International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 2 (2018) pp. 977-982

A Study on the Recovery of Iron from Copper Slag with Temperature

Kwang-Myoung Hwang[1], Jin-Sung Lee[2], Hyun-Mook Choi[3], Min-Jung Kang[4], Dong-Gi Yoo[5]
Sae-Kwon Heo[6], Jei-Pil Wang[7]*

,QXWUR&RRSHUDWLRQ)RXQGDWLRQ6LOODD8QLYHUVLW\%XVDQ5HSXEOLFRI.RUHD
***HQHUDO*UDGXDWH6FKRRO6LOODD8QLYHUVLW\5HSXEOLFRI.RUHD**
HS DUWPHQWRI*UHHQ&KHPLFDO(QJLQHHULQJ6LOODD8QLYHUVLW\%XVDQ5HSXEOLFRI.RUHD
HSDUWPHQWRI0HWDOOXUJLFDO(QJLQHHULQJ3XNRQJ1DWLRQDO8QLYHUVLW\%XVDQ5HSXEOLFRI.RUHD
HSDUWPHQWRI*UHHQ&KHPLFDO(QJLQHHULQJ6LOODD8QLYHUVLW\%XVDQ5HSXEOLFRI.RUHD
2UFLG, V

&RUUHVSRQGLQJDXWKRU

Abstract

Copper smelting slag is an industrial by-product obtained from the process of smelting copper, and about 1.5 million tons of smelting slag is generated annually. Since the copper smelting slag contains high content of Fe, Cu and valuable metals, interest in recycling it is increasing. The high Fe content in the copper smelting slag can be used as a high-value element that can replace the foundry pig iron. Therefore, this study was intended to recover Fe-Cu alloy from the copper smelting slag by a high-temperature reduction method. To this end, the basic properties and thermodynamic reaction behaviors of the copper smelting slag were examined, and the recovery behavior of Fe and Cu from the copper smelting slag according to reaction temperature was observed. As a result, it was confirmed that the whole of the slag should smelted to recover the Fe-Cu alloy, and that slag smelting behavior became active with increasing reaction temperature. The whole of Fe in the slag was recovered at the reaction temperature of 1600℃ and the recovery rate of Fe and Cu was increased with increasing reaction temperature.

Keywords: Copper, Slag, Smelting, Reduction, Fe-Cu alloy

INTRODUCTION

With industrial development, the treatment of industrial by-products became an issue in various industries. In the Korea's copper smelting industry, the treatment of copper smelting slag also becomes an issue, and about 2.2 tons of slag is generated from the process of smelting 1 ton of copper. [1]. In Korea, about 700,000 tons of copper is manufactured annually, indicating that about 1.5 million tons of copper smelting slag will be generated annually [2-4].

The copper smelting slag contains not only a small amount of the residual Cu which was not recovered from the smelting process but also SiO2, Al2O3, CaO, and 35-45 wt.% of Fe. In Korea, the copper smelting slag is currently being simply recycled as building aggregate and cement raw material, etc. or landfilled due to the lack of processing technology. However, since landfill sites are limited due to environmental pollution, and the use of aggregates with a large specific gravity is limited due to a large iron content in the copper smelting slag, the treatment of copper smelting slag became an issue. In addition, recycling or landfilling a slag with high content of iron and a valuable metal such as copper results in an economic loss. In recently years, several processes for recovering iron from the copper smelting slag have been proposed. For the proposed process, there are the technology of the concentration and separation of the iron components by magnetic separation, and a secondary smelting process to recover alloy phase iron by adding a reducing agent by dry smelting method. However, the magnetic separation is not effective for recovery, and the alloy recovered in the dry smelting process consumes energy for remanufacturing steel raw materials through secondary smelting due to a small amount of Cu added. Therefore, there is a lack of technology that can be commercialized by recycling the copper smelting slag [5-14].

On the other hand, a high Fe content in the copper smelting slag can be used as a high-value element that can replace foundry pig iron. Typical foundry pig iron is manufactured by adding various alloy elements depending on the application in the composition of C> 3.40% Si 1.40 to 1.80%, Mn 0.30 to 0.90%, P <0.450% and S <0.050%. 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. Recently, since there is a shortage in supply compared to the demand for foundry pig ion domestic market, the foundry pig iron is being imported from China, Russia and other countries. However, if foundry pig iron is manufactured from 1.5 million tons of copper smelting slag generated annually, the substitution effect of imported resources and the possibility of utilizing by-products are expected to be high [15-17].

Therefore, this study was conducted to manufacture Fe-Cu alloy for manufacturing foundry pig iron by separating Fe and Cu from the copper smelting slag with high content of iron by a high-temperature reduction method. The pig iron and slag recovered from copper smelting slag were analyzed by SEM-EDS (Energy Dispersive X-ray microscopy) and XRD (X-ray diffraction), respectively.

International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 2 (2018) pp. 977-982
 http://www.ripublication.com

EXPERIMENTAL METHOD AND MATERIAL

Experimental Material

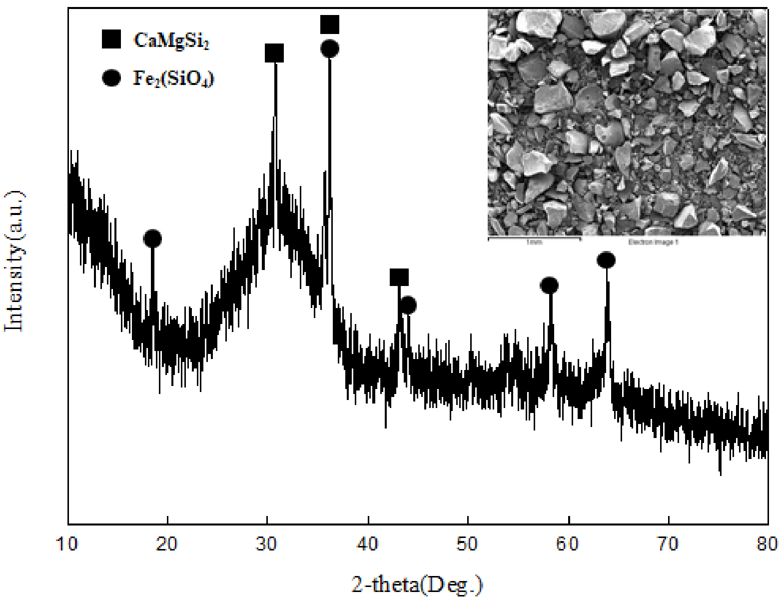
The copper smelting slag used in this experiment was a slag from a domestic copper smelter, which was generated during smelting and refining by a continuous copper smelting method. The shape and physical properties of the copper-smelting slag vary depending on the cooling method, and are classified into slow cooling slag and rapid cooling slag. Most of the copper smelters, including the domestic copper smelters, the copper smelting slag is treated through a water granulation process. 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 chemical composition and 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. Since most of the copper smelting slag forms an oxide phase, XRF oxide composition analysis was performed to examine the most stable oxide phase composition ratio. The content of Fe_2O_3, SiO_2, and CaO, which are typical components of the copper smelting slag formed by the continuous copper smelting process, were about 75%, and the Fe content was about 38%.

Experimental Apparatus

Fig. 2 is a schematic diagram of a high-frequency induction melting furnace used in this experiment. The high frequency induction melting furnace consists of chiller, controller and heater. The chiller keeps the total temperature of the high frequency induction furnace below 30°C. To cool the high frequency induction furnace, a large amount of distilled water is injected into the chiller through the water-cooled tube of the high frequency induction furnace, the high frequency induction heating furnace is rotated, the heated cooling water is returned to the cooling unit, and the heat is released through the upper fan. 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. The heater is an induction furnace using a heating method by high frequency induction, and the experimental process temperature of 1600°C can be reached within 1 minute depending on the voltage.

Fig. 3 is a schematic diagram of a box furnace where high frequency induction is generated. It was designed to facilitate charging from the top, and the charging area was a high frequency magnetic field area. To block the external oxidizing atmosphere, U.H.P Ar gas was charged into the box furnace to maintain an inert atmosphere. The high frequency induction coil is a method of inducing eddy currents to the conductor for heating, and in this study, a graphite crucible was used as the conductor.



Element	Weight %
Fe_2O_3	38.51
SiO_2	21.17
CaO	16.25
Al_2O_3	7.75
ZnO	6.27
MgO	2.61
CuO	2.09
MnO	1.34
P_2O_5	1.11
Na_2O	1.02
TiO_2	0.72
K_2O	0.58
Cr_2O_3	0.58

Figure 1. XRD patterns and chemical composition of copper smelting slag

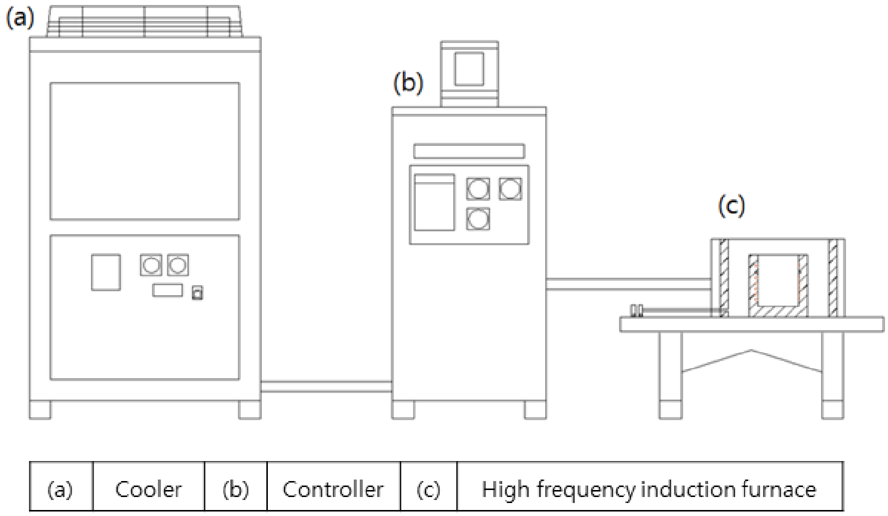


Figure 2. High frequency induction melting furnace apparatus for recovery of Fe, Cu from copper smelting slag

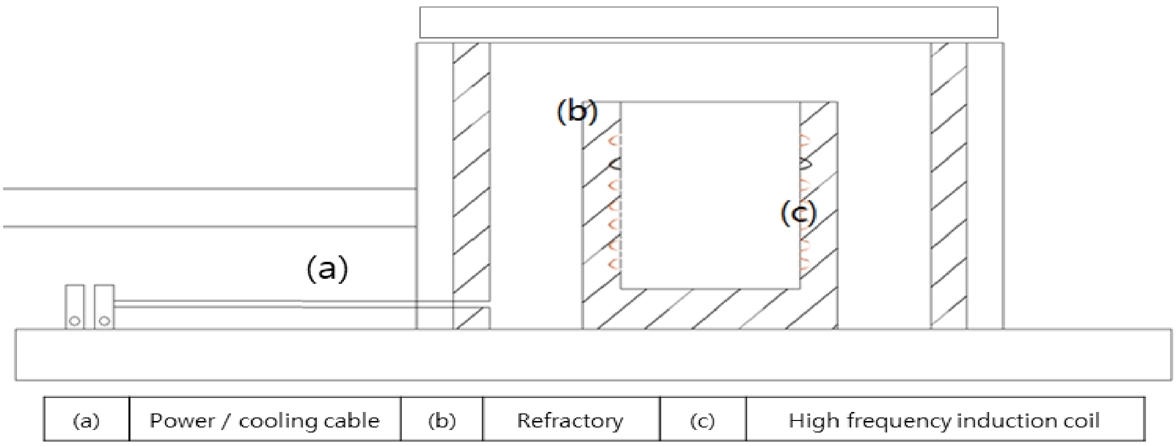


Figure 3. Experimental apparatus for High frequency induction meting

RESULTS AND DISCUSSION

Theoretical Considerations

In this experiment, Fe and Cu contained in the copper smelting slag were recovered to separate the pig iron and the slag. To separate and recover Fe and Cu in oxide state from copper smelting slag, coke was used as a reducing agent, and iron oxide and copper oxide were reduced to a metal phase. Since the copper smelting slag is in an amorphous phase, the Fe component in the slag also does not show an exact oxide phase. Therefore, the thermodynamic feasibility of this study was reviewed based on Fe_2O_3, which is the most stable iron oxide phase. In this study, SiO_2 and CaO were considered to be the most stable oxides in slag. The copper smelting slag used in this study consists of Fe_2O_3, SiO_2, CaO, etc., which affect the melting point, physical and chemical properties of the slag. As shown in Fig.4, the physical properties according to the state diagram were confirmed by predicting the content of Fe_2O_3, SiO_2, and CaO as a ternary system, and the melting point according to the composition was confirmed to be about 1400°C.

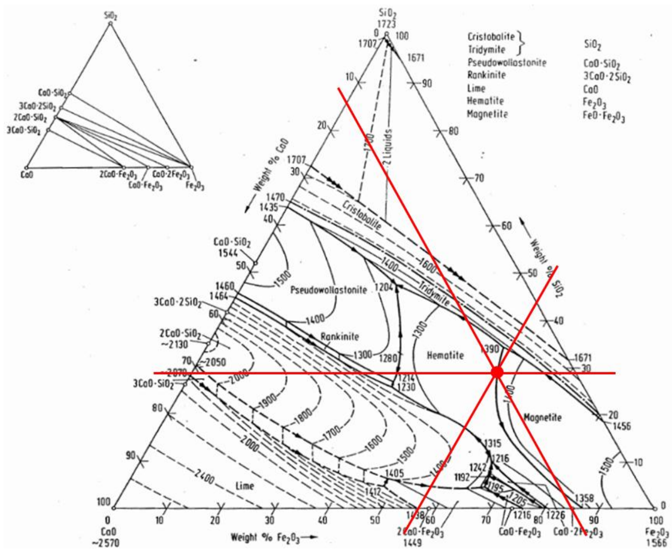


Figure 4. Fe_2O_3-SiO_2-CaO phase diagram

Table 1 below shows the behavior of the reduction reaction between Fe, Cu, Si, Ca, Al and carbon as a reducing agent. It was confirmed that Cu oxide could be reduced to metal phase by carbon across the entire temperature range and that the Fe oxide and the oxides constituting the slag of SiO_2, CaO and Al_2O_3 could not be reduced at temperature 700℃ and 1600℃, respectively. Therefore, in this experiment, the pig iron was separated from the copper smelting slag at the temperature range of 1300 ℃ to 1600 ℃ according to the melting point of the slag and the reduction behavior of the elements constituting the slag. Activated carbon was used as a reducing agent, and the reaction time was fixed to 30 minutes while the carbon equivalent was fixed to 1.5. Fe and Cu formed in a metal phase by reduction are separated by the specific gravity difference with slag consisting of SiO_2, CaO, Al_2O_3, etc., and the slag with a relatively specific gravity floats on the molten metal. Therefore, the pig iron and slag were separated from the copper smelting slag by the high-temperature smelting reduction method. The recovery behavior of Fe and Cu was examined by analyzing the chemical composition of the recovered pig iron and slag after cooling.

Table 1. Gibb's free energy changes of the carbon reduction reaction in the copper smelting slag components

	Fe2O3 + 3C = 2Fe + 3CO(g)			CuO + C = Cu + CO(g)			SiO2 + 2C = Si + 2CO(g)			CaO + C = Ca + CO(g)			Al2O3 + 3C = 2Al + 3CO(g)		
T C	deltaH kcal	deltaS cal/K	deltaG kcal	deltaH kcal	deltaS cal/K	deltaG kcal	deltaH kcal	deltaS cal/K	deltaG kcal	deltaH kcal	deltaS cal/K	deltaG kcal	deltaH kcal	deltaS cal/K	deltaG kcal
0.000	117.370	129.509	81.995	10.794	43.497	-1.087	164.748	85.934	141.275	125.296	46.586	112.571	321.024	138.190	283.277
100.000	117.413	129.693	69.018	10.816	43.581	-5.446	165.062	86.942	132.619	125.350	46.772	107.897	321.672	140.260	269.334
200.000	117.001	128.731	56.092	10.698	43.304	-9.792	165.092	87.024	123.916	125.267	46.579	103.229	321.808	140.603	255.282
300.000	116.321	127.432	43.283	10.490	42.908	-14.103	164.914	86.690	115.228	125.133	46.322	98.584	321.570	140.157	241.240
400.000	115.475	126.074	30.608	10.222	42.478	-18.372	164.572	86.142	106.585	124.991	46.094	93.963	321.114	139.425	227.259
500.000	114.532	124.771	18.066	9.916	42.054	-22.599	164.088	85.474	98.004	125.075	46.213	89.346	320.590	138.700	213.354
600.000	113.528	123.549	5.651	9.585	41.653	-26.784	163.361	84.594	89.498	124.972	46.087	84.731	320.077	138.076	199.516
700.000	112.533	122.467	-6.646	9.240	41.279	-30.930	162.914	84.110	81.063	124.928	46.039	80.126	324.654	142.975	185.518
800.000	112.489	122.424	-18.890	8.887	40.933	-35.041	162.445	83.651	72.675	124.947	46.057	75.521	324.007	142.342	171.252
900.000	112.072	122.054	-31.115	8.532	40.617	-39.118	161.464	82.760	64.374	126.944	47.850	70.809	323.308	141.720	157.049
1000.000	111.677	121.744	-43.322	8.183	40.332	-43.165	160.949	82.339	56.119	126.815	47.744	66.030	322.567	141.114	142.908
1100.000	110.773	121.061	-55.462	11.012	42.408	-47.221	160.431	81.947	47.905	126.676	47.639	61.260	321.791	140.527	128.826
1200.000	109.887	120.438	-67.536	10.635	42.144	-51.448	159.910	81.581	39.729	126.526	47.534	56.502	320.982	139.959	114.802
1300.000	109.020	119.868	-79.551	-1.605	33.989	-55.075	159.389	81.238	31.588	126.364	47.428	51.754	320.144	139.409	100.833
1400.000	108.586	119.586	-91.500	-2.186	33.631	-58.456	158.868	80.918	23.481	126.190	47.320	47.016	319.280	138.876	86.919
1500.000	107.862	119.166	-103.437	-2.768	33.293	-61.802	170.303	87.712	14.777	126.001	47.211	42.290	318.392	138.361	73.058
1600.000	113.614	122.346	-115.558	-3.350	32.974	-65.115	169.725	87.395	6.022	125.797	47.098	37.574	317.481	137.861	59.247
1700.000	112.673	121.856	-127.768	-3.933	32.671	-68.398	169.140	87.090	-2.702	125.576	46.984	32.870	316.549	137.376	45.485
1800.000	111.730	121.390	-139.930	-4.517	32.382	-71.650	166.051	85.548	-11.303	125.340	46.867	28.178	315.595	136.905	31.771
1900.000	110.782	120.944	-152.046	-5.102	32.107	-74.874	165.182	85.139	-19.837	125.087	46.748	23.497	314.622	136.446	18.104
2000.000	109.831	120.516	-164.119	-5.688	31.843	-78.072	164.311	84.747	-28.331	124.819	46.627	18.828	313.629	136.000	4.481

In this experiment, pig iron and slag containing Fe and Cu and slag in the copper smelting slag were separated. 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 SiO_2, CaO, Al_2O_3, etc. by specific gravity difference with the slag. The recovery behavior of Fe and Cu was observed according to the reaction temperature changes at 1300℃, 1400℃, 1500℃ and 1600℃ under the same coke ratio and reaction time.

Fig. 5 shows the smelting behavior of slag and its product with increasing reaction temperature at 1300℃, 1400℃, 1500℃ and 1600℃. 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% 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. The recovered pig iron weighed 8.2g, 13.1g and 22.6g, respectively, and the recovery weight was about 31%, 50% and 86%, respectively. The recovery rate of pig iron varied greatly depending on the reaction temperature.

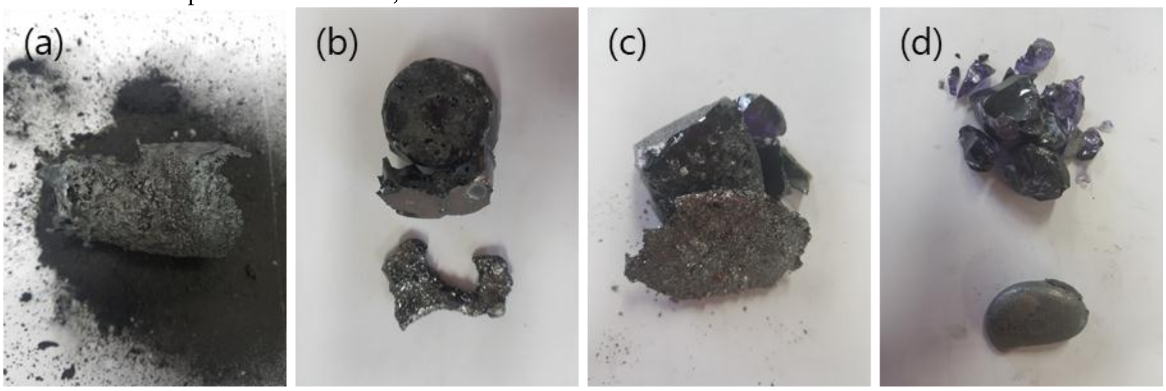
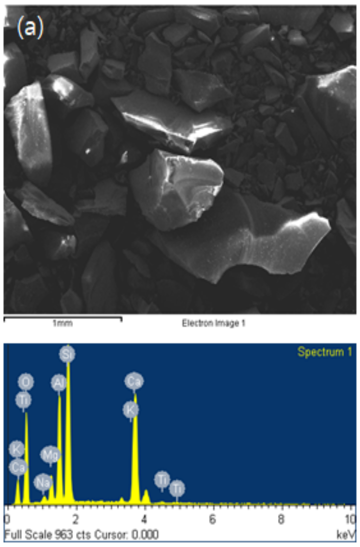


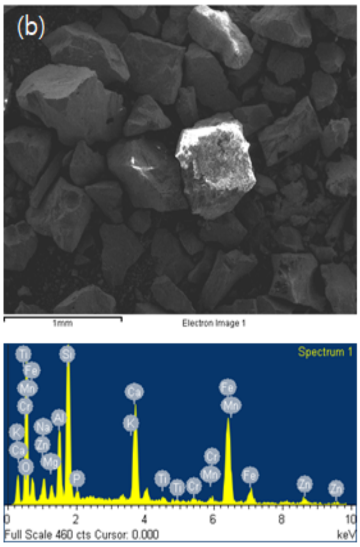
Figure 5. Smelting behavior of slag according to reaction temperature (a) 1300℃, (b) 1400℃, (c) 1500℃, and (d) 1600℃

Fig. 6 shows SEM- EDS results of the chemical composition of the slag in a glassy shape recovered from 100g copper smelting slag by high-temperature reduction at a reaction temperature of 1600°C and the slag in sponge shape which was not smelted at a reaction temperature of 1400°C. The main components are Si, Ca and Al slag, and it was confirmed that the whole of glassy slag was reduced and separated from slag. In addition, the slag in a sponge shape without being smelted and adhered at a high temperature contained about 22.87 wt.% of Fe. In the solid slag, Fe was not separated from the slag. These results indicated that the whole of slag should be smelted to recover Fe content in the copper smelting slag.

Table. 2 shows SEM-EDS 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 condition. It was confirmed that there was no significant difference 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. Table. 3 shows the SEM-EDS results of the chemical composition of the 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℃, 1500℃ and 1600℃, the Fe content in the slag was decreased to 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.



Element	Weight. %
O	50.47
Na	1.04
Mg	2.93
Al	10.01
Si	17.03
K	0.46
Ca	17.74
Ti	0.33



Element	Weight. %
O	39.52
Na	2.14
Mg	1.42
Al	5.53
Si	12.58
P	0.94
K	0.46
Ca	9.53
Ti	0.54
Cr	0.54
Mn	0.86
Fe	22.87
Zn	3.07

Figure 6. Slag recovered by high-temperature reduction of 100g copper smelting slag at the reaction temperature of 1400°C (a) Glassy slag, (b) Solid slag

Table 2. Analysis 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 condition

Element	Reaction temperature	Si	P	Cr	Mn	Fe	Cu
Weight. %	1400℃	5.53	3.84	1.33	1.43	84.75	3.11
	1500℃	4.09	4.00	0.99	1.12	86.17	3.62
	1600℃	2.94	4.62	1.25	0.81	87.45	2.93

Table. 3. Analysis results of the chemical composition of the slag separated from copper smelting slag by high temperature reduction according to the change of reaction temperature condition

Element	Reaction temperature	O	Na	Mg	Al	Si	K	Ca	Ti	Fe
Weight. %	1400℃	42.41	1.26	1.90	6.92	15.43	0.33	14.16	0.31	17.28
	1500℃	44.23	1.16	2.08	7.89	16.57	0.60	15.25	0.51	11.71
	1600℃	49.16	1.08	2.83	9.82	18.57	0.46	17.52	0.56	-

CONCLUSION

This basic study for recovering Fe and Cu contained in copper smelting slag was intended to manufacture the pig iron by reducing valuable metal in the copper smelting slag and separating it from the slag at the same time. 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. The main components of the copper smelting slag were SiO_2, CaO, Fe_2O_3, and the thermodynamic reaction behavior was predicted based on this. Based on the smelting behavior and the thermodynamic reaction of slag, the reaction temperature conditions were divided into 1300℃, 1400℃, 1500℃ and 1600℃. At the reaction temperature of below 1,400 ℃, the whole copper smelting slag was not smelted, and some agglomerated, showing a mass in a sponge form. In addition, since a large Fe content remained inside, it was confirmed that the whole of the slag should be smelted to recover Fe from the copper smelting slag. At the temperature of 1500℃, the whole of the slag was smelted but about 11.71 wt.% of Fe remained. To increase the reduction reactivity and fluidity of the slag, experiments were conducted at the temperature of 1600℃. No Fe was detected in the slag recovered at the reaction temperature of 1600℃, and the pig iron recovered under the above conditions showed the recovery rate of about 86% Finally, Fe-Cu alloy for casting was manufactured by separating the Fe and Cu in the copper smelting slag from the slag by high-temperature smelting reduction method.

ACKNOWLEDGEMENT

This research was supported by the Ministry of Trade, Industry and Energy(MOTIE), KOREA, through the Education Program for Creative and Industrial Convergence(Grant Number N0000717).

REFERENCE

[1] Bipra Gorai, R.K. Jana, Premchand, 2003: Characteristics and utilisation of copper slag –- a review, Resourcesm Conservation and Recycling 39, pp. 299-313.

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

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

[4] S.W. Ji and C.H. Seo, “"The application of copper smelting slag as concrete aggregate”", J. of the Korean Recycled Construction Resources Institute 2 (2006) 68.

[5] Huiting Shen, E. Forssberg, 2003: An overview of recovery of metals from slag, Waste Managment, 23, pp. 933-949.

[6] Norrgran, D., Wernham, J., 1991: Recycling and secondary recovery applications using an eddy-current separator. Miner. Metall. Process. 11, pp. 184-187.

[7] Yucel, O., Addemir, O., Tekin, A., Nizamoglu, S., 1992: Recovery of cobalt from copper slags, Miner. Process. Extr. Metall. Rev. 10(1), pp. 93-99.

[8] Agrawal, A., Sahoo, K.L., Ghosh, S., Pandey, B.D., 2007: United states patent 2007/0283785 A1. Busolic, D., Parada, F., Parra, R., Sanchez, M., Palacios, J.,

[9] Yucel,O., Sahin, F., Sirin, B., Addemir, O., 1999: A reduction study of copper slag in DC arc furnace. Scand. J. Metall. 28(3), pp. 93-99.

[10] Ke-qing Li, Shuo Ping, Hong-yu Wang, Wen Ni, Recovery of iron from copper slag by deep reduction and magnetic beneficiation, International Journal of Minerals, Metallurgy, and Materials, November 2013, Volume 20, Issue 11, pp 1035–1041

[11] Banza, A., Gock, E., kongolo, K., 2002: Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction. Hydrometallurgy 67, pp 63-69.

[12] Veasey, T., 1997: An overview of metals recycling by phisical separation methods. Proc. Inst. Mech. Eng. E J. Process Mech. Eng. 211(1), pp. 61-64.

[13] Hino, M., 2011: Recovery of iron from copper flash smelting slags. Miner. Process. Extr. Metall. (Trans. Inst. Min. Metall. C) 120(1), pp. 32-36.

[14] Gyurov, S., Kostova, Y., Klitcheva, G., Ilinkina, A., 2011: Themal decomposition of pyro-metallurgical copper slag by oxidation in synthetic air. Waste Manag. Res. 29(2), pp. 157-164.

[15] Jung Ho Heo, Yongsug Chung, Joo Hyun Park, Recovery of iron and removal of hazardous elements from waste copper slag via a novel aluminothermic smelting reduction (ASR) process, Journal of Cleaner Production, Volume 137, 20 November 2016, Pages 777-787

[16] Jeon Jun Ya, Current Foundry Pig Iron and Impurities of Steel Scrap, Effect of High Purity Pig Iron on Casting Property, Journal of Korea Foundry Society, v.28 no.2, 2008, pp.52 - 56

[17] Takashi Noda, Kohei Taniguchi, Masaru Fukuda, Development and Utility of High Purity Pig Iron on Foundry Material, Journal of Korea Foundry Society, v.31 no.4, 2011, pp.175 - 179