The Effect of Oxygen and Hydroxide Ion on Electrochemical Leaching Behavior of Tin

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The dissolution of tin from waste Pb-free solder was electrochemically investigated in NaOH solution. Two oxidation peaks were observed in a cyclic voltammetry test in 1 kmol m⁻³ NaOH solution at less than 45°C, and the peaks indicate the oxidation of tin to Sn²⁺ and Sn²⁺ to Sn⁴⁺, whereas only one peak was observed at 75°C resulting from the direct oxidation of tin to Sn⁴⁺. The increase in NaOH concentration and the introduction of oxygen enhanced the dissolution of tin in NaOH solution with less than 0.5 kmol m⁻³ whereas that of tin decreased with increasing NaOH concentration further to 1.5 kmol m⁻³ and the decrease in the dissolution of tin was accelerated by introducing oxygen. An optimum waste solder alkaline electrolysis process was found to be at more than 75°C and around 0.5 kmol m⁻³ NaOH based on the cyclic voltammetry and constant current experiment. [doi:10.2320/matertrans.M2012311]

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1. Introduction

Waste lead-free solder has been mainly recycled by pyrometallurgical processes such as melting and repowdering. The pyrometallurgy treatment has a good reputation for simplicity and mass treatment, whereas it has disadvantages such as high energy consumption, hazardous gas emission, and difficulty in separating and purifying valuable metals.¹⁾ Therefore, alternative recycling processes using hydrometallurgical methods were required to recycle the waste lead-free solder. However, there have been a few studies on the dissolution behavior of lead-free solder.

Electrolytic methods are useful ways to recover the valuable metals from the waste lead-free solder, and promising routes to investigate the dissolution behaviors of the waste lead-free solder. Main component of lead-free solder is tin and the market share of Sn–Ag–Cu series, which contains 4% Ag and 0.8% Cu, has been found to increase to 70% for reflowing the lead-free solder.²⁾ It is important to understand the leaching behavior of tin for recycling of waste Pb-free solder. There have been many studies for tin dissolution as follows; Bodensteiner proposed a process for selectively leaching tin from a highly concentrated KOH–K₂SnO₆ electrolyte using the anode solution method to dissolve tin.³⁾ Lee *et al.* and Kekesi *et al.* performed fundamental research on the leaching behavior of pure tin in NaOH solution as well as on the leaching of tin using the anode solution method in NaOH solution. They reported the tin leaching efficiency of 91–96% with anode current efficiency of 75–85%.^{4,5)} The dissolution of tin could be expressed as shown in eq. (1).^{4,5)}

The standard Gibb's free energy of eq. (1) is –118.92 kcal/mol; indicating that the reaction is spontaneous process.⁵⁾ As can be seen in eq. (1), oxygen and hydroxide

ion play a great role in the dissolution of tin. The present study is aim to examine the effect of oxygen and hydroxide ion on the dissolution of tin from waste lead-free solder in alkaline NaOH solution over pH 9 using electrochemical approach.

2. Experiments

2.1 Preparation of specimen and electrolyte

Waste lead-free solder was obtained from a recycling company in Korea, and it contained 88–93% Sn, 2% Ag and less than 0.5% Cu. An anode electrode was prepared with the solder as follows; the solder was dry-liquefied for 30 min at 400°C and casted and rolled into a strip with thickness of 1 mm. The strip was then cut into an adequate size and polished with No. 1200 sandpaper. The polished surface was washed with ultrasonic cleaning in alcohol and then masked with a plating masking tape. The exposure surface of the anode electrode was 4 cm². For the cathode, 99.9% titanium with an exposure surface of 30 cm² was used. The electrolyte was prepared using extra pure grade NaOH from Junsei Chemicals and deionized water with a resistivity of 17 MΩ·cm or greater.

2.2 Electrochemical experimental

The cyclic voltammetry test was performed using 500 mL of 0.1 to 1.5 kmol m⁻³ NaOH electrolyte in a water jacket, which was connected to a water bath to maintain temperature (25, 45 and 75°C). The anode electrode, Ag/AgCl electrode and Pt wire, which were used as working, reference counter electrodes, respectively, were equipped in electrolyte cell (K0264 Micro Cell Kit, AMETEK, Inc., USA), and potentiostat/galvanostat (273A, EG&G, USA) were used to perform the cyclic voltammetry test and to control voltage. The potential was increased firstly from the open circuit potential (OCV) to +1.5 V (occasionally +1.9 V), and then decreased in the negative direction to –1.9 V, and finally returned to OCV. The scan rate was varied from 50 to

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Fig. 1 Cyclic voltammetry of the waste lead-free solder as function of solution temperature (1 kmol m⁻³ NaOH, Scan rate; 50 mV s⁻¹).

200 mV s⁻¹. The constant current test was conducted in 0.1 to 1.5 kmol m⁻³ solution at 10 mA cm⁻² and 25 °C for 24 h in order to measure the amount of tin dissolved by examining the difference in weight before and after the test.

In the experiments above, 10 ml min⁻¹ of oxygen was introduced into the reactors to investigate the effect of oxygen on the dissolution of tin.

3. Results and Discussion

The electrolysis behavior of the waste solder in 1 kmol m⁻³ NaOH solution was examined at 25–75 °C, and the results of cyclic voltammetry performed were shown in Fig. 1. Two peaks (Peaks 1 and 2) were observed during the dissolution reaction at 25 and 45 °C, and peaks 1 and 2 represent the oxidation of tin into tin(II) and tin(II) into tin(IV), respectively, as the following equations.

It can be seen that peak 1 and peak 2 decline rapidly around -0.75 and -0.5 V (vs. Ag/AgCl), respectively, and this would be due to an insoluble film of tin such as SnO or Sn(OH)₄ formed on the electrode surface as Shams El-Din reported.⁶⁾ Peak 3 was observed during the dissolution reaction at 75 °C. This suggests that tin was oxidized directly into SnO₃²⁻ without undergoing the oxidation reaction into SnO in eq. (2) as the following equation.⁶⁾

Peak 4, where current is increasing dramatically to around 1.7 V (vs Ag/AgCl), represents electrolysis of water, and peak 5 indicates the reduction reaction of the tin dissolved through the anodic reaction showed in peak 1–3. Peak 6 shows the evolution reaction of hydrogen.

Figure 2 presents the result of cyclic voltammetry performed in 0.1, 0.5 and 1.0 kmol m⁻³ NaOH solution at 200 mV s⁻¹ scan rate. As shown in Fig. 2, only one peak was observed between -1 to 0 V at 0.1 to 1.0 kmol m⁻³ NaOH concentration and 200 mV s⁻¹ scan rate. This result would be due to the direct oxidation of Sn into SnO₃²⁻ without undergoing the oxidation reaction into SnO with increasing scan rate from 50 to 200 mV s⁻¹. The oxidation current generated from the dissolution of the waste solder increased with increasing NaOH concentration from 0.1 to 0.5 kmol m⁻³, but it decreased with increasing NaOH

Fig. 2 Cyclic voltammetry of the waste lead-free solder as function of NaOH concentration (25 °C, Scan rate; 200 mV s⁻¹).

Fig. 3 Cyclic voltammetry of the waste lead-free solder with and without introducing oxygen. (a) NaOH 0.1 kmol m⁻³, (b) NaOH 0.5 kmol m⁻³, (c) NaOH 1.0 kmol m⁻³.

concentration further to 1.0 kmol m⁻³. The effect of oxygen introduction on the dissolution of tin was investigated with cyclic voltammetry test in the 0.1, 0.5 and 1.0 kmol m⁻³ NaOH solution. As can be seen Fig. 3, cyclic voltammetry

Fig. 4 Anodic dissolution amount of the waste lead-free solder with and without introducing oxygen (24 h, 25°C, 10 mA cm⁻²).

data indicate that the amount of anodic current is greater in 0.1 and 0.5 kmol m⁻³ NaOH solutions with introducing oxygen than without injecting oxygen, whereas, in 1 kmol m⁻³ NaOH solution, the introduction of oxygen decreased the amount of anodic current.

Constant current tests were performed to examine the amount of anodic dissolution in 0.1 to 1.5 kmol m⁻³ NaOH solution with and without oxygen introduction for 24 h. The constant current was adjusted to 10 mA cm⁻² because 10 mA cm⁻² in the current has used for electro-refining process of tin in Korea. As can be seen in Fig. 4, the increase in NaOH concentration over 0.5 kmol m⁻³ decreased the dissolution of tin, and the introduction of oxygen accelerated the decrease in the dissolution of tin in 1.0 and 1.5 kmol m⁻³ NaOH solutions. As can be seen in eq. (1), it could be expected that the increase in NaOH concentration and the introduction of oxygen accelerate the dissolution of tin. On the contrary in the solution with over 0.5 kmol m⁻³ NaOH, dissolution rate of tin decreased with increasing NaOH concentration and injecting oxygen. Although further study will be required to examine the negative effect of oxygen and hydroxide ion over 0.5 kmol m⁻³ NaOH solution, the dissolution of tin for the recycling of waste lead-free solder is found to be

favorable in 0.5 kmol m⁻³ NaOH solution with oxygen introduction.

4. Conclusions

The dissolution of tin in 1 kmol m⁻³ NaOH was investigated electrochemically to recover tin from waste lead-free solder. Two oxidation peaks were observed in the cyclic voltammetry test at less than 50°C, and this result indicates that the oxidation of tin consists of tin to Sn²⁺ and Sn²⁺ to Sn⁴⁺, whereas only one peak was observed at 75°C resulting from direct oxidation of tin to Sn⁴⁺.

The dissolution of tin increased with increasing NaOH concentration to 0.5 kmol m⁻³ and the introduction of oxygen enhanced the dissolution of tin in less than 0.5 kmol m⁻³ NaOH solution, whereas it decreased with increasing further NaOH concentration and the introduction of oxygen accelerated the decrease in tin dissolution. Based on cyclic voltammetry and constant current experiment, an optimum waste solder alkaline electrolysis process was found to be at more than 75°C and around 0.5 kmol m⁻³ NaOH.

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