

EFFECTS OF VARIOUS SLAG SYSTEMS ON METAL/SLAG SEPARATION OF CCA AND SLAG COMPOSITION ON DESULFURIZATION AND DEPHOSPHORIZATION OF IRON NUGGET

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Keywords: carbon composite agglomerate, desulfurization, dephosphorization, metal-slag separation

Abstract

The reduction experiment of iron ore containing high Alumina content with petroleum coke was carried out in the temperature range of 1673 to 1773K by changing the slag composition. The sulfur and phosphorous content in the reduced iron nugget were measured to investigate the desulfurization and dephosphorization behavior during the reduction. The mineralogy of iron ore and additives to the carbon composite agglomerate (CCA) highly influenced on not only the reduction itself but also the melting, carburization, metal-slag separation, desulfurization and dephosphorization. High basicity of slag retarded the melting of CCA and the metal-slag separation, but enhanced sulfur and phosphorous removal degrees in the separated metal.

Introduction

Low grade irons containing high magnetite and alumina content had not been considered as main sources for conventional iron making process before the depletion of high grade lump ores became a significant issue. In particular, the low grade iron ores cannot be used for blast furnace iron making process by several problems.[1,2] Some iron making processes such as MIDREX, HYL III and rotary kiln have abilities to adopt low grade ores to produce direct reduced iron for electric arc furnace (EAF) operation. But, reducing iron ore of high alumina content is still a challenge even the processed.[3]

Compared to blast furnace process, the process for direct reduced iron can adopt the slag composition in the generous range. The usage of high basicity slag for the reduction of carbon composite iron containing high alumina content was proposed in RHF process.[4] The effect of high basicity slag with high alumina content on the CCA reduction and the metal-slag separation was also investigated.[4,5] It has been known that the high basicity of slag has an advantage to remove sulfur and phosphorous in the reduced iron.[6]

In this study, high basicity slag was adopted to reduce the high alumina containing CCA to investigate the melting, carburization, desulphurization and dephosphorization behaviors in the experiment carried out in the temperature range of 1673K to 1773K.

Sample preparation

As a representative high alumina iron ore, the limonitic laterite iron ore of high alumina and low silica was used. For the reducing carbon source, a petroleum coke of low ash was adopted. The iron ore and the coke were crushed and sieved into powders in the size range of 100~150 μ m. Their chemical composition are shown in the **Tables 1** and **2**, respectively.

Table 1. Chemical composition of limonitic laterite ore used in the present study (mass%).

	T.Fe	Fe ²⁺	M.Fe	SiO ₂	Al ₂ O ₃	Ni	P	S
Limonitic Laterite	42.52	0.42	-	5.11	7.80	1.5	0.03	1.58

Table 2. Chemical composition of petroleum coke used in the lab scale test.

Proximate analysis (mass%)				Ultimate analysis (mass%)				
VM	FC	Ash	IM	C	H	N	S	O
10.97	87.7	0.06	0.68	87.25	3.70	1.03	5.73	2.29

The iron ore mainly contains Al₂O₃ and SiO₂ which would form Al₂O₃-SiO₂ based slag which might have high melting temperature. To control the melting temperature, specific amounts of CaO and SiO₂ were added into the iron ore so that the expected final slag compositions would have low melting temperatures in the CaO-SiO₂-Al₂O₃ slag system. The coke adopted in the experiment contains high sulfur content and low ash content. The high sulfur content in the coke increased the total sulfur content in the CCA and the total sulfur content was used as the initial value to measure desulfurization degree in the iron nugget after the reduction experiment. By adjusting the total basicity and fixing C/O ratio, 4 kinds of CCAs with different mixing condition were prepared for the experiment as shown in **Table 3**.

Table 3. Mixing conditions of the pellets with various slag systems.

	Ore (g)	Petro coke (g)	CaO (g)	SiO ₂ (g)	Al ₂ O ₃ (g)
CCA_origin	3.0	0.47	-	-	-
CCA_A	3.0	0.47	0.36	0.81	-
CCA_B	3.0	0.47	0.47	0.32	-
CCA_C	3.0	0.47	0.18	0.02	-
CCA_D	3.0	0.47	1.21	-	0.73

The slag melting behaviors of the expected chemical compositions induced by the mixing conditions were predicted based on FactSage data base in **Table 4**. [7]

Table 4. Slag liquefying temperatures of samples

	Liquid formation starting temperature (K)	Fully liquefied temperature (K)
CCA_origin	1870	-
CCA_A	1460	1535
CCA_B	1532	1580
CCA_C	1668	1687
CCA_D	1603	1691

In short, CCA_A and CCA_B have lower melting temperatures than CCA_C and CCA_D due to their own chemical compositions.

Experimental Procedure

5g of the each CCA was put into a graphite crucible and heated up to the target temperature in the range of 1673K to 1773K in the air and held for 5, 10, 15 and 20 minutes to observe the melting and reduction behaviors for the given time at the given temperature. After the reaction, the sample was quenched by high purity Argon gas to reduce the change for the further reaction during the cooling. The carbon, sulfur and phosphorus contents in the iron nugget which was separated from the slag were analyzed to analyze the carburization, desulfurization and dephosphorization degree in the reduction process. The slag composition also was analyzed by X-ray fluorescence spectrometry.

Metal-Slag Separation with Different Slag Composition

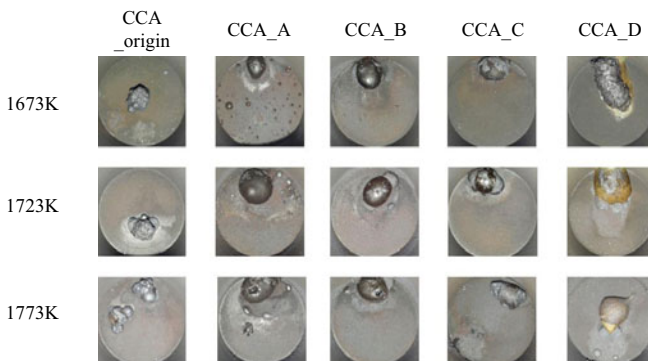


Fig.1. Images of CCAs of different slag compositions with different reaction temperatures

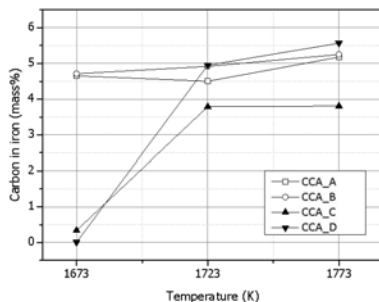


Fig.2. Effect of temperature and slag composition on the carbon content in iron nugget

Figure 1 shows the images of CCAs after the reductions at the given temperatures. Compared to the CCA without additives, the other CCAs showed relatively promoted metal-slag separation behaviors at any temperature. But, at low temperature (1673K), CCA_C and CCA_D showed relatively poor metal-slag separation which might be induced by their high slag melting temperatures as shown in **Table 4**. In detail, the CaO-Al₂O₃ based slag has a high melting temperature than the CaO-SiO₂ based slag, so the direct contact between carbon and reduced iron is retarded by the less liquefied slag.[5] **Figure 2** shows the carbon content change in the iron nuggets depending on the reaction temperatures and slag compositions. As expected from the metal-slag separation behaviors, the carbon content in the iron nuggets obtained from CCA_C and CCA_D at 1673K were particularly lower than those of the other cases. It shows that the metal-slag separation behavior is nicely correlated with the carburization degree of the iron nugget.[5]

During the reduction of CCA and the carburization of iron nugget, an intermediate iron oxide, namely FeO, can be formed. Because of the SiO₂ additions to CCA_A, B and C, they had chance to allow the formation of fayalite (2FeO·SiO₂) which has a low melting temperature of 1483K. [8] To clarify the effect of FeO on the metal-slag separation, the metal-slag separations of the CCAs for given reaction times at 1723K were observed as in **fig.3**. And the FeO contents in the separated slags were measured as in **fig.4**. CCA_D showed the poor metal-slag separation until 10 minutes and it might be induced by the rapid decrease of FeO content.

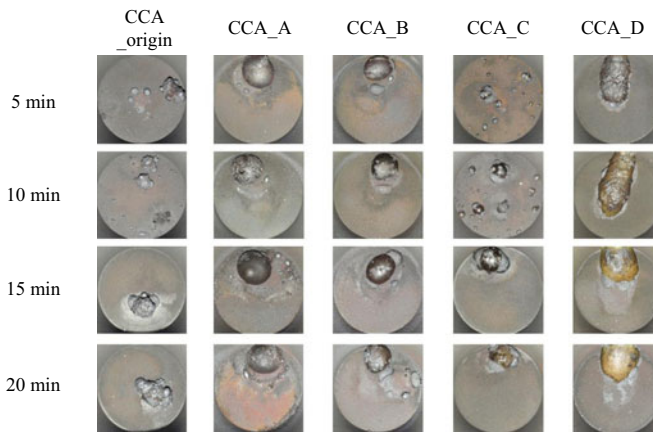


Fig.3. Images of CCAs of different slag compositions with different reaction times at 1723K

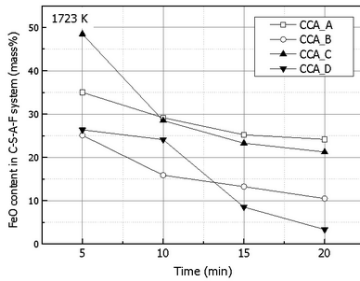


Fig.4. FeO content of separated slags with different reaction times at 1723K.

Desulfurization and Dephosphorization Behaviors in CCA Reduction

The sulfur content in the iron nugget separated from the slag was analyzed. The iron nugget without additives (from CCA_origin) shows the highest sulfur content among the reduced iron nuggets in **fig.5**. Interestingly, the lowest sulfur content was obtained from the iron nugget separated from the CCA_D which has the highest CaO content, i.e, the highest basicity. This results corresponds the well-known fact that the high basicity induces the high desulfurization degree

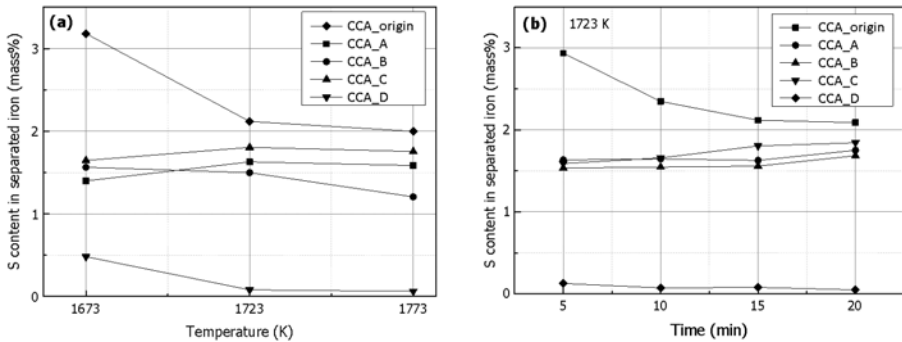


Fig.5. Sulfur content in separated iron nugget at given reaction temperatures and times

In terms of the phosphorus content, similar to the sulfur content, the high basicity induced the effective dephosphorization degree in the iron nugget as shown in **fig.6**. In detail, the phosphorus removal degrees of CCA_B and CCA_D reach at 80%~90%. The degree is much higher than that of any conventional process.[9]

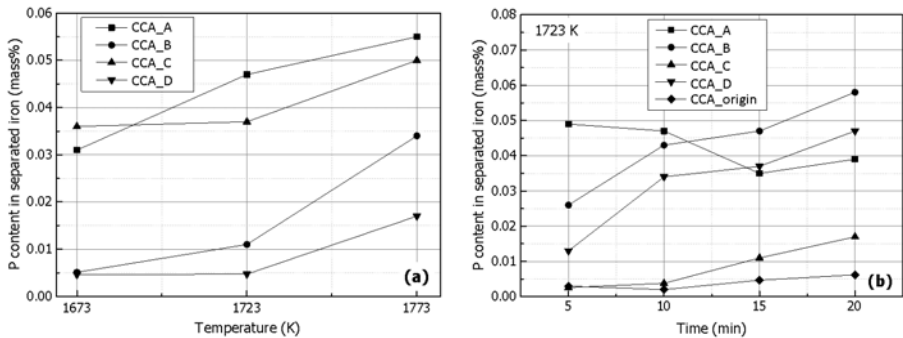


Fig.6. Sulfur content in separated iron nugget at given reaction temperatures and times

Conclusions

From the experimental results, the following conclusions were obtained:

- (1) Iron nugget separated from slag was successfully produced by direct reduction of high alumina containing iron ore with coke of high sulfur and ash.
- (2) The high basicity of slag retarded the metal-slag separation due to the high melting temperature, but, the desulfurization degree is much higher than the other slag compositions.
- (3) More than 80% of the initial phosphorus could be removed from the iron nugget by reducing the high basicity CCA at 1723K.

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