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HIGH Al_2O_3 IRON ORE REDUCTION BY EFFECTIVE USE OF HIGH BASICITY SLAG[1]

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Abstract

To meet the increase of iron ore price and depletion of high grade iron ores, low grade iron ores such as high Al_2O_3 containing iron ore will be forced to use soon. But it is hard to use high Al_2O_3 containing ore for BF process because it deteriorates cold strength and RDI of sinter. Also, high Al_2O_3 in ore increases slag volume and viscosity if we stick to the conventional slag composition. Thus, to effectively use high Al_2O_3 contained ore, a new concept to decrease slag volume and decrease of viscosity is required. To meet this demand, the application of ultra high basicity slag ($CaO-Al_2O_3$ based slag) is investigated in the present study. The in-situ observation of the separation behavior between a high basicity slag, iron and graphite assembly in a small scale experiments by using a confocal laser scanning microscope(CLSM) as well as the relatively large size of pellet with high basicity slag were carried out. The clear slag/metal separation was observed at the temperature around 1350°C. Also, it was confirmed by relatively large pellet experiments that small amount of solid fraction is allowed for metal/slag separation. These results strongly suggest that the application of the ultra high basicity slag can be the plausible alternative approach to use high Al_2O_3 content iron ore in the ironmaking process.

Key words: High Al_2O_3 iron ore; Metal/slag separation; Wetting; Direct reduction.

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1 INTRODUCTION

Due to its high thermal efficiency and production capacity, blast furnaces are widely used to produce pig iron at integrated steel plants. In the conventional blast furnace operation, however, it is hard to utilize high Al_2O_3 containing-iron ores. In the sintering process, the low fluidity due to the high Al_2O_3 produces uneven sinter ore properties in the sintering bed, and the increase of Al_2O_3 tends to produce coarse calcium ferrite phase which brings bonding strength degradation and RDI degradation. In the blast furnace operation, high Al_2O_3 content in the slag causes poor slag charging due to its high viscosity and increase of slag volume as well. For example, despite of the reasonable amount of Fe_2O_3 content, laterite is not utilized as an iron resource due to its high Al_2O_3 content. Thus, to extensively use high Al_2O_3-containing iron ore, alternative slag design must be developed. In DRI process, the slag composition is not so demanding compared with that of BF process. Thus, at this moment, the direct reduction process will be the one of the choice to effectively use high Al_2O_3-containing iron ore. In coal-based direct reduction processes, fine iron ore and coal are agglomerated in the form of carbon composite agglomerate (CCA), and this CCA is reduced to iron by using a rotary hearth furnace or rotary kiln.

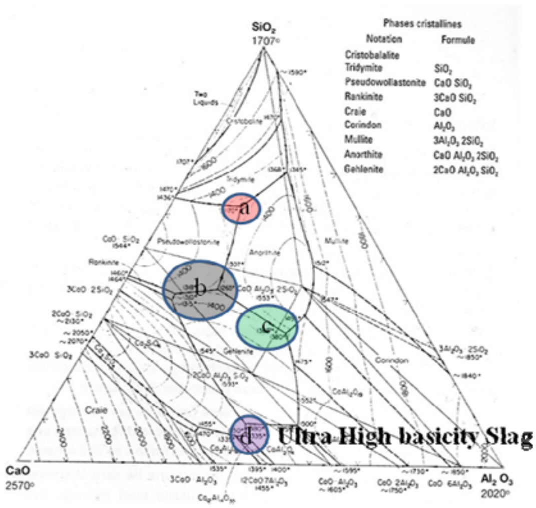

Figure 1 Slag compositions used for direct reduction processes (a), (b) and (c), and ultra high basicity slag(d) for high Al_2O_3 ore direct reduction.

In the CCA reduction process, the good slag/metal separation is practically important to avoid the extra cost and time for their separation. In coal-based direct reduction processes using low Al_2O_3 iron ore, the finally formed slag compositions are in the region of ‘a’, ‘b’ and ‘c’ shown in Fig. 1 due to their low melting temperature and the ease of slag composition control. Consequently, the coal-based direct reduction behaviors with the slag composition ‘a’, ‘b’ and ‘c’ have been extensively studied.(1-6) However, these slag compositions are not suitable for using low Al_2O_3 iron ore.

Among the high Al_2O_3 iron ores, some of them contain low SiO_2 content. If we want to use these high Al_2O_3 containing iron ores, high basicity slag (CaO-Al_2O_3-based slag) composition of ‘d’ region will be much more beneficial than those of ‘a’, ‘b’ and ‘c’ because of small amount of requiring additives and its low slag melting temperature. It

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has been also found that viscosity with the high basicity slag's composition of 'd' region are comparable to those of 'a', 'b' and 'c' regions.(1)

The coal-based direct reduction process consists of several steps of iron ore reduction, iron carburization & melting, slag melting and slag/metal separation. These steps with the slag region 'a', 'b' and 'c' were extensively studied. Ohno et al.(2) investigated the effect of slag/metal separation depending on slag melting temperature and viscosity with slag 'b' and 'c'. Nogueira et al.(3) compared iron/slag separation between low melting temperature slag 'a' and some other high melting temperature slag. He observed the clear slag/metal separation behavior in low melting temperature compared with poor separation in the other case. Recently, Kim, Kim and Sasaki(4) and Kim et al.(7) studied about the role of liquid phase for the enhancement of melting and reduction of CCA by in-situ observation of wetting/separation behavior in the slag composition 'a'.

But none of them focused on the slag 'd' which can be one of the plausible solutions to use high Al_2O_3 ore for the direct reduction of CCA. Although Ono, Tanizawa and Usui(8) studied the rate of iron carburization by carbon in slag through carbon/slag and slag/metal reactions at 1450°C using 'd' slag composition, they didn't focus on direct carburization between carbon and iron which is much faster and thus much more important in iron/slag separation than carburization through slag.

In the present study, as a first step to effectively use high Al_2O_3 iron ore, the role of ultra high basicity slag on the wetting and slag/metal separation behaviors in CCA pellet were investigated.

2 EXPERIMENTAL - MATERIALS AND METHODS

Synthetic slag was prepared by melting cold pressed mixture of chemical grade CaO, Al_2O_3 and SiO_2 pellet at 1500°C with Ar atmosphere. After holding for 24 hours at 1500°C, the molten slag was quenched by pouring to a Cu plate to make glassy materials and X-ray fluorescence analysis was used to confirm the slag composition. Compositions of the synthetic slag were shown in Table 1. A particular type of high Al_2O_3 with low SiO_2 iron ore contains some amount of Cr_2O_3. To find the effect of Cr_2O_3 on slag/metal separation behavior, 1, 2 and 4 mass% of Cr_2O_3 was added in slag C1, slag C2 and slag C4 respectively. Generally, Cr_2O_3 increases melting temperature of the $CaO-SiO_2-Al_2O_3$ based slag as shown in Table 1.

Table 1 Composition of synthetic slag

Sample	Content(mass %)					Melting T(°C) (Calculated)
	CaO	SiO_2	Al_2O_3	Cr_2O_3	CaO/SiO_2	
Slag C0	52.0	6.6	41.4	0	7.9	1376.76
Slag C1	51.5	6.5	41.0	1	7.9	1371.34
Slag C2	50.9	6.5	40.6	2	7.9	1468.26
Slag C4	49.9	6.3	39.8	4	7.9	1581.04

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For the in-situ observation of metal/slag wetting and separation behavior, the same method used by Kim, Kim and Sasaki(4) was used. Iron disks (Diameter: 1.0 mm, Thickness: 0.5mm) were prepared by polishing a sliced iron block from an iron rod. Graphite disks (Diameter: 1.0 mm, Thickness: 0.5mm) were prepared by punching a graphite plate. A piece of slag C0 or slag C1 was placed between iron and graphite disk as shown in Figure 2. The bottom of the Al_2O_3 crucible was coated with boron nitride in order to eliminate the interaction between sample and the crucible surface. In-situ observation of the interaction between iron, high basicity slag and graphite at high temperature was carried out by using a confocal laser scanning microscope (CLSM) combined with an image furnace. The sample was heated up to 1400°C at a heating rate of 200°C/min under purified Ar atmosphere. The behaviors of samples were recorded at a frame rate of 15 frame/sec.

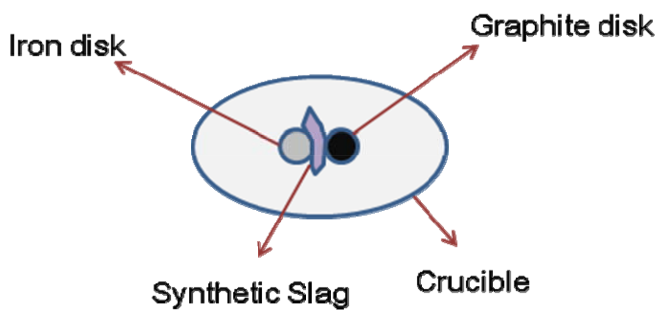

Figure 2 Schematic for the sample assembly.

The wetting and slag/metal separation behavior is found to be strongly influenced by the surface tension of slags and metals.(4,5) The effect of the surface tension is dominant in a small scale, but it is decreased with the size. Thus, to evaluate the size effect on the slag/metal separation, the observation of the melting behavior using a large size pellet mixed with slag, Fe and graphite powders were carried out. The pellet with 5mm diameter was produced by cold pressing 0.05g mixture of iron powder(~150um), synthetic slag(45~100um) and graphite powder(~50um). The slag mixing ratio to iron was fixed to 0.61, and the carbon mixing ratio to iron was set to 1,3,5 and 10 based on one real ore composition. At the experiments with the pellets, slag samples of C0, C1, C2 and C4 were used. The pellet was heated to 1100°C at a 300°C/min rate and 1500°C at a 75°C/min rate in the image furnace under purified Ar atmosphere. The melting and separation behavior was investigated by the CLSM in-situ observation.

3 RESULTS AND DISCUSSION

Figure 3 shows wetting and separation behavior between iron disk, graphite disk and high basicity slag C0 at 1400°C. Once slag starts to melt, good wettability between molten slag and solid iron was shown in Figure 1 (b) and (c). This wetting induced the contact between graphite and the solid iron is carburized by the introduced direct contact with graphite. By this carburization process, iron melting temperature decreases so that the iron melting started before the temperature reached to the melting point of pure iron. After iron melting, the molten iron and slag were separated as shown in Figure 1 (d).

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Similar experiments were carried out at 1350°C or using slag C1 but all the cases showed the same results with that of C0. These results were similar with the results reported by Kim, Kim and Sasaki.(4) From these results, it was confirmed that iron/slag wetting and separation with high basicity slag occurred without difficulties (Slag composition of 'd' in Figure 1).

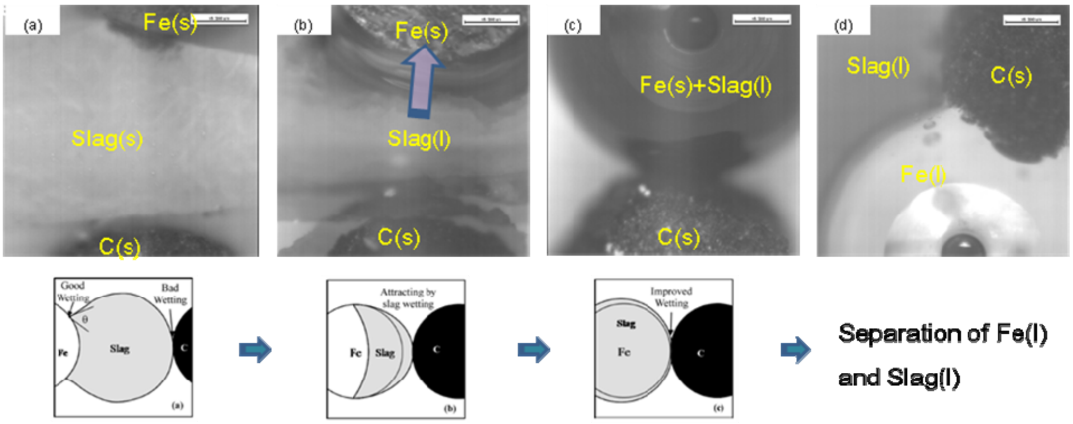

Figure 3 Wetting and separation behavior between high basicity slag, iron disk and graphite disk observed by CONFOCAL.

For the pellet samples, slower heating rate than the previous 200°C/min was used to see the temperature dependence on the metal/slag separation. Since iron does not melt at the temperature under 1100°C, the sample behaviors at temperature from 1100°C to 1400°C were mainly observed. No metal/slag separation was observed for the samples with the carbon mixing ratio 1 or 3 possibly due to the lack of carburizing source. Although small amount of iron melting was observed at around 1150°C by direct carburization, most of part was still remained as solid state even at 1400°C. As a result, the pellet maintained their shape throughout the experiments and no separation between slag and iron was observed. On the other hand, the separation was clearly observed at higher carbon mixing samples (5mass% and 10mass%).

Figure 4 shows iron melting and slag/metal separation behavior of 5mass% carbon mixing pellet. At around 1150°C, the iron started to melt by carburization. With increase of temperature, the slag started to melt and consequently dispersed molten iron sphere entrapped in unmolten solid slag merged together to form large iron sphere. Finally, iron and slag was separated as shown in the last image of Figure 4. There was almost no difference between 5mass% and 10mass% carbon mixing samples in the separation behavior. The only difference was that the iron surface after the experiment was contaminated by unreacted carbon in the case of 10mass% carbon mixing sample due to the excess graphite. The mixing of 5mass% to iron seems to be enough for the separation.

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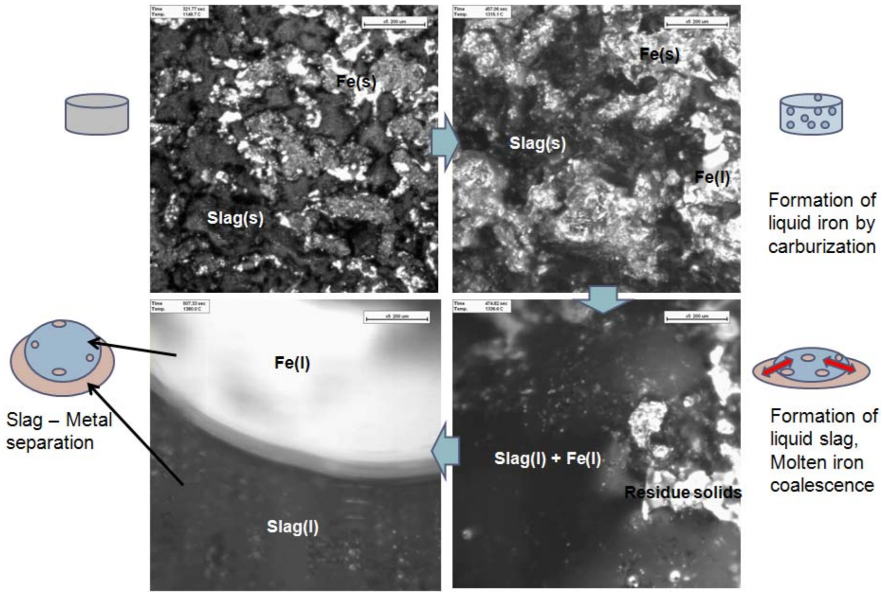

Figure 4 Iron melting and slag/metal separation behavior of 5wt% carbon mixing pellet.

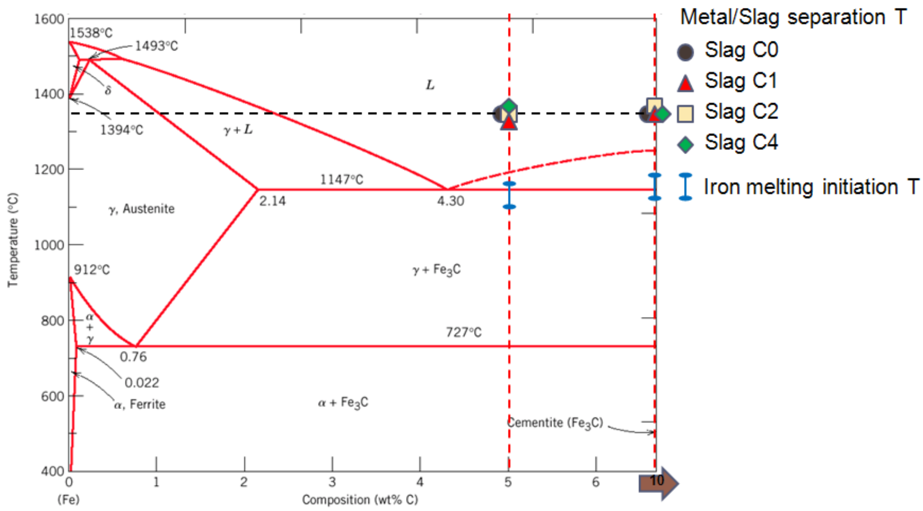

Figure 5. Iron melting initiation temperature and metal/slag separation temperature.

The temperature of iron melting initiation and metal/slag separation temperature were plotted in Figure 5. It is obvious that iron melting initiation temperature has no relation with the carbon mixing ratio or slag composition. The intriguing thing is that metal/slag separation temperature was almost the same regardless of Cr_2O_3 content (or melting temperature of Cr_2O_3 containing slag). It is because Cr_2O_3 forms very small amount of solid fraction throughout the experimental condition so that the effect on the slag viscosity or liquid fraction is negligible. The separation took place even before the temperature reaches slag melting temperature. The result tells that not a full state of melting is required for the metal/slag separation which is well agreed with Ohno's result.[2)] In the all experiments, the separation temperature was found to be 1350°C.

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4 CONCLUSIONS

In the present study, the role of CaO-Al_2O_3 based-slag system with high basicity, low melting temperature and low viscosity on the CCA melting behavior was investigated to utilize high Al_2O_3 containing fine ore. CLSM combined with image furnace was used to observe the behaviors of iron melting by carbon and wetting/separation behavior between synthetic high basicity slag, graphite and iron assembly. Iron melting and separation of molten iron/slag using the high basicity slag system were confirmed by in-situ observation. To evaluate the size effect, the melting behavior of a relatively large size pellet (mixture of high basicity slag, Fe powder and graphite powder) of 5 mm dia. was investigated. The clear slag/metal separation was also observed at the temperature around 1350^{o}C. It was also found that the full melting of the slag was not necessary for the slag/metal separation, or a small amount of solid fraction in the molten slag did not affect the metal/slag separation. All these results indicate that high Al_2O_3 iron ore can be effectively used as a new iron resource by applying CaO-Al_2O_3 based slag.

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