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Manufacture of Foundry Pig Iron from Copper Smelting Slag

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Abstract

The copper smelting slag is an industrial by-product obtained by cooling and crushing the by-products from the process of smelting copper. Since the slag contains ceramics such as SiO_2, Al_2O_3, CaO, etc. and a large iron content (34~45%), it can be recycled as a resource. However, there are many difficulties in the process of recovering the iron. This study was intended to analyze the effect of reaction time on Fe content in slag in the process of manufacturing foundry pig iron (Fe-Cu) from the copper slag by a dry smelting reduction method. No residual Fe was observed in the slug after 30 minutes of smelting.

INTRODUCTION

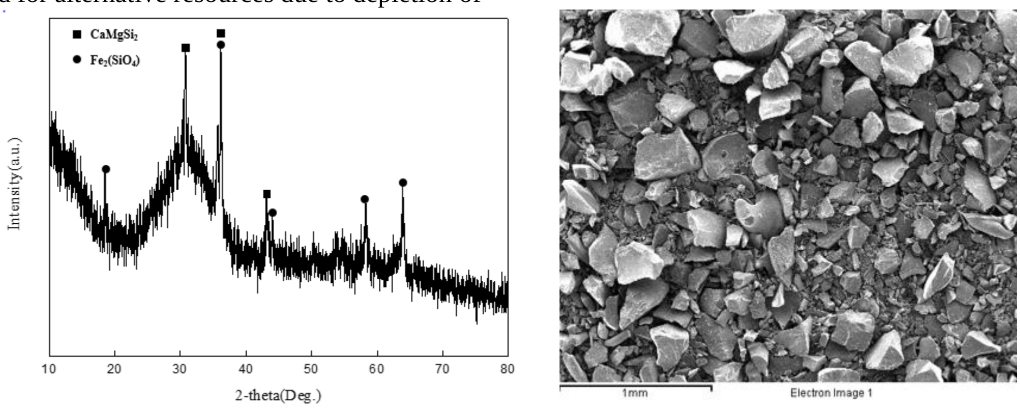
The copper smelting slag is an industrial by-product obtained by cooling molten slag, which is a by-product generated in the process of smelting copper in a flash furnace or a continuous furnace, in water and crushing it.1) It is known that about 2 tons of slag is generated from the manufacture of 1 ton of cooper 2), and about 1,5million tons of copper slag are generated from copper smelters in Korea. The copper slag contains not only ceramic components such as SiO_2, Al_2O_3 and CaO but also a large iron content (35~45%), which can be used as raw material of iron. 3) However, in Korea, it is simply recycled as agent for roadbed or additives for cement and bricks, or is landfilled. With increased global interest in environment and resources in recent years, recycling technologies of various by-products are being promoted, and efforts to treat and recycle slag generated in the production process are appropriately being made in Korea.4) The need for alternative resources due to depletion of natural resource is increasing, but its limitations are gradually appearing, indicating the possibility of utilizing by-products such as copper slag will increase 5~7). Various processes for recovering iron from copper have been proposed up to date and the proposed processes can be divided into physical separation process and dry smelting process. However, it has been reported that the physical separation is not effective in separating and recovering the iron, and the dry smelting process is difficult to use because it requires a high temperature of 1673K and increases the cost of process. Therefore this study was conducted to manufacture the foundry pig iron (Fe-Cu) from copper smelting slag, and to analyze the effect of reaction time on Fe content in the process of manufacturing pig iron.

EXPERIMENTAL METHOD

Experimental Material

In this study, the waste copper slag from G company was used. X-Ray fluorescence analysis and X-Ray diffraction were used to analyze the components of the copper smelting slag. In addition, X-ray fluorescence analysis and energy dispersive spectroscopy were used to analyze 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, Fe_2O_3 is about 40 wt.%, SiO_2 is about 21 wt.%, CaO is about 16 wt.%, and Al_2O_3 is about 7 wt.%. Fig. 1 (a) and (b) show the results of X-ray diffraction and SEM-EDS of the waste copper slag used in this study.



(a) **(b)**

Figure 1. XRD patterns (a) and SEM-EDS results (b) of the particle of the copper slag before the reduction reaction

Table. 1. Chemical composition of the copper slag used in this study.(XRX)

Element (Wt. %)												
Fe_2O_3	**$Si0_2$**	**CaO**	**Al_2O_3**	**ZnO**	**MgO**	**CuO**	**MnO**	**P_2O_5**	**Na_2O**	**TiO_2**	**K_2O**	**Cr_2O_3**
38.51	21.17	16.25	7.75	6.27	2.61	2.09	1.34	1.11	1.02	0.72	0.58	0.58

Experimental Apparatus

Fig. 1 is a schematic diagram of the high-frequency induction furnace used in the process. The experimental temperature of 1600°C can be achieved within 1 minute. The installation space was small and the additional equipment such as dust collector was miniaturized to reduce the difficulty and cost of the process. This equipment consists of units: cooler (a), controller (b), and high frequency induction furnace (c). Cooler is an equipment that cools heat generating components such as power supply and heating coil, and is necessary equipment because the temperature rises above 1600℃ in the experiments using high frequency. Controller is an equipment that controls the process temperature and reaction time, and conditions can be set according to the adjustment of wattage. The induction furnace was designed as sealed type to control dust and emission gas, and to maintain the inside of the furnace in an Ar gas atmosphere.

Figure 2. Experimental apparatus for removal and recovery of arsenic from gold concentrate.

Experimental Method

In this experiment, Fe and Cu oxides contained in the slag were separated into slag and pig iron (Fe-Cu) for recovery by reducing them to Fe-Cu alloy. In the experimental process, the copper slag and the reducing agent carbon were mixed at a certain ratio and then charged into the crucible, and the waste copper slag was reduced in the high frequency induction furnace. The experiment was conducted at the reduction temperature of 1600 ℃ and in an Ar gas atmosphere. For the amount of carbon used as a reducing agent, the amount of carbon necessary for reduction was calculated by analyzing the content of Fe, Cu, and Mn which can form an alloy by reduction. In consideration of the possibility of oxidation by oxygen, 1.5 times of the amount calculated was used in the experiment. The reduction reaction behavior of oxides was observed using HSC. It was thermodynamically confirmed that Cu oxide could be reduced to metal phase by C across the entire temperature range and and Fe oxide and SiO_2 could be reduced to a metal phase at 700°C and at 1700°C respectively. The thermodynamic reaction formulas are as follows (1, 2, 3).

$Fe_2O_3 + 3C = 2Fe + 3CO(g)$ $\Delta G_{700℃} = -6.646 kcal$ (1)

$CuO + C = Cu + CO(g)$ $\Delta G_{0℃} = -1.087 kcal$ (2)

$SiO_2 + 2C = Si + 2CO(g)$ $\Delta G_{1700℃} = -2.702 kcal$ (3)

To analyze the residual Fe content in the slag by reaction time, element contents in the slag were analyzed at 5, 10, 15, 20, and 25 minutes after slag smelting. Finally, properties of the slag and cast iron (Fe-Cu) separated by dry smelting reduction were analyzed. The components of the samples after dry smelting reduction were analyzed by X-ray diffraction.

EXPERIMENTAL RESULTS AND CONSIDERATIONS

In this study, the changes in the residual Fe content in the slag were examined according to the reaction time when separating and recovering the slag and pig iron (Fe-Cu) from the pig iron using a dry smelting reduction method. Here, reducing agent coke was mixed with the sample at the ratio of 9 g per 100 g (total quantity of charging sample: 200 g), and the mixture was charged into a crucible. And then the reaction time was changed to 5 minutes, 10 minutes, 15 minutes, 20 minutes, and 25 minutes, respectively under the same condition as above.

Table. 2 shows the components of the slag obtained by reduction. Fig. 4 shows the residual Fe content in the slag recovered by reduction reaction based on Table. 2. As shown in Table. 2 and Fig. 4, it was found that the Fe_2O_3 content in the slag was decreased as the reaction time considered in this study was increased from 5 minutes to 25 minutes. When the reaction time was 5 minutes, the content of original sample was decreased from to 38.51 wt.% to 19.55 wt.% and only about 2 wt.% remained at 25 minutes.

Table. 2. XRF analysis results of slag by timeslot (wt. %)

Element	Weight %				
	5 minutes after smelting	10 minutes after smelting	15 minutes after smelting	20 minutes after smelting	25 minutes after smelting
SiO_2	35.9432	39.0488	42.4491	44.9266	46.2493
CaO	21.2649	22.5585	25.5539	26.1175	26.5678
Fe_2O_3	19.5529	14.3199	8.6884	4.4716	3.8815
Al_2O_3	11.1952	12.5388	12.9748	14.3574	14.4895
MgO	3.5358	3.6987	4.4611	4.0977	3.8815
Na_2O	2.3889	1.9345	1.9807	2.1488	2.5573
MnO	1.4541	1.4314	1.8644	1.5116	1.6205
Cr_2O_3	1.0023	1.2131	1.1693	0.7277	0.7521
TiO_2	-	1.0933	-	-	0.9919
K_2O	0.7702	0.8638	0.8583	1.0269	-
P_2O_5	0.8757	0.7271	-	-	-
ZnO	2.0169	0.572	-	-	-

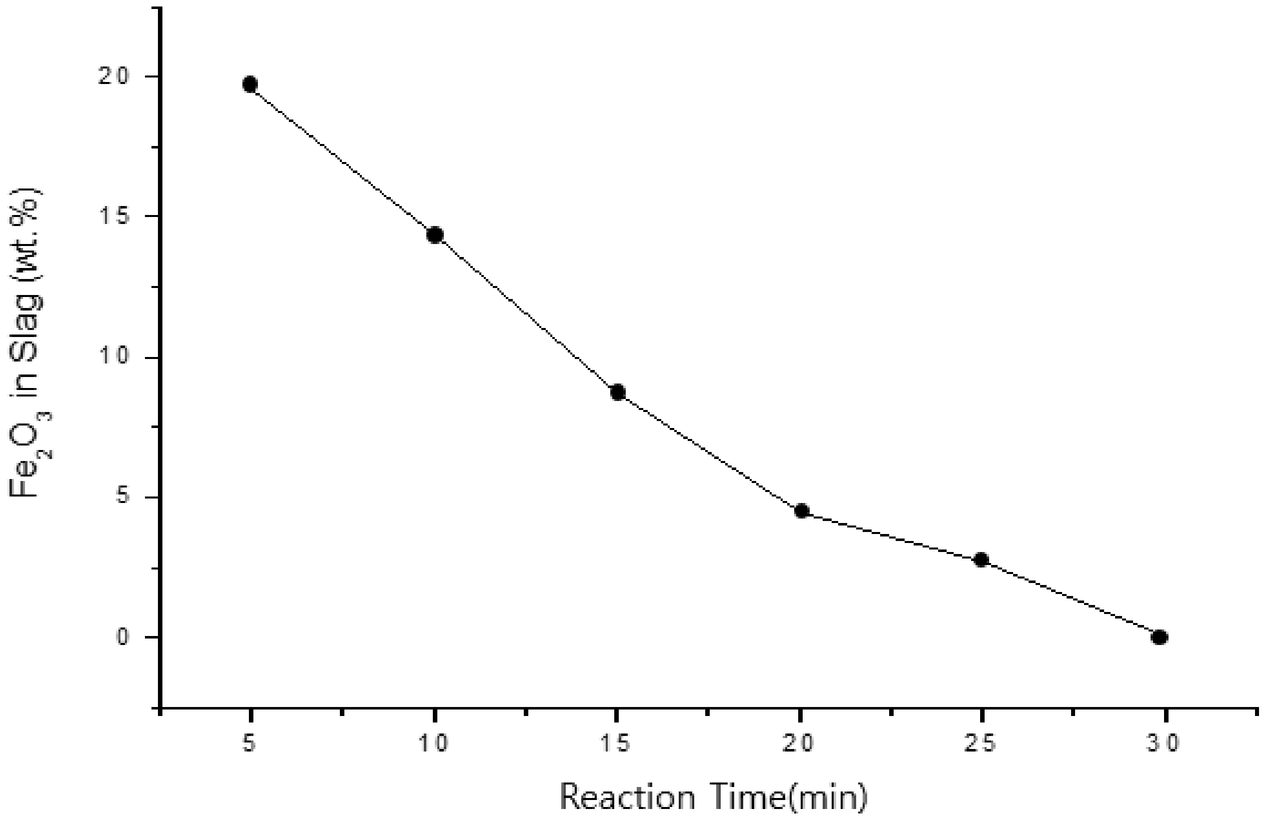


Figure 3. Fe_2O_3 content in the slag by reaction time

Table. 3. Components of the pig iron (Fe-Cu) and slag recovered after 30 minutes of reaction time (wt. %)

EDS results of pig iron	
Element	Weight %
Si	2.94
P	4.62
Cr	1.25
Mn	0.81
Fe	87.45
Cu	2.93
Totals	100.00
O	50.47
Na	1.04
Mg	2.93
Al	10.01
Si	17.03
K	0.46
Ca	17.74
Ti	0.33
Totals	100.00
Fe	Not detected
Cu	Not detected

Table 3 is shows the chemical composition of the pig iron (Fe-Cu) obtained by separating and recovering the pig iron (Fe-Cu) from waste copper slag by a dry smelting reduction method.

CONCLUSION

In this study, the changes in the residual Fe content in the slag were examined according to the reaction time when separating and recovering the slag and pig iron (Fe-Cu) from the pig iron by a dry smelting reduction method. To examine the Fe content in the slag according to the reaction time in the reduction heat treatment process, the slag was recovered at intervals of 5 minutes after slag smelting, and the element content was analyzed. With increasing reaction time, the Fe content in the slag was decreased to 19.55 wt.% after 5 minutes and to 2.69 wt.% after 25 minutes from 38.51 wt.%. And no Fe was observed from the reaction time of 30 minutes. As a result, it was confirmed that the optimum condition for the reduction process was from 30 minutes + from slag smelting. The Fe content of the pig iron (Fe-Cu) obtained under these conditions was 87.45 wt.%. All these processes examined by XRD and XRF analysis were accompanied by thermodynamic behaviors.

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