for 120 min. The addition of NaCl or Cu powder was used to separate Ag from Cu in the solution. The addition of 2 kg·m⁻³ of NaCl or 125 kg·m⁻³ of Cu powder to the leaching solution at 30°C led to the successful recovery of 3755 g·m⁻³ of Ag. Thus, the results showed that Sn, Ag and Cu could be separated and recovered from waste Pb-free solder by the proposed recycling process.

[doi:10.2320/matertrans.M2012268]

(Received August 2, 2012; Accepted September 6, 2012; Published November 2, 2012)

Keywords: lead-free solder, tin, silver, nitric acid leaching, recycling

1. Introduction

Tin–lead (Sn–Pb) solder has been predominantly used as the interconnecting material in electronic packaging due to its outstanding solderability and reliability.^{1,2)} However, lead is known to be a toxic material that can have negative impacts on both the environment and the human body. The EU's directives relating to the waste of electrical and electronic equipment (WEEE) and the restriction of the use of certain hazardous substances (RoHS) regulate the use of lead in electric and electronic equipment.^{3,4)} Thus, Sn–Pb solder has been substituted by various Pb-free solders, such as the 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 of solders.¹⁾ The market share of the Sn–Ag–Cu series of solders has reached to approximately 70% in the reflowing of the lead-free solders.^{1,2,5)}

Waste Sn–Pb solder has been recycled using a lead refining process which consists of melting and re-powdering processes.⁶⁾ Similarly, the majority of Pb-free solders have been reused as solders by simple melting processes. RICOH Microelectronics Co. Ltd. and Tottori University of Environmental Studies co-developed a recycling process for waste Pb-free cream solder, wherein the solder is melted at 220–230°C followed by the separation of the organic flux and metal components by specific gravity difference. However, these pyrometallurgical processes have disadvantages, such as the consumption of high energy and the emission of carbon dioxide and harmful gases generated from the combustion of the organic flux.⁶⁾ Furthermore, it is difficult to recover metals as individual components in the pyrometallurgical processes.

Hydrometallurgical routes have been recognized as alternative processes for waste solder recycling. Rhee and co-

workers investigated the feasibility of Sn recovery from lead frame scrap using sodium hydroxide with sodium persulfate as an oxidant.⁷⁾ Mecucci and Scott reported the recovery of Sn, Pb and Cu from scrap printed circuit boards (PCBs) using nitric acid, where the contents of Sn and Pb were approximately 0.4 and 0.3 mass%, respectively, in the PCBs (i.e., they were minor components in the PCBs).⁸⁾ Takahashi and co-workers developed the recycling process of solder paste using organic solvents such as toluene, even though such organic solvents are harmful to the environment. However, there are very few studies on the recovery of metals as individual components from waste Pb-free solders.

The demand for solder is gradually decreasing in Korea because most of the manufacturing facilities are moving to China. On the contrary, the demand for Sn, Ag and Cu is increasing in the plating industry and in the high-tech electronics industry. Therefore, we aimed to develop a recycling process for the waste solder of the Sn–Ag–Cu series using nitric acid leaching. We examined the behavior of these metals and the subsequent recovery of each metal component (i.e., Sn, Ag and Cu). The effects of the parameters, namely nitric acid concentration, leaching temperature, pulp density, and agitation speed, on the dissolution of Sn, Ag and Cu are discussed. In addition, we investigated the precipitation of Ag by adding NaCl or Cu powder to separate Ag and Cu from the nitric acid leaching solution.

2. Experimental

2.1 Materials

Waste Pb-free solder, obtained from a recycling company in Korea, was generated from the manufacturing processes of electronic appliances. The chemical composition of the solder is given in Table 1. It contained 87.7% Sn, 3.09% Ag and 0.85% Cu as the main components. The X-ray pattern (see Fig. 1) of the solder shows the presence of phases, such as

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Table 1 Chemical composition of the waste Pb-free solder.

| Elements | Sn | Ag | Cu | Bi | Pb |
|----------|------|------|------|-------|-------|
| mass (%) | 87.8 | 3.09 | 0.85 | 0.022 | 0.021 |

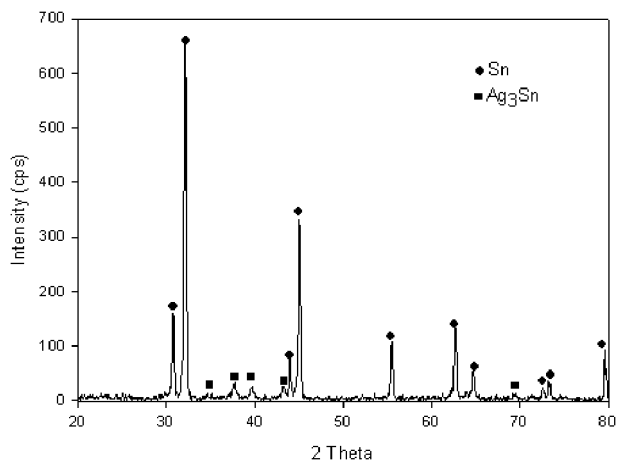


Fig. 1 XRD pattern of the waste Pb-free solder used in this study.

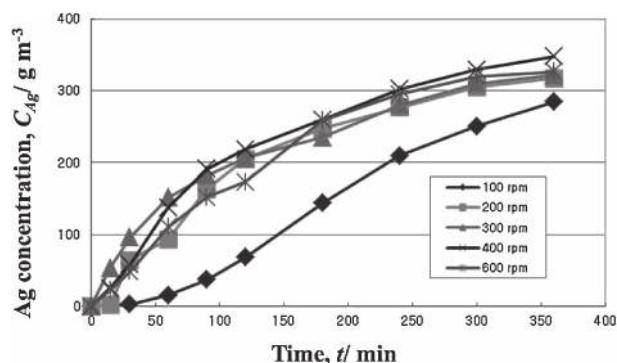
Sn and Ag_3Sn . All the chemicals used in this study were of reagent-grade.

2.2 Leaching procedure

The leaching experiments of the waste Pb-free solder in HNO_3 solution were carried out in a 500 dm³ three-necked Pyrex glass reactor equipped with a heating mantle to maintain temperature. The reactor was fitted with an agitator and a reflux condenser. The reflux condenser was inserted into one port of the reactor to avoid solution loss at high temperatures. In a typical run, 200 dm³ 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 sample of the solder powder with a particle size of less than 125 μm was then added to the reactor in all the experiments, except for the pulp density test. The agitator was set at 100–600 rpm. During the experimental run, a sample of 3 cm³ of the solution was withdrawn periodically at various time intervals (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. At the end of the leaching period, the entire volume remaining in the reactor was filtered, and then dried overnight at 105°C for XRD and chemical analyses.

2.3 Separation tests for Ag and Cu

The two types of separation tests for Ag and Cu were performed with NaCl and Cu powders. The leach solution used in these tests were obtained under the following leaching conditions: 400 rpm agitation speed, 2 kmol·m⁻³ HNO_3 concentration, 75°C temperature and 10% pulp density. The separation tests were conducted in a 250 cm³ Pyrex reactor equipped with a water jacket for temperature control. In the NaCl addition tests, 0.2 or 0.4 g of NaCl were added to 100 cm³ of the leach solution at 400 rpm and 30°C. The Cu addition tests were performed using both the leach

Fig. 2 Effect of agitation speed on the dissolution of Ag from the waste solder in 1 kmol·m⁻³ HNO_3 at 50°C.

solution and a simulated leach solution, which was prepared by dissolving AgNO_3 (Junsei Chemical Co., Japan) and nitric acid. To 100 cm³ volume of leach solution, 0.75, 1.0 or 1.25 g of Cu were added at an agitation speed of 400 rpm at various temperature (30, 50 and 70°C). For the measurements of the concentrations of Ag and Cu, 2 cm³ of solution was sampled with a syringe and was prepared for analysis following the same procedure as mentioned above (section 2.2).

2.4 Analytical methods

The sample solutions were analyzed by an atomic absorption spectrometer (AA, SpectrAA400, Varian Inc.) and an inductively coupled plasma-atomic emission spectrometer (ICP-AES, JY-38 plus, Jobin Yvon Ltd.). The precipitates were also characterized by an X-ray diffractometer (D-max-2500PC, Rigaku Co.) or field emission gun scanning electron microscope (MIRA 3 FEG-SEM, TESCAN Co.).

3. Results and Discussion

The nitric acid leaching experiments of the waste Pb-free solder at agitation speeds in the range of 100–600 rpm were carried out to examine the effect of the liquid film boundary diffusion surrounding the solid particles on the leaching efficiency of the solder in 1 kmol·m⁻³ HNO_3 at 50°C. As seen in Fig. 2, the leaching rates of Ag are independent of the agitation speeds faster than 200 rpm; the leaching rates of Cu showed a similar behavior (data not shown). Therefore, in all the subsequent leaching experiments, a working agitation speed of 400 rpm was employed to ensure effective particle suspension in the solution while minimizing the effect of the liquid film boundary diffusion surrounding the solid particles.

Figures 3 and 4 show the effect of temperature on the dissolution of Ag and Cu from the waste solder in 1 kmol·m⁻³ HNO_3 solution. The dissolution temperature was varied in the range of 30–90°C, while all the other parameters were kept constant. As seen in the figures, the higher temperatures yielded higher dissolution efficiencies of Ag and Cu from the solder. The concentrations of Cu increased rapidly and reached plateaus for all temperatures. The dissolution efficiency of Ag was extremely slow at 30°C, but the efficiencies enhanced with increasing temperature from 50 to 90°C. The Ag concentration increased to

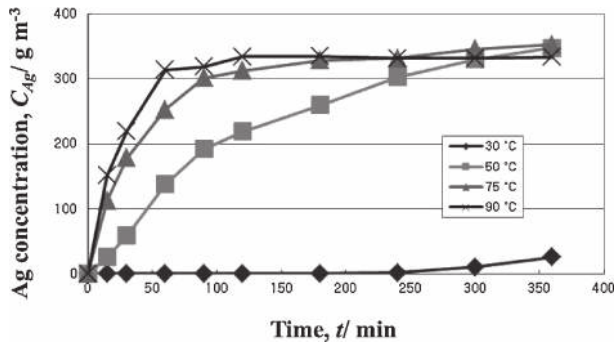


Fig. 3 Effect of temperature on the dissolution of Ag from the waste solder in $1 \text{ kmol}\cdot\text{m}^{-3}$ HNO_3 at 400 rpm.

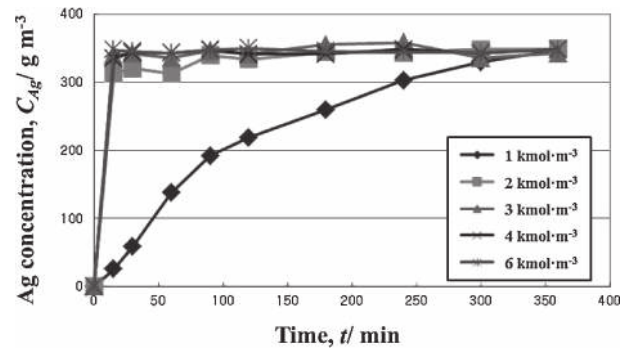


Fig. 5 Effect of HNO_3 concentration on the dissolution of Ag from the waste solder at 50°C and 400 rpm.

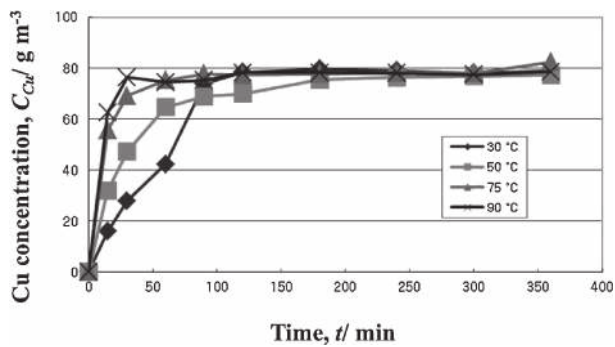


Fig. 4 Effect of temperature on the dissolution of Cu from the waste solder in $1 \text{ kmol}\cdot\text{m}^{-3}$ HNO_3 at 400 rpm.

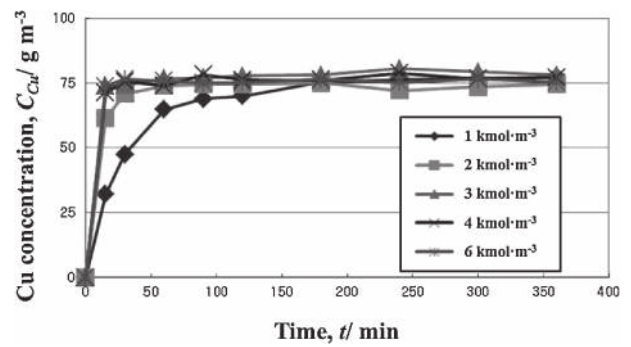
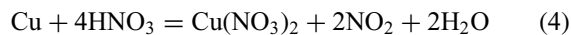
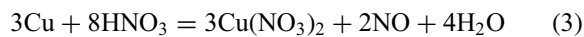
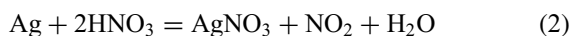
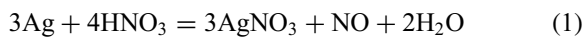


Fig. 6 Effect of HNO_3 concentration on the dissolution of Cu from the waste solder at 50°C and 400 rpm.

$302.2 \text{ g}\cdot\text{m}^{-3}$ within 240 min at 50°C , while it reached to $313.7 \text{ g}\cdot\text{m}^{-3}$ within 60 min at 90°C .

The dissolution of Ag and Cu from the solder was investigated at varying HNO_3 concentrations ($1\text{--}6 \text{ kmol}\cdot\text{m}^{-3}$) at 50°C . Figures 5 and 6 show the effect of HNO_3 concentration on the dissolution of Ag and Cu, respectively. The concentrations of both metals increased with leaching time at $1 \text{ kmol}\cdot\text{m}^{-3}$ HNO_3 , whereas the concentrations remained almost constant at HNO_3 concentrations above $2 \text{ kmol}\cdot\text{m}^{-3}$. The dissolution of Ag and Cu in nitric acid can be represented by the following reactions:



where the stoichiometry varies according to nitric acid concentration and the reactions (2) and (4) are predominant at higher HNO_3 concentrations.^{9,10}

The effect of pulp density, ranging from 40 to $100 \text{ kg}\cdot\text{m}^{-3}$, was investigated under the leaching conditions of $2 \text{ kmol}\cdot\text{m}^{-3}$ HNO_3 , 400 rpm, and 75°C . As shown in Figs. 7 and 8, the concentrations of Ag and Cu reached plateaus within 15 min for pulp densities of 40 and $50 \text{ kg}\cdot\text{m}^{-3}$. For a pulp density of $100 \text{ kg}\cdot\text{m}^{-3}$, the concentrations of Ag and Cu increased gradually for 120 min then remained constant. The leaching recovery of Ag and Cu was found to be greater than 99% after 120 min for a pulp density of $100 \text{ kg}\cdot\text{m}^{-3}$ in $2 \text{ kmol}\cdot\text{m}^{-3}$ HNO_3 at 400 rpm at 75°C .

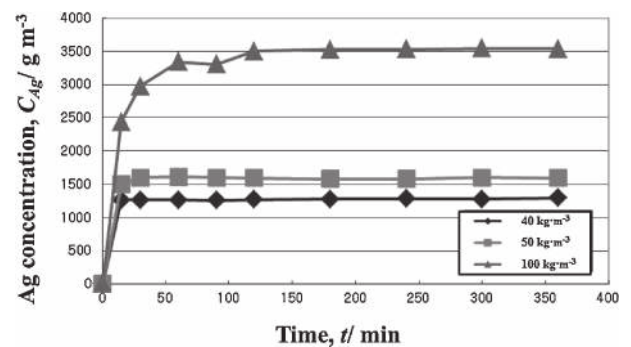


Fig. 7 Effect of pulp density on the dissolution of Ag from the waste solder in $2 \text{ kmol}\cdot\text{m}^{-3}$ HNO_3 at 75°C and 400 rpm.

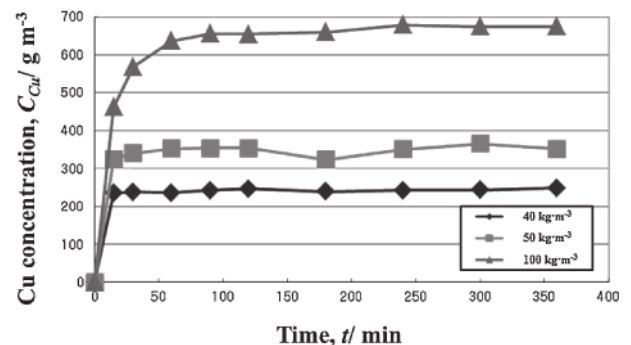


Fig. 8 Effect of pulp density on the dissolution of Cu from the waste solder in $2 \text{ kmol}\cdot\text{m}^{-3}$ HNO_3 at 75°C and 400 rpm.

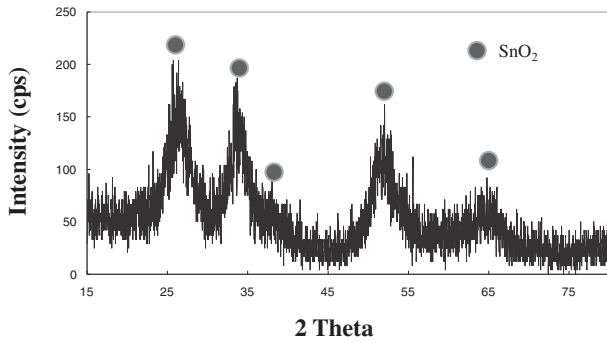


Fig. 9 XRD pattern of the precipitate obtained from leaching in $1 \text{ kmol}\cdot\text{m}^{-3} \text{ HNO}_3$ at 50°C and 400 rpm .

In all the nitric leaching experiments, the tin concentrations were extremely low. The tin component in the waste Pb-free solder precipitates as stannic acid during nitric acid leaching, as shown in the following reactions:

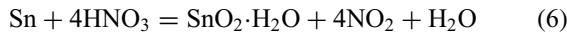
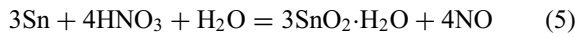
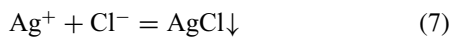


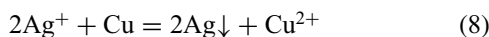
Figure 9 shows the XRD patterns of the precipitate obtained from the nitric leaching experiment in the $1 \text{ kmol}\cdot\text{m}^{-3} \text{ HNO}_3$ at 50°C and 400 rpm ; it was identified as stannic oxide. This result suggests that the tin component can be successfully separated from Ag and Cu during leaching.

The process of separating Ag and Cu was investigated by adding either NaCl or Cu powder to the leach solution obtained under the following leaching conditions: $2 \text{ kmol}\cdot\text{m}^{-3} \text{ HNO}_3$ concentration and 10% pulp density stirred with an agitation speed of 400 rpm at 75°C . The initial concentrations of Ag and Cu in the leach liquor were 3755 and $855 \text{ g}\cdot\text{m}^{-3}$, respectively. The silver ion has been found to precipitate by reacting with the Cl^- ion in the following reaction:



Because $34.8 \text{ mol}\cdot\text{m}^{-3}$ of Cl^- is required to precipitate $3755 \text{ g}\cdot\text{m}^{-3}$ of Ag, 0.2 g and 0.4 g of NaCl were added to 100 cm^3 of the leach solution. In Fig. 10, the Ag concentrations decreased rapidly while the Cu concentrations remained almost constant (data not shown). The standard Gibbs free energies of Ag^+ , Cl^- and $\text{AgCl}_{(s)}$ are given in Table 2.¹¹⁾ The solubility product (K_{sp}) of AgCl was calculated to be $10^{-22.59}$, using the data at 25°C in Table 2. This result indicates that the Ag ions precipitate easily and rapidly as AgCl because the solubility of AgCl is extremely low.

Cementation is the process of precipitating the metals from a solution using the electrochemical reaction between two metals.¹²⁾ The cementation process using Cu powder precipitates Ag, as shown in the reaction below:



where the standard redox potential of eq. (8) was calculated to be $+0.46 \text{ V}$.¹³⁾

In eq. (8), $17.4 \text{ mol}\cdot\text{m}^{-3}$ of Cu (0.11 g of Cu added to 100 cm^3 of leach solution) is required to precipitate $3755 \text{ g}\cdot\text{m}^{-3}$ ($34.8 \text{ mol}\cdot\text{m}^{-3}$) of Ag.

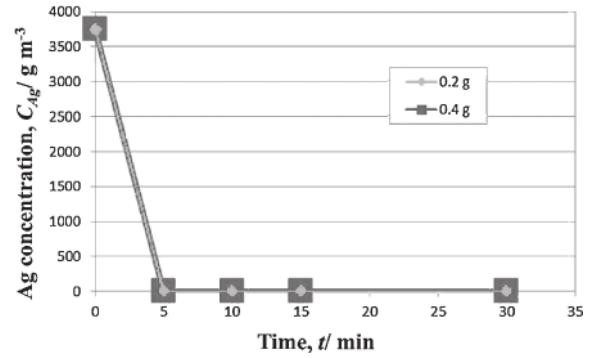


Fig. 10 Behavior of Ag in the leach solution with the addition of 0.2 or 0.4 g of NaCl.

Table 2 Standard Gibbs free energies (kJ mol^{-1}) of Ag^+ , Cl^- and $\text{AgCl}_{(s)}$ at 25°C .¹¹⁾

| Components | Ag^+ | Cl^- | $\text{AgCl}_{(s)}$ |
|--------------|---------------|---------------|---------------------|
| ΔG^0 | 77.16 | -131.0563 | -109.86 |

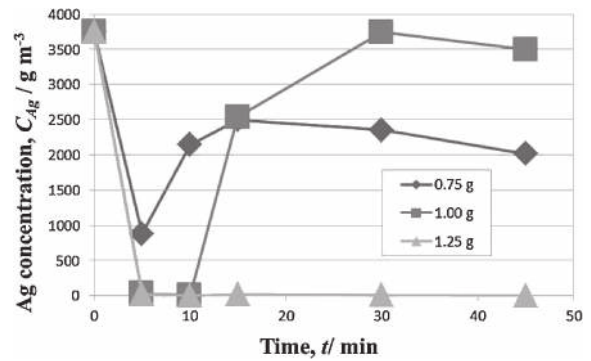


Fig. 11 Behavior of Ag during the cementation process with the addition of various amounts of Cu.

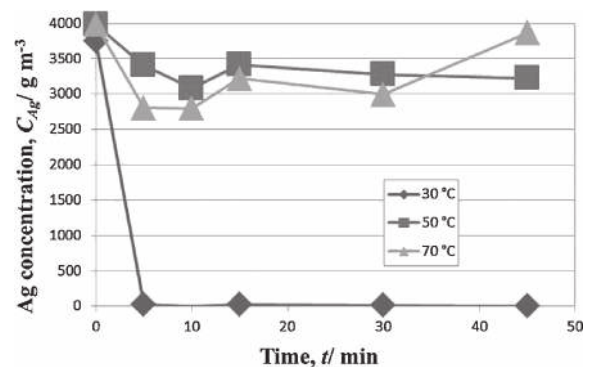


Fig. 12 Effect of temperature on the removal of Ag from the leach solution with 1.25 g of Cu powder.

As shown in Fig. 11, the Ag concentrations first decreased then increased with the addition of 0.75 g and 1.0 g of Cu powder; 0.75 g of Cu is 7 times more than what is required in eq. (8) and was added to the leach solution at 30°C . On the other hand, the Ag concentration decreased and then remained constant, close to zero, with the addition of 1.25 g of Cu powder. Figure 12 shows the effect of temperature on the behavior of Ag during the cementation process with the

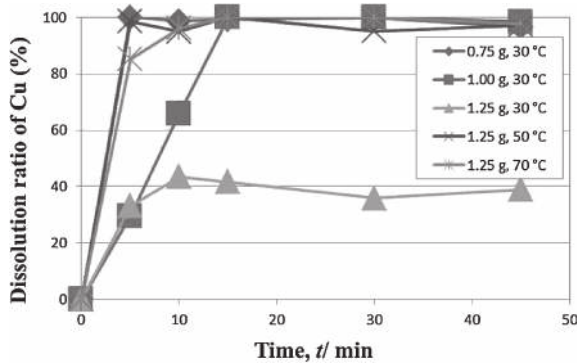


Fig. 13 Removal ratio of Cu in the experiments shown in Figs. 11 and 12.

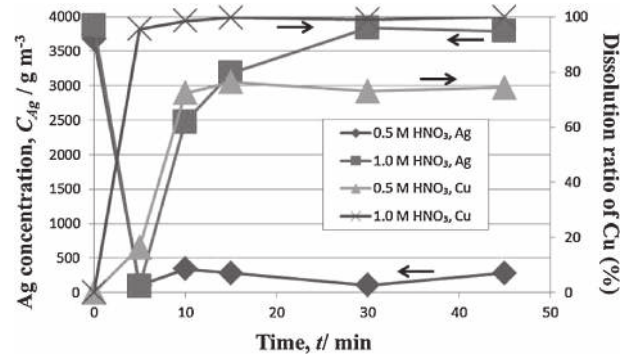


Fig. 15 Behavior of Ag and the removal ratio of Cu in the simulated leach solution with 0.5 or 1.0 kmol·m⁻³ HNO₃ at 30°C.

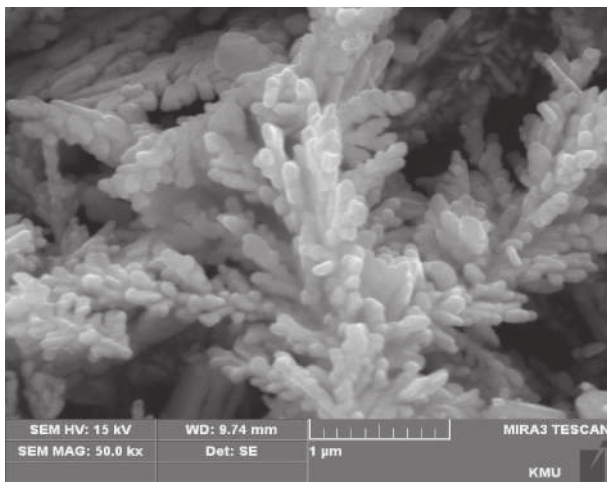


Fig. 14 SEM image of Ag cemented by 1.25 g of Cu powder at 30°C.

addition of 1.25 g of Cu powder. The Ag concentrations decreased slightly at 50 and 70°C, whereas it decreased rapidly and then remained constant (close to zero) at 30°C. These results indicate that Ag ions can be precipitated successfully at 30°C with the addition of 1.25 g of Cu and that the removal ratio of Ag decreased with increasing temperature and decreasing the amount of Cu added. Figure 13 shows the behavior of Cu for the experimental results presented in Figs. 11 and 12. The dissolution percent of Cu increased to 40% at 30°C with the addition of 1.25 g of Cu; it increased rather slowly with the addition of 1.00 g of Cu at the same temperature, compared to that obtained at other experimental conditions. These results have a good correlation with the behavior of Ag removal. The Ag concentration decreased rapidly almost to zero in 5 min, and remained constant for the addition of 1.25 g of Cu at 30°C with 1.25 g. On the other hand, for the addition of 1.00 g of Cu at the same temperature, Ag concentration almost reached zero only at 5 and 10 min (Fig. 11). As seen in Fig. 14, the SEM image of the Ag precipitate cemented by the addition of 1.25 g of Cu powder at 30°C shows dendrite-like growth.

During HNO₃ leaching, NO or NO₂ gases are generated as an end product. Considering the amounts of Sn, Ag and Cu shown in Table 1, 1.07 and 3.09 kmol·m⁻³ of HNO₃ are required for NO [eqs. (1), (3) and (5)] and NO₂ [eqs. (2), (4)

and (6)] gas generation, respectively. Because it is difficult to determine the residual HNO₃ concentration after the reactions in eqs. (1)–(6), the effect of HNO₃ concentration on the behavior of the Ag ion during the cementation process with Cu powder was investigated using a simulated leach solution. The initial concentration of Ag was 3677 g·m⁻³ and the concentrations of HNO₃ used were 0.5 and 1 kmol·m⁻³; 1.0 g of Cu powder was added to 100 cm³ of the simulated leach solution at 30°C. Figure 15 shows the behavior of Ag and the dissolution ratio of Cu for 0.5 and 1.0 kmol·m⁻³ HNO₃. Ag concentration decreased and then increased for 1.0 kmol·m⁻³ HNO₃, whereas it decreased and remained almost constant for 0.5 kmol·m⁻³ HNO₃. The dissolution ratios of Cu increased to approximately 75 and 99% for 0.5 and 1.0 kmol·m⁻³ HNO₃, respectively. These behaviors are in good agreement with the results given in Figs. 12–14. These results suggest that there was no excess HNO₃ available to leach Ag cemented because 0.5 kmol·m⁻³ HNO₃ was not able to oxidize all Cu (leaching efficiency 75%) whereas HNO₃ would still be enough to oxidize the cemented Ag even after almost Cu was dissolved in 1.0 kmol·m⁻³ HNO₃ solution. It is thus reasonable to suggest that the re-dissolution of Ag depends on the residual HNO₃ concentration.

Based on the above results, a recycling process for the waste Pb-free solder is proposed, as shown in Fig. 16. Silver and copper are dissolved by nitric acid leaching and then recovered by precipitation with NaCl or cementation with Cu powder, followed by subsequent electro-winning. Further work is required to recover Sn metal from the stannic oxide present in the leaching residue.

4. Conclusions

The nitric acid leaching process for the treatment of waste lead-free solder, followed by the separation of Ag and Cu, was investigated to recover Sn, Ag and Cu as individual components.

The dissolution of Ag and Cu was independent of agitation speed faster than 200 rpm, but increased with increasing temperature and HNO₃ concentration. The concentration of tin was extremely low in all the nitric acid leaching experiments, and the XRD result indicated that tin precipitates as stannic oxide or stannic acid. The Ag and Cu components were successfully separated from Sn by nitric acid leaching.

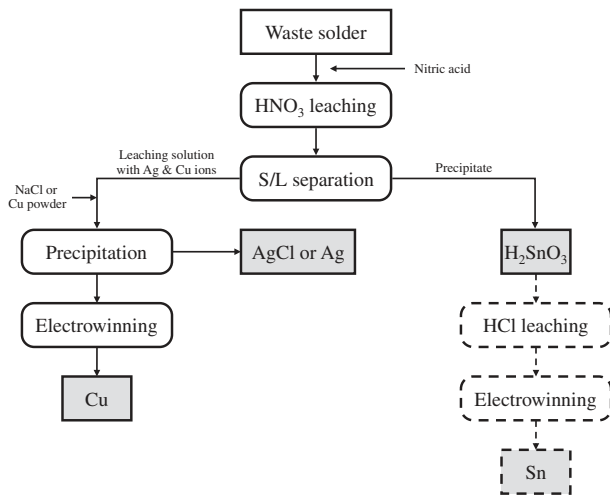


Fig. 16 Schematic diagram of the recycling process of waste Pb-free solder proposed in this study.

To precipitate Ag ions from the leach solution, the additions of NaCl or Cu powder were investigated. The addition of $2 \text{ kg}\cdot\text{m}^{-3}$ of NaCl could remove $3755 \text{ g}\cdot\text{m}^{-3}$ of Ag successfully. In the cementation process with Cu powder, $125 \text{ kg}\cdot\text{m}^{-3}$ of Cu powder precipitated Ag ions at 30°C . The precipitated Ag re-dissolved into the leach solution as temperature increased and the amount of added Cu decreased. The re-dissolution of Ag depended on the concentration of HNO_3 remaining after the nitric acid leaching of waste Pb-free solder. Thus, Ag could be separated successfully from Cu by the addition of NaCl or Cu powder, and Cu could be recovered by electro-winning from the Ag-free solution.

Acknowledgement

The paper is based on the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Knowledge Economy of Korea.

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