A High Temperature Process for Extracting Valuable Metals from Waste Electric and Electronic Scraps (WEES)

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In the view points of resource recycling and environment protection it is necessary to extract the valuable metals from waste electric and electronic scraps (WEES) which contain considerable amounts of valuable metals such as copper, tin, gold, and silver. In present work, a novel process to extract valuable metals such as copper and tin from WEES by smelting with the addition of waste copper slag as a slag formative has been developed. The process uses only waste copper slag without using any additional flux components as slag formatives. In each set of experiment, crushed WEES were melted with waste copper slag for 30 min at 1623 K in air atmosphere. Based on proposed process flow-sheet, up to 90% of copper and 80% of tin contained in the raw materials were extracted as a Cu-Fe-Sn alloy phase at the input ratio of 50 : 50 of WEES and waste copper slag. [doi:10.2320/matertrans.M2009062]

Keywords: waste electric and electronic scraps (WEES), waste copper slag, copper, tin, recycling

1. Introduction

More than half million tons of waste electric and electronic scraps (WEES) per year have been generated in Korea, which contains considerable amounts of valuable metals such as copper, tin, gold, and silver as well as large amount of plastics. Specially, it has been reported that the WEES generated from waste computers contains the precious metals 700 – 1,100 ppm.¹–⁵) Therefore, many processes have been developed to extract the valuable metals from WEES in the viewpoint of resource recycling and environment protection. A number of processes for extracting valuable metals from the solid wastes have been investigated. The developed processes are broadly classified into hydrometallurgical and pyrometallurgical processes.²–⁹) In the hydrometallurgical process, the valuable metals contained in WEES is first leached into acid or alkali solutions, and then concentrated by using various methods like precipitation, cementation, and solvent extraction.⁵,⁸) In the pyrometallurgical process, WEES is melted with several flux components as slag formatives. The molten WEES containing valuable metals contacts with a molten metal pool into which the valuable metals dissolve and accumulate. The molten metal is called as collector metal. Commonly used collector metals include iron, copper, nickel, lead-copper and nickel matte.⁵,⁸) And then, the extracted valuable metals must be further treated in order to separate and purify them. Among the above processes, the pyrometallurgical process is effective for extracting valuable metals from WEES in large-scale treatment. However, the pyrometallurgical process needs large amount of additional flux components as slag formatives to easily melt the WEES. Large amount of waste slag were thus generated from conventional pyrometallurgical processes because it only uses waste copper slag as a slag formative. In this study, laboratory scale studies were carried out to see the feasibility of the novel pyrometallurgical process.

2. Experimental Procedure

2.1 Choice of the slag system

To estimate the melting temperature of the WEES used in this work, the chemical composition was investigated through previously reported data.⁶,⁹,¹⁰) The isothermal liquidus line of the ternary slag system consisting of three main slag components contained in the WEES is shown in Fig. 1. The dot in the figure represents the weight-percent composition based on the total mass of just the three main slag-forming oxides contained in the WEES used in this study. The complete composition of the WEES will be presented subsequently in this paper. So, it was expected that the melting temperatures of the WEES used in this work would be over 1673 K. That means a lot of energy might be necessary to dissolve and extract the valuable metals contained in the WEES into a molten alloy phase. Thus, suitable fluxes are needed to lower their melting temperatures. However, the additional amounts of fluxes must be as small as possible because it is undesirable to generate large amounts of waste slag that requires disposal.

With this in mind, an FeO-CaO-SiO₂ slag system was chosen to extract valuable metals such as copper and tin from WEES by smelting with adding only waste copper slag as a slag formative because the waste copper slag contains large amounts of slag formatives such as Al₂O₃, CaO, FeO and SiO₂ as shown in Table 1 later. Currently, large amount of the waste copper slag has been discarded from the slag cleaning furnace of copper smelting furnace. It is thus desirable to reuse the waste copper slag in the viewpoint of resource recycling. Figure 2 represents isothermal line of FeO-CaO-SiO₂ slag system at 1573 K. Also, displayed in this figure is the target slag composition region that will be used to calculate the input ratio of WEES and waste copper slag in the reduction smelting step.

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2.2 Experimental procedure

Smelting experiments were carried out using a box type furnace (having SiC heating elements) under air atmosphere. The temperature was measured by a Pt-13 pct Rh/Pt thermocouple. A uniform temperature profile of \(250^\circ C\) was achieved over the input material. Figure 3 shows the schematic diagram of experimental apparatus used in this study.

The WEES used in the study were first crushed under 5 cm to insert easily into a melting crucible before doing the reduction smelting, followed by the addition of waste copper slag. The addition amounts of waste copper slag used for experimental purpose were calculated by considering the chemical compositions of FeO, CaO, and SiO\(_2\) contained in the WEES to achieve the suitable slag composition region shown in Fig. 2. The reduction agents such as coal and coke were not added because the WEES contains considerable amount of plastic which can be used to maintain the reduction atmosphere of furnace during the smelting. In general, it is reported that WEES contains about 19% plastics even if the content varies with the function and age of the appliance as well as the design chosen. However, the content of plastics contained in the WEES used in the study was not verified. In the study, the mixing ratios of WEES and waste copper slag were 40 : 60 and 50 : 50. Since the amount of product alloy decreases as the addition of waste copper slag increases, a mixing ratio beyond 40 : 60 was not investigated. About 100 g of the solid wastes was used for each run. The mixture was charged in an alumina crucible (10 cm height and 7 cm inner diameter), and fed to the reactor in the furnace. The reduction smelting started at 1623 K and lasted 30 min. During the experiments, it was not possible to avoid partial erosion of the crucible.

Materials used in the study were the WEES of waste computers and waste copper slag of copper smelter generated in Korea. The waste copper slag is discarded from the slag cleaning furnace of Mitsubishi copper smelter at LS-Nikko copper smelter INC. in Korea. Table 1 presents the average chemical compositions of the WEES and waste copper slag used in this work. The WEES contains about 18% Cu and 2% Sn, and the waste copper slag mainly contains FeO, SiO\(_2\), Al\(_2\)O\(_3\), and CaO components and less than 1% for copper.

Samples before and after the smelting reaction were analyzed for Cu, Sn, Al, Ca, and Mg by the inductively coupled plasma (ICP) method (JY-38 Plus, Jobin-Yvon Equipment Co., London, UK). Also, the total iron and divalent iron contents in the slag specimens were determined by titration with K\(_2\)Cr\(_2\)O\(_7\), the SiO\(_2\) content by a gravimetric analysis method.

In the present study, the extraction ratios of copper and tin were defined as:

![Fig. 1 The 1673 K isothermal line in the SiO\(_2\)-CaO-Al\(_2\)O\(_3\) slag system used to predict the melting temperature of the used WEES (mass%). (The dot represents the mass% composition based on the total mass of just the three main slag-forming oxides contained in the used WEES [Table 1].)](image1)

![Fig. 2 The 1573 K isothermal line of FeO-CaO-SiO\(_2\) slag system (mass%). (Circle represents the target composition region that will be used to calculate the input ratio of WEES and waste copper slag in the reduction smelting step.)](image2)

![Fig. 3 Schematic diagram of experimental apparatus used in this study.](image3)

![Table 1 Average compositions of waste electric and electrical scrap (WEES) and waste copper slag (WCS) used in the study (mass%).](image4)
where, $E_M$ is the extraction ratio of M metal, $A_M$ is the weight (g) of M metal concentrated into the molten metal phase (alloy phase), and $S_M$ is the weight (g) of M metal remained in the slag phase.

3. Results and Discussion

In the smelting experiment, the input material started melting at around 1523 K 10 min., after it was inserted in the furnace. The experiment lasted about 30 min., after which the molten product was cooled in air. Generally, WEES in the smelting is divided into three phases: gas, slag, and alloy phases. Figure 4 shows the average mass distribution of the input WEES among three phases. The mass distribution was calculated by weighing the slag and alloy phases obtained after the reduction smelting and measuring the weight change before and after the reduction smelting. The figure indicates that the WEES is divided to the alloy phase of 19.9%, the slag phase of 45.0%, and the gas phase of 35.2% for the mixing ratio of 40 : 60 (WEES : waste copper slag) and the alloy phase of 25.4%, the slag phase of 39.7%, and the gas phase of 34.9% for the mixing ratio of 50 : 50 (WEES : waste copper slag), by weight. Here, the gas phase may contain many chemicals such as Zn, Cl, Sb, As, etc. Table 2 presents the chemical compositions of the slags obtained from the charge materials. As shown in the table, the slag compositions are a little different with the target slag composition region displayed in Fig. 2. That might be the reason why the composition variation of the WEES and waste copper slag is relatively large. Based on the slag compositions shown in Table 2, the separation of the molten phase into slag and alloy phases was expected to be somewhat difficult because of the viscosity of the slag. Although it was not measured in this study, the viscosity of the slag was estimated to be <30 poise at around 1673 K based on previously reported data. However, all the molten phases obtained in this work were easily separated into slag and alloy phases. This may be due to the fact that the wettability between the slag and alloy phases is low. Table 3 presents the mass and chemical compositions of the alloy phases obtained from the experiments. As shown in Table 3, the alloy phase was mainly composed of copper, tin and iron. Here, most iron in the alloy phase might be reduced from the waste copper slag which contains considerable iron oxide compounds. The average weight of the alloy obtained was about 7.9 g for the mixing ratio of 40 : 60 (WEES : waste copper slag) and 12.7 g for the mixing ratio of 50 : 50 (WEES : waste copper slag). Figure 5 shows the average extraction percentages of copper and tin. It is shown in the figure that the extraction percentage of copper is higher than that of tin for all the mixing ratios of WEES and waste copper slag. The average obtained extraction percentages were >85% for copper and >75% for tin for the mixing ratio of 40 : 60 (WEES : waste copper slag) and >90% for copper and >80% for the mixing ratio of 50 : 50 (WEES : waste copper slag). The reason why the extraction percentage of copper is high compared that of tin might be due to the difference of the affinity with oxygen for copper and tin as shown in Fig. 6. Figure 6 represents the predominance phase diagram of Cu-Sn-O system. Here, circle indicates the

![Fig. 4 Average mass distribution of the charge materials among three product phases (alloy, slag, and gas phases).](image-url)

### Table 2 Chemical compositions of slags obtained from the charge materials.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$A_2O_3$</th>
<th>CaO</th>
<th>$T_1Fe$</th>
<th>$Fe^{2+}$</th>
<th>$Fe^{3+}$</th>
<th>MgO</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 A2 A3 A4 A5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1 B2 B3 B4 B5</td>
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<th>Input ratio</th>
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<th>$T_1Fe$</th>
<th>$Fe^{2+}$</th>
<th>$Fe^{3+}$</th>
<th>MgO</th>
<th>SiO$_2$</th>
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<td>40 : 60</td>
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<td>8.85</td>
<td>6.42</td>
<td>28.97</td>
<td>21.65</td>
<td>7.32</td>
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<td>37.77</td>
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<td>8.27</td>
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<td></td>
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<td>13.76</td>
<td>23.67</td>
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<td>13.45</td>
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<td>7.55</td>
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</table>

*WCS = waste copper slag
- The balance consists of small amount of other oxides and unoxidized metals.
oxygen potential region in the slag phase under the experimental conditions. The oxygen potentials in the slag phase were calculated by eq. (4) through assaying Fe$^{2+}$ and Fe$^{3+}$ concentrations in the slag phase. Equation (4) was obtained as follows:

Reaction (2) is an equilibrium reaction between FeO and FeO$_{1\frac{1}{2}}$ in a slag phase, and eq. (3) is the standard Gibbs free energy of reaction (2).

$$4(\text{FeO})_{\text{slag}} + \text{O}_2(g) = 4(\text{FeO}_{1\frac{1}{2}})_{\text{slag}}$$

$$\Delta G^{\circ} = -507,300 + 212.0T \ (J/mol)$$

$$= -RT \ln(\alpha_{\text{FeO}_{1\frac{1}{2}}} / \alpha_{\text{FeO}} \cdot P_{\text{O}_2})$$

Here, $\alpha_{\text{FeO}}$ and $\alpha_{\text{FeO}_{1\frac{1}{2}}}$ are the activities of FeO and FeO$_{1\frac{1}{2}}$. So, eq. (4) could be induced from eq. (3) when the activity coefficients of FeO$_{1\frac{1}{2}}$ and FeO in a slag phase are assumed to be equal in a certain temperature range.

$$\ln P_{\text{O}_2} \ (\text{in slag bath}) = \frac{\Delta G^\circ}{RT} + 4 \ln \left(\frac{\text{mass\% of Fe}^{3+} \text{ in slag}}{\text{mass\% of Fe}^{2+} \text{ in slag}}\right)$$

Thus, the oxygen potential in the slag phase can be calculated by using eq. (4) and Fe$^{2+}$ and Fe$^{3+}$ concentrations in the slag phase as shown in Table 3. The oxygen potential was calculated at $1.9 \times 10^{-6} - 1.3 \times 10^{-2}$ atm. Regarding Fig. 6, the affinity with oxygen for tin is higher than that for copper. Therefore, it was considered that the extraction percentage of copper obtained is found higher than that of tin.

Based on the above studies, a novel pyrometallurgical process for extracting copper and tin from WEES by utilizing waste copper slag as a slag formative has been suggested and presented in Fig. 7. In the proposed process, the extracted copper and tin metals must be further treated to separate and purify them individually. The process uses only waste copper slag as a slag formative. Therefore, the proposed process is simple and economical when compared with conventional processes, and has additional benefits of reusing waste copper slag and reducing the generation amount of waste slag.
4. Conclusions

A pyrometallurgical study to develop a process for the extraction of copper and tin from waste electric and electronic scraps (WEES) by utilizing waste copper slag as a slag formative was carried out. Based on the experimental results, a novel process flow-sheet was proposed. In the smelting process, WEES was found to be divided into three phases: the alloy phase of 26%, the slag phase of 40%, and the gas phase of 34%, by weight. Up to 90% of copper and 80% of tin contained in the WEES were also extracted as a Cu-Fe-Sn alloy phase at the input ratio of 50 : 50 of WEES and waste copper slag by the proposed process. The proposed pyrometallurgical process uses only waste copper slag as a slag formative. Therefore, the process is simple and economical compared with conventional processes.

Acknowledgement

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REFERENCES