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Leaching of tin from waste Pb-free solder in hydrochloric acid solution with stannic chloride

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ABSTRACT

A hydrochloric acid (HCl) leaching process with stannic chloride ($SnCl_4$) was proposed to leach Sn from waste Pb-free solder containing Sn, Ag, and Cu, where the oxidant stannic ion (Sn^{4+}) oxidizes Sn metal into stannous ion (Sn^{2+}). When Sn reagent-grade powder was leached in HCl solution with $SnCl_4$, the leaching efficiency of Sn increased rapidly and the oxidation-reduction potential decreased with leaching time. In the leaching tests of Pb-free solder, the effect of factors such as the agitation speed, HCl concentration, pulp density, and temperature on the leaching behaviors of metals was investigated. The leaching efficiencies of Sn increased rapidly in the beginning of leaching with increasing agitation speed, HCl concentration, and temperature. The difference in the leaching efficiencies was negligible after 90 min under the following conditions: HCl concentration of 1–3 kmol m^{-3}, agitation speed of 300–600 rpm, and temperature of 50 °C or 70 °C. Although the pulp density was increased from 1% to 2%, the Sn concentration dissolved did not exceed 10,500 g m^{-3} because of the lack of oxidant, and the increase in the initial concentration of Sn^{4+} as the oxidant could accelerate the leaching of Sn. A Sn leaching efficiency of greater than 99% was achieved in 1 kmol m^{-3} HCl with 10,000 g m^{-3} Sn^{4+} at 400 rpm and 50 °C with 1% pulp density within 90 min. Ag was not detected in any of the leaching tests. Although the leaching solution contained 24.5 g m^{-3} of Cu, the addition of Sn powder was successful in removing Cu from the solution via a cementation reaction. Thus, a Sn leaching solution was successfully obtained from Pb-free solder via HCl leaching with $SnCl_4$.

1. Introduction

Lead–tin (Pb–Sn) solder is known for its outstanding solderability and reliability as an interconnecting material in electronic packaging (Ma and Suhling, 2009; Pan et al., 2005). However, the use of Pb has been strictly restricted because of its toxicity (Marino et al., 1997; Tsunekawa et al., 2008); thus, various Pb-free solder series have been developed using Sn, Ag, Cu, Bi, Sb, and Zn (Ma and Suhling, 2009). The market share of Sn–Ag–Cu series increased to approximately 70% for reflowing Pb-free solder (Ma and Suhling, 2009; Pan et al., 2005; Turbini et al., 2001). There are increasing demands for recycling processes of waste Pb-free solder.

Tin and lead are known for their low melting points; thus, simple melting processes can be used to reuse the waste solder as recycled solder (Yoo et al., 2012). However, there are concerns regarding the hazardous gas emission resulting from the incineration of the resin or organic flux in the solder. Furthermore, valuable metals, generally, could be recovered as alloys in pyrometallurgical processes. Hydrometallurgical methods have been recognized as alternative processes for the recycling of waste Pb-free solder.

Rhee et al. (1994) and Kim et al. (2012) reported the dissolution behavior of Sn under basic conditions to recover Sn from Pb frame scrap (Rhee et al., 1994) and waste Pb-free solder (Kim et al., 2012). A few studies have also been performed on the recycling of waste Pb-free solder under acidic conditions. Yoo et al. (2012) and Mecucci and Scott (2002) investigated nitric-acid leaching to recover valuable metals from waste Pb-free solder (Yoo et al., 2012) and printed circuit boards (Mecucci and Scott, 2002); however, these methods could result in NOx emissions. Kim et al. (2014) reported the separation of Sn, Ag, and Cu from Pb-free solder using hydrochloric acid (HCl) leaching with hydrogen peroxide. Hydrogen peroxide is relatively unstable (Antonijevic et al., 1997; Barik et al., 2012); thus, it is difficult to manage the recycling process.

In the present study, a new recycling process for Pb-free solder is proposed using HCl and stannic chloride ($SnCl_4$), where Sn^{4+} was used as an oxidant and the process was not reported. The leaching behaviors of Sn, Ag, and Cu were investigated during the HCl leaching. The effects of parameters such as the agitation speed, HCl concentration, pulp density, and leaching temperature on the leaching efficiencies were examined. In addition, the precipitation of Cu resulting from the

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addition of Sn powder was investigated to separate Cu and Sn from the HCl leaching solution.

2. Experimental

2.1. Materials

The waste Sn–Ag–Cu series Pb-free solder powders were obtained from a recycling company in Korea; they were generated from the fabricating processes of printed circuit boards for electronic home appliances. The waste solder was ground and dry-sieved using a 150-μm (100-mesh) sieve to remove trash, and the remaining solder contained 90.2% Sn, 4.11% Ag, and 0.65% Cu as its main components as well as 0.022% Bi and 0.021% Pb as minor components; no other metals were detected. All the chemicals used in this study were of reagent grade.

2.2. Leaching procedures

The leaching tests of the waste Pb-free solder were performed in a 500-dm^3 three-necked Pyrex glass reactor using a heating mantle to maintain the temperature. The reactor was fitted with a reflux condenser and an agitator. 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 (0.5–3 kmol m^{-3} HCl) with 10,000 or 15,000 g m^{-3} Sn^{4+} was poured into the reactor and allowed to reach thermal equilibrium (30–70 °C) with an agitation speed of 200–600 rpm. Before the leaching tests began, nitrogen gas was introduced for 1 h to reject air and continuously during the tests, and 2 g Sn powder (200 mesh, Junsei Chemical Co. Ltd.) or the solder powder was added to the reactor in all the experiments except for the pulp density test. During the experiment, 3 cm^3 of the solution was withdrawn periodically at a desired time interval (15–120 min) with a syringe. The sample was filtered using a 0.45-μm membrane filter, and then, the filtrate was diluted with 5% HNO_3 solution for Cu and Ag analyses and with 15% HCl solution for Sn analysis.

2.3. Separation test of Cu and Sn

The separation tests for Cu and Sn were performed by adding the Sn powder. The leaching liquor was obtained under the following leaching conditions: 400 rpm agitation speed, 1 kmol m^{-3} HCl concentration, 10,000 g m^{-3} Sn^{4+}, 70 °C temperature, and 1% pulp density. The separation tests were conducted in a 250-cm^3 Pyrex reactor, which was equipped with a water jacket for temperature control. Sn powder (0.25 g) was added to 100 cm^3 of the leaching solution at 400 rpm and 30 °C, and nitrogen gas was introduced. To measure the concentrations of Cu, 2 cm^3 of solution was sampled with a syringe and was prepared for analysis following the same procedure described in Section 2.2.

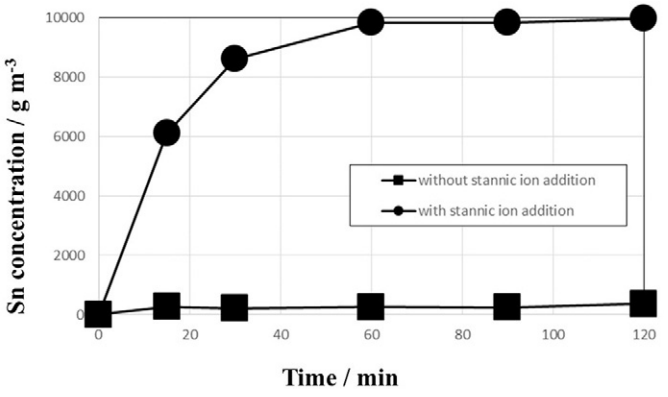

Fig. 1. The effect of $SnCl_4$ addition on the dissolution of Sn powder in 1 kmol m^{-3} HCl with and without 10,000 g m^{-3} Sn^{4+} at 50 °C and 400 rpm with 1% pulp density.

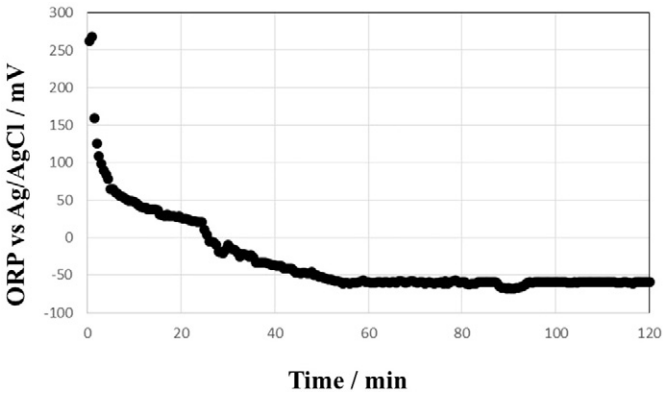

Fig. 2. ORP (vs. Ag/AgCl) variation during Sn powder dissolution in 1 kmol m^{-3} HCl with 10,000 g m^{-3} Sn^{4+} at 50 °C and 400 rpm with 1% pulp density.

2.4. Analytical methods

The oxidation-reduction potential (ORP) (vs. Ag/AgCl) was measured during Sn reagent-grade powder leaching test using an ORP meter (Orion 3 star plus pH meter, Thermo Fisher Scientific Inc.). The sample solutions were analyzed using atomic absorption spectrometry (AA7000, Shimadzu Co. Ltd.) and inductively coupled plasma-atomic emission spectrometry (ICP-AES, JY-38 Plus, Jobin Yvon Ltd.).

3. Results and discussion

In general, for leaching processes of metals from e-wastes, oxidants are required to dissolve metals into metal ions. In previously reported leaching procedures for waste Pb-free solder (Yoo et al., 2012; Kim et al., 2014), HNO_3 and H_2O_2 were used to oxidize Sn, Ag, and Cu in the waste Pb-free solder; however, there are disadvantages such as the emission of NOx gas or self-decomposition of H_2O_2. In this study, stannic chloride ($SnCl_4$) was proposed as a new oxidant for Sn metal oxidation, and to investigate the effect of $SnCl_4$ addition on the leaching efficiencies of Sn, leaching tests of Sn reagent-grade powder were performed in 1 kmol m^{-3} HCl with and without 10,000 g m^{-3} Sn^{4+} at 50 °C and 400 rpm with 1% pulp density.

As illustrated in Fig. 1, the Sn concentration remained low in the leaching solution without $SnCl_4$, whereas the leaching efficiency of Sn with the addition of $SnCl_4$ addition increased rapidly and then gradually to more than 99% within 60 min. Fig. 2 presents the ORP results measured during the leaching test with 10,000 g m^{-3} Sn^{4+}. The ORP

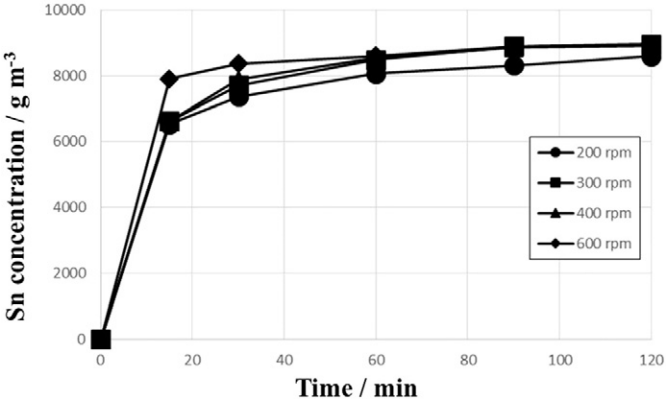

Fig. 3. The effect of the agitation speed on the dissolution of Sn from Pb-free solder in 1 kmol m^{-3} HCl with 10,000 g m^{-3} Sn^{4+} at 50 °C and 200–600 rpm with 1% pulp density.