Copper slag is a by-product obtained during smelting and refining of copper. Copper smelting slag typically contains about 1 wt.% copper and 40 wt.% iron depending upon the initial ore quality and the furnace type. Main components of copper slag are iron oxide and silica. These exist in copper slag mainly in the form of fayalite (2FeO·SiO₂). This study was intended to recover pig iron from the copper smelting slag by reduction smelting method. At the reaction temperature of below 1400°C the whole copper smelting slag was not smelted, and some agglomerated, showing a mass in a sponge form. The recovery behavior of pig iron from copper smelting slag increases with increasing smelting temperature and duration. The recovery rate of pig iron varied greatly depending on the reaction temperature.

Keywords: copper slag, reduction, pig iron, fayalite, recovery

1. Introduction

Today, under the rapid technical and technological developments all production and services have been automatized, leading to annual growth in metal copper consumption. For example, in Korea, production of conductive copper products has reached approximately to 700,000 tons in recent years. In cooper industry, cooper products are produced from natural and secondary raw materials. During the processing, pure cooper and much copper slag is produced. 2.2 to 3 tons of copper slag is generated per ton of copper production and 1.5 million tons of copper slag is generated in Korea every year [1-3].

Dumping or disposal of copper slag causes wastage of metal values and leads to environmental problems. In particular, the dumping requires wide area and leads to many negative impacts such eroding and damaging land surface, solid and gas substances polluting the atmosphere [4]. Therefore, scientists all over the world had paid special attention to recycle the copper slag and developed several technologies. The common management options for copper slag are recycling of production of value added products such as abrasive tools, roofing granules, cutting tools, abrasive, tiles, glass, road-base construction, railroad ballast, asphalt pavements etc. But, these methods can’t efficiently recover high content of iron and valuable metal in copper smelting slag.

Copper slag differs by chemical composition and structure, depending on the type of processing. Copper smelting slag typically contains about 1 wt.% copper and 40 wt.% iron depending upon the initial ore quality and the furnace type. Significant amounts of silica and minor amounts of other elements (e.g., zinc, titanium, lead and arsenic) are also associated with copper slag [5]. Elements have oxidized form and little amount of sulphide are contained in the copper slag. Slag elements are in oxide form and some sulphides may also present in the slag phase. Main components of copper slag are iron oxide and SiO₂, these exist in copper slag mainly in the form of fayalite (2FeO·SiO₂). The molten copper slag is managed near the smelter site. It is quenched with water resulting in a glassy, granulated, amorphous material [5].

The processing technologies are different depending on the metals to be recovered from copper slag. Magnetic separation and reduction smelting method are used to recover and separate the iron from copper slag. Magnetic separation is not efficient due to its difficult method of fayalite. But, reduction smelting method requires a large amount of energy. It is possible to recover the pig iron with low content of copper from copper smelting slag with high content of iron by a high-temperature reduction method. Copper is contained in casting iron, it improves nature of carbon graphitization, fluidity of cast iron, hardness and strength of casting iron [7].

The recovering of pig iron from copper smelting slag for any fabrication and manufacturing process purposes, will be more economical and completely recycled. Therefore, this study was conducted to manufacture the foundry pig iron from copper smelting slag by using the high temperature reduction method.

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2. Experimental method

2.1. Experimental material

In this study, the waste copper slag from G Company was used. The slag used in this study is a cooling slag, which has undergone water granulation process. The slag has irregular fine irregularities of 1 to 3 mm with a black glassy luster. Fig. 1 shows the XRD analysis results of the copper smelting slag used in this experiment. In the copper smelting slag, peaks of peculiar to amorphous phase of glass were observed.

X-Ray fluorescence analysis and X-Ray diffraction were used to analyse the components of the copper smelting slag. In addition, X-ray fluorescence analysis and energy dispersive spectroscopy were used to analyse the components of the samples obtained from the experiment. Table 1 is an analytical table of the chemical composition of the waste copper slag from G company used in this study. As shown in Table 1, Fe₂O₃ is about 40 wt.%, SiO₂ is about 21 wt.%, CaO is about 16 wt.%, and Al₂O₃ is about 7 wt.%. 

2.2. Experimental apparatus

Reduction smelting experiments were performed in high-frequency induction furnace. The high frequency induction furnace consists of cooler, controller and heater box. The installation space was small and the additional equipment such

![Fig. 1. XRD patterns (a) and SEM-EDS results (b) of the particle of the initial copper slag](image)

**TABLE 1**

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>ZnO</th>
<th>MgO</th>
<th>CuO</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>K₂O</th>
<th>Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, wt.%</td>
<td>38.51</td>
<td>21.17</td>
<td>16.25</td>
<td>7.75</td>
<td>6.27</td>
<td>2.61</td>
<td>2.09</td>
<td>1.34</td>
<td>1.11</td>
<td>1.02</td>
<td>0.72</td>
<td>0.58</td>
<td>0.58</td>
</tr>
</tbody>
</table>

![Fig. 2. Schematic diagram of experimental apparatus](image)
as dust collector was miniaturized to reduce the difficulty and cost of the process. The entire controller of the high frequency induction melting furnace controls the heating temperature of the high frequency induction melting furnace by regulating the voltage. Fig. 2 is a schematic diagram of heater box where high frequency induction is generated. It provides enclosed equipment, eliminates dust and fume gas from the furnace and argon gas was charged into the heater box to maintain an inert atmosphere. A carbon crucible was placed inside heater box and the temperature was measured using a thermocouple.

2.3. Experimental procedure

In the experimental process, the copper slag with irregular fine irregularities of 1 mm to 3 mm and reducing agent activated carbon were mixed with the sample at the ratio of 9 g per 100 g, and then charged into the carbon crucible. Experiment was heated up to necessary temperature for 20 minutes and reduction smelting process was fixed for 30 minutes. Experimental media was Ar gas atmosphere to blow with pressure of 300 cc/min.

In experiment, when copper slag was smelted at the high temperature, Fe₂O₃, CuO and some oxides were reduced, formed to metal phase and molten pig iron is generated. Unreduced oxides such as SiO₂, CaO and Al₂O₃ etc., formed the secondary slag and the slag with a relatively specific gravity floats on the molten pig iron.

The copper slag mainly consists of fayalite and melts at lower temperature of approximately 1200°C. But, the secondary slag consists of eutectic compound of CaO-SiO₂-Al₂O₃ with a large amount of SiO₂ and some of CaO and Al₂O₃. Therefore, the experiment was conducted within range of 1300 to 1600°C temperature, with high recovery and separation of molten pig iron and secondary slag.

3. Results and discussion

In the reduction smelting process of copper smelting slag, direct reduction with solid carbon and indirect reduction with CO gas are observed. In reduction process, solid carbon converts to CO gas by the following reaction at temperatures above 900°C [8].

\[
\begin{align*}
C + O₂ & = CO₂ \\
C + CO₂ & = 2CO \\
2C + O₂ & = 2CO
\end{align*}
\]

Blowing argon gas of 300 cc/min into furnace forms atmosphere with deficiency of oxygen and unavailability of oxidation. As a result of 1 and 2 reactions of carbon oxidation, atmosphere of furnace changes to reducing atmosphere of CO gas. At this atmosphere, iron oxide can be fully reduced within temperature range of 1300 to 1600°C as shown in diagram of the equilibrium of the systems Fe-O-CO in Fig. 3.

Copper smelting slag that was used in this study contains 16 wt.% CaO. Thus, it was considered that slag consists of Fe₂SiO₄ (fayalite), Ca₂SiO₄ (calcium orthosilicate) and CaFeSiO₄ and Fe₂O₃ [9]. In reduction smelting process, iron oxide is reduced from fayalite decomposition by the following reaction.

\[
\begin{align*}
\text{Fe₂SiO₄} + CO & = 2\text{Fe} + \text{SiO₂} + CO₂ \\
\text{FeO} + CO & = \text{Fe} + 2\text{CO₂} \\
\text{Fe₂SiO₄} + 2\text{C} & = 2\text{Fe} + \text{SiO₂} + 2\text{CO} \\
\text{FeO} + \text{C} & = \text{Fe} + \text{CO}
\end{align*}
\]

CaO in the slag supports the decomposition of fayalite and impacts on reduction of iron oxide. Copper oxide is easily reduced in reduction process.

\[
\begin{align*}
\text{Fe₂SiO₄} + 2\text{CaO} + 2\text{C} & = \text{Ca₂SiO₄} + 2\text{Fe} + 2\text{CO} \\
\text{CuO} + CO & = 2\text{Cu} + \text{CO₂} \\
2\text{CuO} + \text{C} & = 4\text{Cu} + \text{CO₂}
\end{align*}
\]

Reduction behavior of iron oxide to be reduced from fayalite decomposition was examined by thermodynamic analysis using HSC 5.1 chemistry software. It determined that as a result of thermodynamic analysis in Fig. 4, iron can be reduced from decomposition of fayalite in reduction smelting process and moreover, due to impact of CaO, reduction of iron in fayalite is more intensified.
The experiment was conducted according to the reaction temperature changes at 1300°C, 1400°C, 1500°C and 1600°C under the same solid carbon ratio and reaction time. Activated carbon was used as a reducing agent to reduce the Fe and Cu oxides in the slag, and the reduced Fe and Cu were separated from the slag consisting of SiO₂, CaO, Al₂O₃, etc. by specific gravity difference with the slag.

Fig. 5 shows the smelting behavior of slag and its product with increasing reaction temperature at 1300°C, 1400°C, 1500°C and 1600°C. In the slag recovered by high temperature smelting reduction at the reaction temperature of 1300°C, an area where the inter-granular agglomeration occurred, was observed, but general smelting shape was not observed. Unreacted powder accounted for 58 wt.% of the total weight, and no pig iron was separated from the slag. When examining the smelting behavior at the reaction temperatures of 1400°C, 1500°C and 1600°C, the whole slag was smelted and a glassy shape was observed, and the pig iron separated from the slag formed a mass. There covered pig iron weighed 8.2 g, 13.1 g and 22.6 g, respectively, and the recovery weight was about 31 wt.%, 50 wt.% and 86 wt.% respectively.

Table 2 shows the SEM-EDS results of the chemical composition of the secondary slag separated from copper smelting slag by high temperature reduction according to the change of reaction temperature condition. The main constituent elements were measured as slag components of Si, Ca and Al. With increasing reaction temperature at 1400°C, 1500°C and 1600°C, the Fe content in the slag was decreased from 17.28 wt.% to 11.71 wt.% At the reaction temperature of 1600°C, Fe in the slag could not be measured, indicating complete separation from the slag. The recovery rate of pig iron varied greatly depending on the reaction temperature.

Table 3 shows EDS-SEM results of the chemical composition of the pig iron separated from copper smelting slag by high temperature reduction according to the change of reaction temperature conditions and about 85 wt.% of Fe and 3 wt.% of Cu were recovered indicating the formation of Fe-Cu alloy.

In the experiment, recovery of iron and copper was conducted completely at 1600°C, in this case, glassy secondary slag with content of about 46 wt.% SiO₂, 26 wt.% CaO and 14 wt.% Al₂O₃ was formed. Fig. 6 shows SEM-EDS results of the chemical composition of the slag in a glassy shape recovered from 100 g copper smelting slag by high-temperature reduction at a reaction temperature of 1600°C.

Experiment to separate and recover the pig iron from copper smelting slag was conducted for 20 minutes of heating process and 30 minutes of reduction smelting process at the different reaction temperatures. Reduction behaviour of iron oxide was analyzed with frequency of 5 minutes at temperature 1600°C.
during 30 minutes of reduction process. In the first 5 minutes, content of Fe$_2$O$_3$ two times decreased and reached 19.55 wt.%. Then, with increasing reduction time, Fe$_2$O$_3$ content in the slag was decreased to only 3.88 wt.% Fe$_2$O$_3$ after 25 minutes. But, copper oxide in the slag was not determined in analysis of the sample during the first 5 minutes and copper oxide was fully reduced and dissolved to metal phase. To analyze the residual Fe$_2$O$_3$ content in the slag by reduction time, element contents in the slag were analyzed at 5, 10, 15, 20, and 25 minutes after slag smelting.

Fig. 7 shows content changes of main components in the slag at temperature 1600°C during reduction time. While content of iron oxide in the slag decreased following the increase of reduction time, on the contrary, content of SiO$_2$, CaO and Al$_2$O$_3$ in the slag increased.

4. Conclusions

This study analyzed the experiment to recover pig iron from copper smelting slag on the basis of reduction smelting method. Activated carbon was used as a reducing agent, and the smelting behavior of slag with the change of the reaction temperature condition was examined and the recovery rate of the pig iron from the slag was measured. As determined by thermodynamic analysis, CaO impacted on reduction of iron from decomposition of Fe$_2$SiO$_4$ (fayalite) and formed main component Ca$_2$SiO$_4$ (calcium orthosilicate) in the secondary slag. At the reaction temperature below 1400°C, the whole copper smelting slag was not smelted, and some agglomerated, showing a mass in a sponge form. It was confirmed that the whole of the slag should be smelted to recover Fe from the copper smelting slag. To increase the reduction reactivity and fluidity of the slag, experiments were conducted at the temperature of 1600°C. No Fe was detected in the slag recovered at the reaction temperature of 1600°C.

Reduction behavior of iron oxide was analyzed with frequency of 5 minutes at temperature 1600°C during 30 minutes of reduction process. In the first 5 minutes, content of Fe$_2$O$_3$ decreased two times and reached 19.55 wt.%. Then, with increasing reduction time, Fe$_2$O$_3$ content in the slag was decreased to only 3.88 wt.% Fe$_2$O$_3$ after 25 minutes and iron was not determined in 30 minutes. Finally, the recovery of pig iron from copper smelting slag by high temperature reduction method and the usage in fabrication process proves that it can be more economical and completely recycled.

Acknowledgement

This work was supported by the Ministry of Trade, Industry &Energy (MOTIE, Korea, Grant Number 10077570).

REFERENCES


