URTNASAN ERDENEBOLD[1], CHOI MOO SUNG[1], JEI-PIL WANG[1*]

MANUFACTURE OF LOW SULPHUR PIG IRON FROM COPPER SLAG

Copper slag differs by chemical composition and structure, depending on the type of processing. Copper slag typically contains about 1 wt.% copper and 40 wt.% iron depending upon the initial ore quality and type of furnace used. The aim is to produce a typical foundry pig iron with the chemical composition of C > 3.40 wt.%, Si 1.40 to 1.80 wt.%, Mn 0.30 to 0.90 wt.%, P < 0.03 wt.% and S < 0.03 wt.% from copper slag. But foundry pig iron manufactured from copper slag contains a high sulphur content. Therefore, this study examines how to conduct desulphurization. Desulphurization roasting and reduction smelting with desulphurization additives used to remove sulphur from the copper slag. The results showed that desulphurization effect of desulphurization roasting is poor but when combined with reduction smelting with CaO addition is possible to manufacture low sulphur pig iron from copper smelting slag.

Keywords: copper slag, desulphurization, roasting, sulphur, basicity

1. Introduction

In the copper industry, the copper products are produced from natural and secondary raw materials. During processing, pure copper and copper slag are 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 [1-5]. Copper slag differs by chemical composition and structure, depending on the type of processing. Copper slag usually contains about 1 wt.% copper and 40 wt.% iron depending on the initial ore quality and the furnace type. Significant amounts of SiO_2, FeO, CaO, Al_2O_3 and minor amounts of other elements (e.g., zinc, titanium, lead, and arsenic) are also associated with copper slag [5]. 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 SiO_2, these exist in copper slag mainly in the form of fayalite ($2FeO \cdot SiO_2$). A sulphur in the copper slag exists in form of FeS and Cu_2S.

In our previous study "Recovery of Iron from Copper Slag", experiments on the recovery of iron from copper slag with a high content of iron were performed using reduction smelting at high-temperatures under the holding temperature and holding time factors. The results confirmed that the iron can be reduced 100% and pig iron can be recovered at a temperature of 1600°C

and a holding time 30 of minutes through the reduction smelting [6]. The purpose of that study on the manufacture of foundry pig iron contained copper slag was to produce a typical foundry pig iron with a chemical composition of C > 3.40 wt.%, Si 1.40 to 1.80 wt.%, Mn 0.30 to 0.90 wt.%, P < 0.03 wt.% and S < 0.03 wt.%. In particular, Cu is used as an additive element to improve mechanical properties such as hardness, abrasion resistance and corrosion resistance in the foundry pig iron products. High sulphur content in the cast iron negatively affects the mechanical properties of cast iron. Consequently, we aimed to recover low sulphur pig iron.

The copper smelting slag from G Company used in this study contained 0.207 wt.% of sulphur. In our previous experiment, it observed that is impossible to produce pig iron with the required sulphur composition using only the reduction smelting with reducing agent solid carbon additives.

Desulphurization is a widely used method in metallurgical process and it includes desulphurization roasting before processing the raw materials and desulphurization with additives during the processing. Therefore, this experiment was conducted to test the effect on the desulphurization rate of desulphurization roasting under holding temperature and time factors, and reduction smelting with desulphurization additives.

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2. Experimental method

2.1. Experimental materials

In this study, copper slag from G Company was used. The slag is a cooling slag, which has undergone a water granulation process. Fig. 1 shows the real image and XRD analysis results of the copper slag used in this experiment. The copper slag was consisted in forms of ($2FeO \cdot SiO_2$) and monticellite ($CaMgSiO_4$) according to the XRD patterns.

X-Ray fluorescence analysis and SEM-Energy dispersive spectrometer were used to analyze the components of the copper smelting slag. Table. 1 is an analytical table of the chemical composition of the copper slag used in this study by XRF analysis. 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.%. The results of SEM-EDS analysis on the powder particle of the copper slag indicated that it contains of 26.14 wt.% of Fe and 0.67 wt.% of Cu, and results are illustrated in Fig. 2. In addition, the inductively coupled plasma (ICP) atomic emission spectroscopy analysis was used to evaluate the sulphur in the copper smelting slag, which revealed that the copper smelting slag contains 0.207 wt.% of sulphur.

2.2. Experimental Apparatus

2.2.1. Desulphurization roasting

The desulphurization roasting experiments were performed in a tube furnace. Fig. 3 presents a schematic diagram of the

TABLE 1

Chemical composition of copper slag from G company

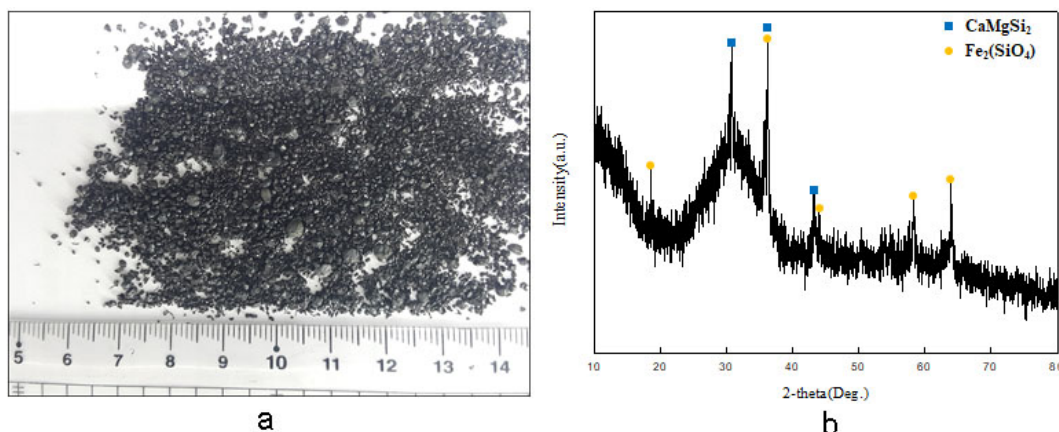| Element	Fe$_2$O$_3$	SiO$_2$	CaO	Al$_2$O$_3$	ZnO	MgO	CuO	MnO	P$_2$O$_5$	Na$_2$O	TiO$_2$	K$_2$O	Cr$_2$O$_3$
Content, wt.%	38.51	21.17	16.25	7.75	6.27	2.61	2.09	1.34	1.11	1.02	0.72	0.58	0.58

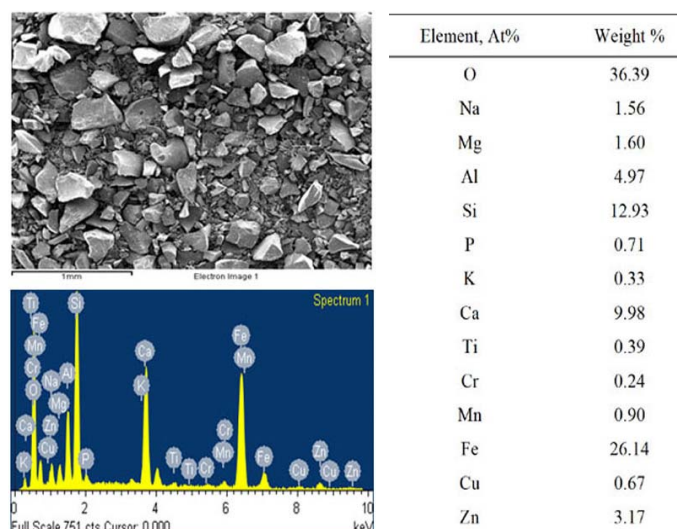Fig. 1. Real image (a) and XRD patterns (b) of the copper slag from G company

Fig. 2. Particle and chemical composition of the copper slag by SEM-EDS analysis

tube furnace in order to roast the removal of the sulphur from copper slag. In Fig. 3, (A) is a SiC heater that receives electricity and causes resistance to increase the temperature inside. (B) is a thermocouple that measures and controls the temperature inside furnace. (C) is a crucible, which in this experiment was made of
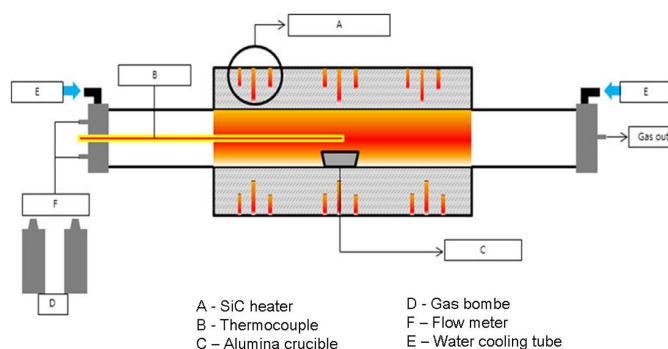

Fig. 3. Schematic diagram of experimental apparatus

aluminum and was where the specimen to be tested was placed. (D) is the gas bomb where the gas to be injected is appropriately positioned; Ar and O_2 gas bombs were used for this experiment, and these gases were injected through the flow meter (F), which controlled the amount of gas injected. (E) shows the placement of a water cooling tube, which minimized deformation of the equipment due to the high temperatures.

2.2.2. Reduction smelting

The reduction smelting experiments were performed in a high-frequency induction furnace. The high-frequency induction furnace consisted of a cooler, controller and heater box. The installation space was small and the additional equipment such as dust collector was miniaturized to reduce the difficulty and cost of the process. The temperature of the high-frequency induction furnace was controlled by regulating the voltage. Fig. 4 is a schematic diagram of a heater box where high-frequency induction is used in the experiment. The heater box enclosed the equipment and eliminated dust and flue gases from the furnace. Argon gas was released into the heater box to maintain an inert atmosphere. The alumina crucible was used to provide the conditions necessary to avoid a chemical reaction between the copper slag and crucible during the experimental process. Electricity was conducted through the thermo-generator and the φ26 alumina crucible was placed inside it using the φ45 graphite crucible. Then the crucibles were placed inside the heater box and the temperature was measured using a thermocouple.

1. Argon gas tank
2. Flowmeter
3. Ar gas inlet
4. Thermocontroller
5. Thermocouple
6. lid
7. Copper coil
8. Ar gas outlet
9. Graphite crucible
10. Molten slag
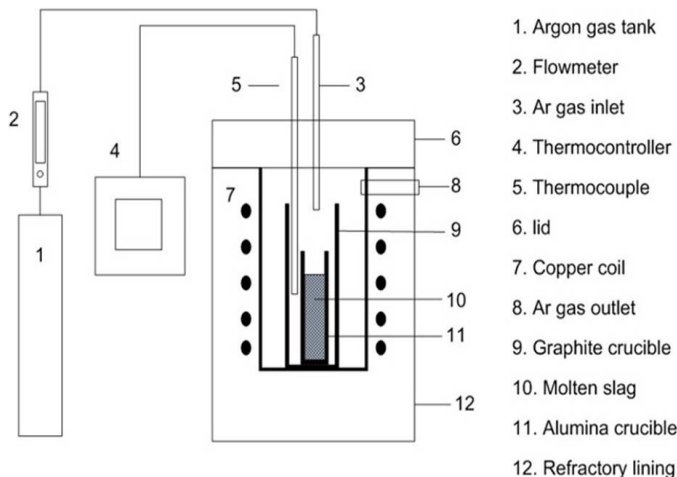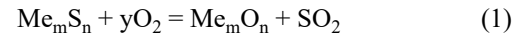11. Alumina crucible
12. Refractory lining

Fig. 4. Schematic diagram of experimental apparatus

2.3. Experimental Procedures

2.3.1. Desulphurization roasting

The copper slag contained a certain amount of sulphur content and the sulphur phase in the copper slag existed in form of FeS and Cu_2S. Most of the sulphur can be removed by oxidising it to SO_2 gas. The sulphur in the solid copper slag present as Me_mS_n can be oxidized according to the following reaction:

$$Me_mS_n + yO_2 = Me_mO_n + SO_2 \qquad (1)$$

In desulphurization roasting, 50 g of copper slag was put into the alumina crucible and then placed inside tube furnace. Than the desulphurization roasting experiment was conducted at holding temperatures of 500°C, 700°C and 900°C for 1 to 9 hours under 400 cc/min air blow.

2.3.2. Reduction smelting with CaO addition

During the reduction smelting process, copper slag with fine irregularities of 1mm to 3mm and 9 g of reducing agent solid carbon per 100 g of copper slag were mixed with CaO additives. The mixture with a $B = \dfrac{\%CaO + \%MgO + \%MnO}{\%SiO_2 + P_2O_5} = 0.8 - 1.2$ ratio of CaO powder per 100 g of copper slag was, and then put into the alumina crucible. We estimated a necessary amount of CaO to add by the molecular weight calculator (molar mass). In the case of $(\%CaO + \%MgO + \%MnO)/(\%SiO_2 + P_2O_5)$ ratio is equal to 1, the amount of CaO to add was estimated at 15 wt.%. Then, the amount of CaO additives was calculated of 5 g, 10 g, 15 g, 20 g and 25 g according to the ratio B = 0.8, 0.9, 1.0, 1.1, respectively.

The alumina crucible was placed inside a graphite crucible. Then, the crucibles were placed inside the heater box. The experiment was heated up to the necessary temperature of 1600°C for 180 minutes and reduction smelting process continued for 30 minutes of holding time. Ar gas was blown into the crucible under a rate 300 cc/min during this process.
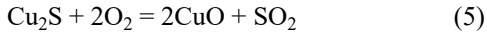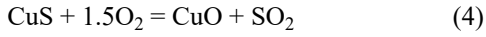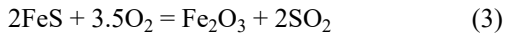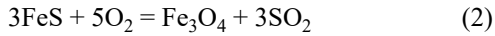
In this reduction smelting, when copper slag was smelted at the high temperature of 1600°C, Fe_2O_3, CuO and some oxides were reduced, and formed to a metal phase and molten pig iron was generated. Unreduced oxides such as SiO_2, CaO, and Al_2O_3 etc, formed the secondary slag, which is reformed slag, and floated on the molten pig iron. The structure of reformed slag is also called secondary slag from the initial copper slag is completely converted to $CaO-SiO_2-Al_2O_3$ slag system.

3. Considerations and results

3.1. Desulphurization roasting

The copper smelting slag used in this study contains 0.207 wt.% of sulphur. First, we attempted to remove the sulphur from the copper slag at low amount of sulphur necessary to below 0.05 wt.% using common method of roasting at high temperatures under air blow. The desulphurization roasting is one of metallurgical process involving gas-solid reactions at less than melting point of the sulphides and oxides with the purpose of purifying the metal components in the raw material. The sul-

phur in the solid copper slag present as FeS and Cu_2S, CuS can be oxidized according to the following reaction:

$$3FeS + 5O_2 = Fe_3O_4 + 3SO_2 \qquad (2)$$

$$2FeS + 3.5O_2 = Fe_2O_3 + 2SO_2 \qquad (3)$$

$$CuS + 1.5O_2 = CuO + SO_2 \qquad (4)$$

$$Cu_2S + 2O_2 = 2CuO + SO_2 \qquad (5)$$

The experiment was conducted at 500°C, 700°C and 900°C for 9 hours and the sample was checked every 2 hours, respectively. Fig. 5 is the results of the ICP analysis for sulphur content in the sample of the copper slag after desulphurization roasting depended on the temperature and time factors. As results of the roasting experiment, the sulphur content in the copper slag sample small decreased and after 3 hours at 500°C, the sulphur content just reached a minimum level of 0.129 wt.%. In this experiment, it could not remove the sulphur from the copper slag by high-temperature roasting. Therefore, we analyzed the surface chemistry of the copper smelting slag using XPS (X-ray photoelectron spectroscopy) analysis.
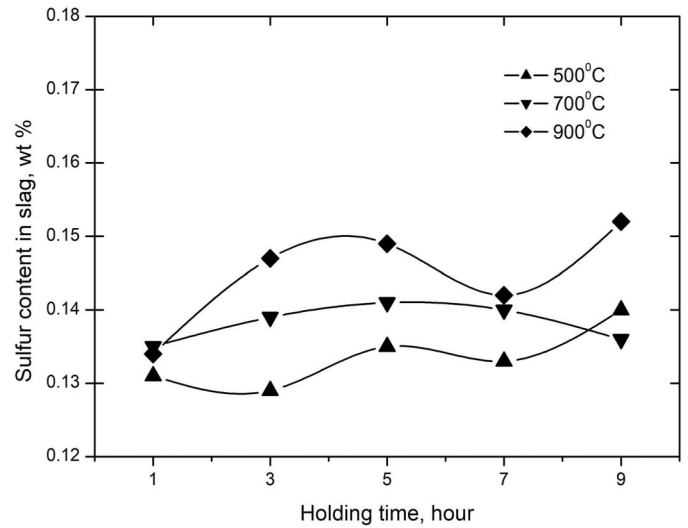

Fig. 5. Results of ICP analysis for sulphur content in the sample of the copper slag after desulphurization roasting depended on temperature and time factors
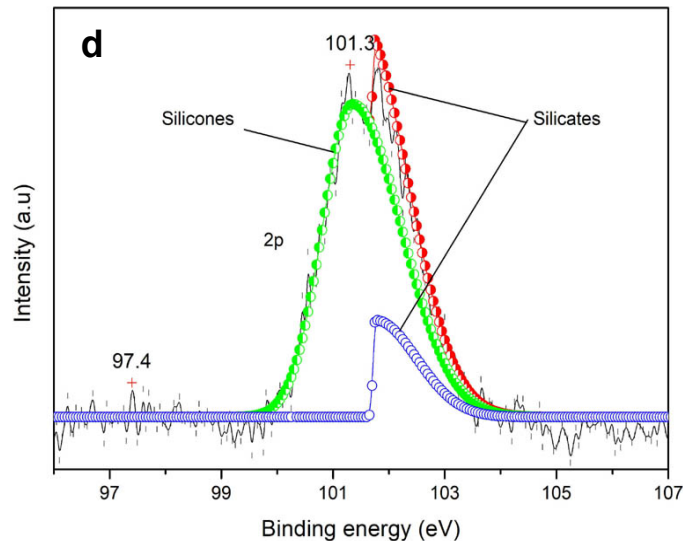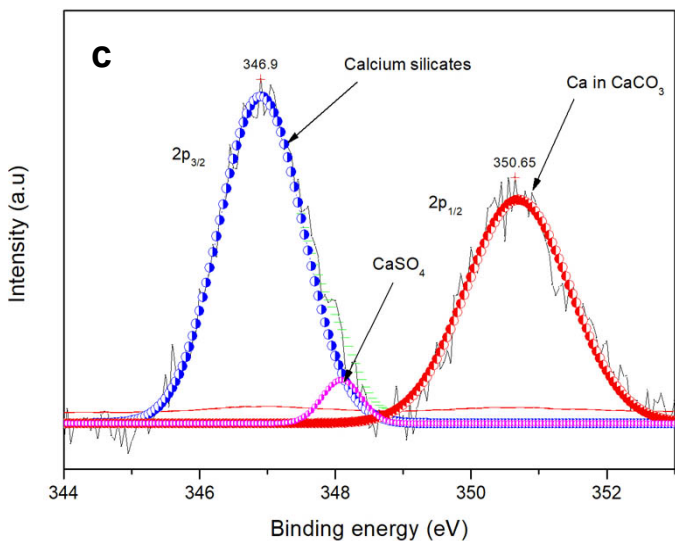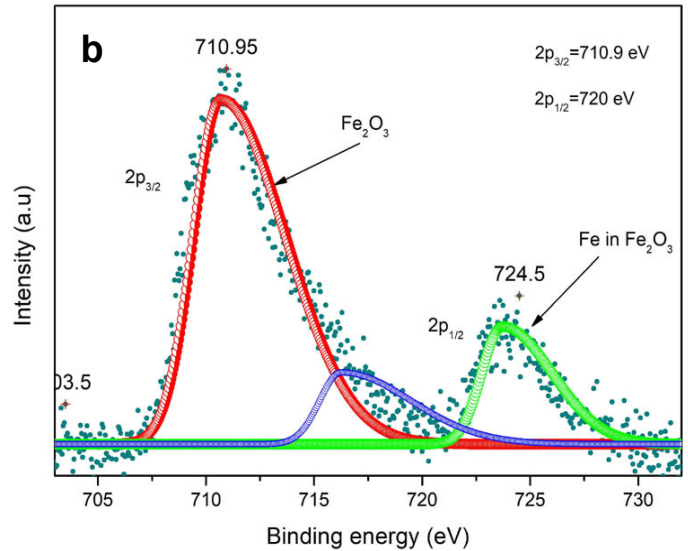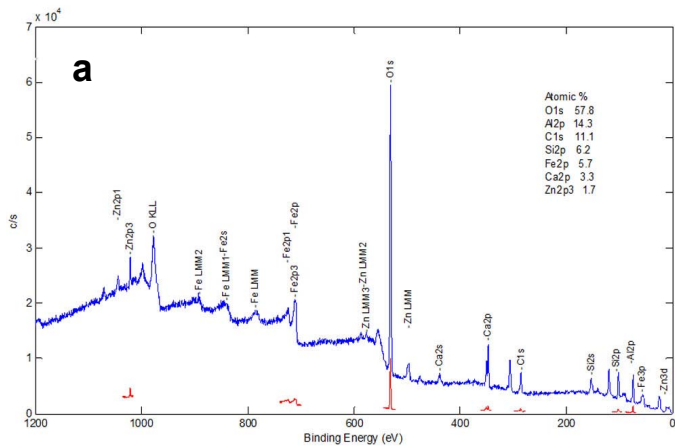

Fig. 6. Result of XPS analysis for surface of the copper smelting slag: (a) Wide scan result of XPS for all elements, (b) Iron peaks, (c) Calcium peaks and (d) Silicon peaks analysed by XPS

Fig. 6a is a wide scan for all elements in the copper slag used to examine the existing atoms. In the case of the copper slag, strong oxygen (O1s), aluminium (Al2p), iron (Fe2p), calcium (Ca2p), silicon (Si2p) and zinc (Zn2p$_{3/2}$) signals are registered. Rather intensive iron (2p) and silicon (Si2p) peaks were detected as well.

The two peaks in the iron species 700~730 eV range as shown in Fig. 6b. A literature survey indicate that iron exists in copper slag as forms of iron oxides and iron metasilicate. The two peaks for iron oxide ions agree with reported peaks in as survey by John F. Moulder et al. [7]. Fig. 6c shows the Ca2p$_{3/2}$ and 2p$_{1/2}$ spectra of the copper smelting slag samples. The *BE* Ca2p$_{3/2}$ values for reference calcium silicates and CaSO$_4$ are reported as 346.7±1.0 eV and Ca2p$_{1/2}$ for Ca in CaCO$_3$ values in the 350.65 eV, respectively by Moulder and Stickle. Therefore, the calcium exists as calcium silicates and CaCO$_3$ in the copper slag. The *BE* of Si 2p values for silicates and silicones were detected as 101.3±1.0 eV, thus the shift between the binding energies of silicates and silicones is 1.0 eV as shown in Fig. 6d. The peak of silicates is slightly higher than that silicones peak. This indicates that silicon mainly exists as silicates in the copper slag.

In the results of the XPS analysis, the main components of copper slag are FeO, SiO$_2$ and CaO, these exist in the copper slag mainly in the form of fayalite (2FeO·SiO$_2$) and calcium silicates (CaO·SiO$_2$). This solid quarts fayalite slag with a glassy surface does not react to structural and chemical reactions at less than melting point of the copper slag and high chemically stable. The roasting consists of thermal gas-solid reactions on surface of solid materials. But, the structure of glas-like material is most stabiliser network form with strong bonds [8,9], therefore, it is hardly reacted with gases. In the desulphurization roasting, the transfer of sulphur through the glassy copper slag would be extremely slow due to glass structure hence the extent of sulphur removal from copper slag would be slow. Consequently, we proved that sulphur oxidation in copper slag is impossible through high-temperature desulphurization roasting alone.

3.2. Reduction smelting with CaO addition

This experiment was performed to produce foundry pig iron with S < 0.03 wt.% using reduction smelting with CaO additives.

The amount of CaO added was evaluated by the molecular weight calculator (molar mass). The major components of the copper smelting slag are iron oxide, SiO$_2$ and CaO, these exist in copper slag mainly in the form of fayalite (2FeO·SiO$_2$) and calcium silicates (CaO·SiO$_2$). The copper slag contained 38.51 wt.% Fe$_2$O$_3$, 21.17 wt.% SiO$_2$, 16.25 wt.% CaO, 7.75 wt.% Al$_2$O$_3$, 6.27 wt.% ZnO and 2.61 w.t.% MgO. During reduction smelting, the ZnO was completely reduced with carbon at a temperature of 980~1000°C and volatilized zinc was removed from the furnace as fumes. The fayalite (2FeO·SiO$_2$) in the copper slag decomposes under carbon reduction and CaO, and iron oxide is reduced and separates as liquid pig iron according to the following reactions.

$$Fe_2SiO_4 + 2C = 2Fe + SiO_2 + 2CO \qquad (6)$$

$$Fe_2SiO_4 + 2CaO + 2C = Ca_2SiO_4 + 2Fe + 2CO \qquad (7)$$
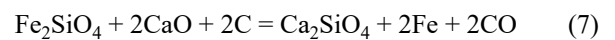
In this case, it was seen that the remaining oxides of SiO$_2$, CaO, Al$_2$O$_3$ and MgO interacted and generated the secondary slag. This secondary slag might be consisted on the considering main compounds as the CaO·SiO$_2$, CaO·FeO·SiO$_2$, 2CaO·Al$_2$O$_3$, 2CaO·SiO$_2$, CaO·FeO·SiO$_2$, CaO·MgO·SiO$_2$, CaO·Al$_2$O$_3$·2SiO$_2$, CaS and etc. [10-14].

The chemically stability of these molecular compounds were analyzed at a temperature 1600°C using the HSC-5 Chemistry program. Table. 2 shows Gibb's free energy changes of the considering main compounds in the secondary slag. After thermodynamic analysis, it discovered that the secondary slag mainly consisted of high chemically stable compounds such as CaSiO$_3$, CaAl$_2$SiO$_6$ and CaMgSiO$_4$.

In the previous reduction smelting by solid carbon, the iron was completely reduced at temperature 1600°C for 30 minutes, and formed to liquid pig iron. The reformed secondary slag in the in the previous experiment contained about 46 wt.% SiO$_2$, 26 wt.% CaO and 14 wt.% Al$_2$O$_3$, and was acid slag. Table 3 shows that chemical composition of the secondary slag in the previous experiments as determined by the X-Ray Fluorescence.

The amount of CaO in the secondary slag was of 25.56 wt.%. We estimated a necessary amount of CaO to add. The percentage used to generate the major compounds of the secondary slag in this experiment and the amount of CaO spent during reduction smelting were calculated by molar mass according to the

TABLE 2

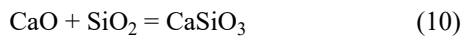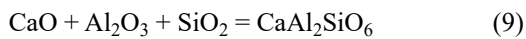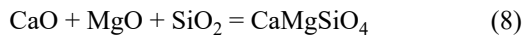Gibb's free energy changes of the considering main compounds in secondary slag at 1600°C

Compound	CaSiO$_3$	Fe$_2$SiO$_4$	CaAl$_2$O$_4$	Ca$_2$Al$_2$O$_5$	CaFeSiO$_4$	CaMgSiO$_4$	CaAl$_2$SiO$_6$	CaS
Delta G, kJ	–91.249	–5.483	19.204	–16.925	229.081	–101.163	–100.55	–8.234

TABLE 3

Chemical composition of the secondary slag in previous experiment

| Element	SiO$_2$	CaO	Al$_2$O$_3$	MgO	MnO	Na$_2$O	TiO$_2$	Cr$_2$O$_3$	MnO	K$_2$O	P$_2$O$_5$
Content,wt.%	46.25	26.56	14.49	3.88	1.62	2.55	1.49	1.25	1.62	0.99	0.90

reaction. Calculations were made per 100 g of materials. The reactions of CaO and major elements are follows:

$$CaO + MgO + SiO_2 = CaMgSiO_4 \quad (8)$$

$$CaO + Al_2O_3 + SiO_2 = CaAl_2SiO_6 \quad (9)$$

$$CaO + SiO_2 = CaSiO_3 \quad (10)$$

The reactions between of CaO and sulfides in the copper slag are follows:

$$CaO + FeS + C = CaS + Fe + CO \quad (11)$$

$$CaO + Cu_2S + C = CaS + 2Cu + CO \quad (12)$$
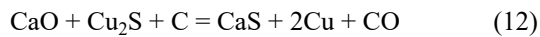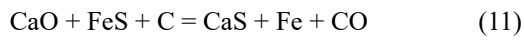
Desulphurization reaction of CaO with dissolved sulhpur in the molten pig iron is follows [15-18]:

$$(CaO) + [S] + [C] = (CaS) + CO(g) \quad (13)$$
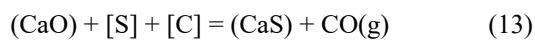
Capability of a slag to remove sulphur from metal is characterized by the distribution coefficient of sulphur:

$$L_s = \frac{(\%S)}{[\%S]}$$

Where: (%S), [%S] – sulphur content in slag and metal.

As the results of the amount of CaO to add was calculated at 17.20 wt.% by a molar mass. According to these calculations, the total amount in secondary slag in this study is 43.77 wt.% and

basicity of secondary slag was B = 1.04. In this case, the secondary slag able to completely dissolve the sulphur in the pig iron.

$$B = \frac{\%CaO + \%MgO + \%MnO}{\%SiO_2 + P_2O_5} = 1.04$$

Then, the amount of CaO additives was calculated according to the ratio B = 0.8, 0.9, 1.0, 1.1 and 1.2 and mixed the estimated amount of CaO powder per 100 g of copper slag. Table 4 shows the amount of CaO to add per 100 g copper slag in this experiment.

In the reduction smelting with CaO addition, the sulphur extremely dissolved to the reformed slag according to the changes of the B ratio condition at 1600°C for 30 minutes. Table 5 is the chemical composition of the slag reformed from copper slag during the reduction smelting with CaO addition as determined by the XRF analysis. As the shown Table 5 it was found that the SiO_2 content in the slag was decreased according to the changes of the B ratio but the CaO content in the slag increased.

Table 6 shows results of EDS analysis of the chemical composition of the pig iron separated from copper smelting slag by high temperature reduction according to the changes of B ratio. It was confirmed that there was no significant difference according to the changes of CaO addition conditions and about 86% Fe and 3% Cu were contained in pig iron. But, the sulphur was not detected in the pig iron, therefore, ICP analysis used to evaluate the amount of sulphur in the pig iron, and its results used on estimate effect of desulphurization rate.

The effect of desulphurization rate increased according to the basicity of the secondary slag increased. Fig. 7 shows the changing desulphurization rate depending on the changes of the slag basicity. When the slag basicity increased above B = 1, the distribution coefficient of sulphur extremely increased up to 180, and the sulphur content in the pig iron was less than 0.001 wt.%,

TABLE 4

Amount of CaO added to copper slag

Basicity, B	0.8	0.9	1.0	1.1	1.2
CaO addition by calculation method, g	4.93	9.55	14.18	18.80	23.43
CaO addition of actual experiment, g	5	10	15	20	25

TABLE 5

Chemical composition of slag reformed from copper slag during reduction smelting with CaO addition according to changes of B ratio

Element, wt.%		SiO_2	CaO	Al_2O_3	MgO	Na_2O	TiO_2	K_2O	MnO	SO_3	BaO	Fe_2O_3	SrO	P_2O_5
CaO addition, g per 100 g of copper slag	5	40.05	37.50	13.45	5.00	1.52	0.91	0.635	0.61	0.30	—	—	—	—
	10	37.42	42.54	13.12	4.40	0.54	0.41	0.18	0.23	0.28	0.66	0.10	0.07	—
	15	31.80	50.86	12.42	4.14	—	.0.24	—	—	0.46	—	—	0.08	—
	20	31.82	50.94	11.80	3.49	—	0.21	—	—	0.45	0.49	0.70	0.07	—
	25	22.36	60.91	11.24	3.50	—	—	—	—	0.55	—	1.14	—	0.28

TABLE 6

Chemical composition of the pig iron separated from copper slag by EDS analysis

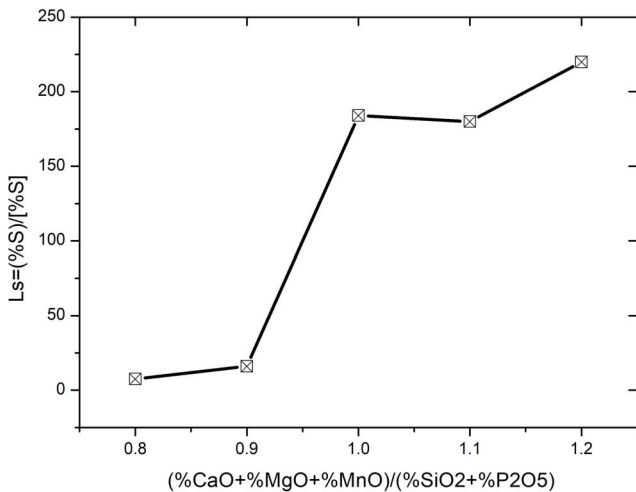| CaO addition, g per 100 g of copper slag	Element, wt.%					
	Si	C	Cr	Mn	Cu	Fe
5	5.53	3.84	1.33	1.43	3.11	84.76
10	4.09	4.00	0.99	1.12	3.62	86.18
15	4.01	4.12	1.24	1.75	3.22	85.66
20	3.63	3.95	0.87	1.30	3.06	87.19
25	2.94	4.62	1.25	0.81	2.93	87.45

Fig. 7. Effect of basicity of secondary slag on sulphur distribution between slag and pig iron at 1600°C for 30 minutes

as the determined by ICP analysis. Consequently, we proved that reformed slag greatly dissolved the sulphur from the molten pig iron during the smelting reduction process with CaO addition when slag basicity was B = 1.0.

4. Conclusions

For this study, an experiment was performed to manufacture foundry pig iron containing S < 0.03 wt.% from copper smelting slag by desulphurization roasting and reduction smelting with CaO addition. Firstly, the desulphurization roasting experiment was conducted at temperatures of 500°C, 700°C and 900°C with over a 9 hours period and sample was checked every 2 hours respectively. As a result of the desulphurization roasting experiment, the sulphur content in the copper slag reduced to a minimum of 0.129 wt.%. It was observed that the fayalite slag with a glassy surface cannot be processed through desulphurization roasting at less than melting point of copper slag.

Next, the reduction smelting with CaO addition experiment was performed at temperature 1600°C for 30 minutes. The main components in the secondary slag were determined to be several compounds as $CaMgSiO_4$, $CaAl_2SiO_6$ and $CaSiO_3$ by thermodynamic analysis. The amount of CaO to add per 100 g of materials was calculated by a molar mass, which was 17.20 wt.%. In this case, the basicity of secondary slag was B = 1.04, when basicity of secondary slag increased 1, the sulphur content in the pig iron was less than 0.001 wt.%, which was determined by the ICP atomic emission spectroscopy analysis. In this study, it was confirmed that it is possible to manufacture low sulphur pig iron from copper smelting slag by reduction smelting with CaO addition.

REFERENCES

[1] LS-Nikko copper inc., Ulju-gun, Ulsan, Korea, Private Communication (September 2012).

[2] Korea Zinc Co., Ltd., Onsan Refinery, Ulju-gun, Ulsan, Korea, Private Communication (May 2012).

[3] S.W. Ji , C.H. Seo, The application of copper smelting slag as concrete aggregate. Korean Recycled Construction Resources Institute 2, 68-72 (2006).

[4] Jei-Pil Wang, Kwang-Myoung Hwang, Hyun-Mook Choi. A Study on the Recovery of Iron from Copper Slag with Temperature, International Journal of Applied Engineering Research 2, 977-982 (2018).

[5] Jei-Pil Wang, Kwang-Myoung Hwang, Manufacture of foundry pig iron from copper smelting slag, International Journal of Applied Engineering Research 2, 973-976 (2018).

[6] U. Erdenebold, H.M. Choi. J.P. Wang. Recovery of pig iron from copper smelting slag by reduction smelting, Arch. Metal. Mater. 63 (4), 1793-1798 (2018).

[7] John F. Moulder, William F. Stickle, Peter E. Sobol, Kenneth D. Bomen, Handbook of X-ray Photoelectron spectroscopy, USA. 80-81 (1992).

[8] LI Lie, Hu Jian-hang, Wang Hua, Smelting oxidation desulfuration of copper slag. Journal of Iron and Steel Research, International, 14-20 (2012).

[9] Bao-jing Zhang, Li-ping Niu, Ting-an Zang, Alternative reduction of copper matte in reduction process of copper slag, ISIJ International, 775-781 (2017).

[10] A.A. Lykasov, G.M. Riss, Recovery of iron from copper smelting slag, Ferrous Metallurgy 9, 597-602 (2016).

[11] Prince Sarfo, Gary Wyss, Guojun Ma, Avimanyu Das, Courtney Young, Carbothermal reduction of copper smelter slag for recycling into pig iron and glass, Minerals Engineering 107, 8-19 (2017).

[12] A.A. Lykasov, G.M. Riss. Recovery of iron from copper smelting slag. Ferrous Metallurgy 9, 597-602 (2016).

[13] Geological survey professional paper 440-L, 58-65 (1964).

[14] Yalong Liao, Juan Zhou, Feirong Huang, Separating and recycling of Fe, Cu, Zn from dumped copper slag by microwave irradiation assisted carbothermic method, Journal of Residuals Science & Technology 13, 155-160 (2016).

[15] G. Siwiec, M. Sozańska, L. Blacha, A. Smalcerz, Behaviour of iron during reduction of slag obtained from copper flash smelting, Metalurgija 54, 113-115 (2015).

[16] J. Kijac, M. Borgon, Desulphurization of steel and pig iron, Metelurgija 47 (4), 347-350 (2008).

[17] Akitoshi Matsui, Yu-ichi Uchida, Naoki Kikuchi and etc., Effects of temperature and oxygen potential on removal of sulfur from desulfurization slag, ISIJ International 57 (6), 1012-1018 (2017).

[18] Verlag Stahleisen, D. Dusseldorf, Slag atlas 2nd Edition (1995).