THE EFFECT OF INITIAL MELT FORMATION ON THE REDUCIBILITY OF IRON ORE AGGLOMERATES¹

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Abstract

In order to utilize the lower quality of iron ore with high Al_2O_3 content, it is important to understand the effect of Al_2O_3 in iron ore agglomerates on their reducibility. The iron ore agglomerates(tablet type) of FeO-CaO-SiO₂-Al₂O₃ were synthesized for the reduction experiments under 30v01%CO- $70v01\%N_2$ gas mixture from 1000 to $1200^{\circ}C$ in the rate of 5°C/min, in which Al_2O_3 content was changed from 0 to 4 mass%. The reducibility in the higher temperature region (> $1100^{\circ}C$) deteriorates by increasing Al_2O_3 content. In-situ observations of the melt formation of slag in artificial iron ore agglomerates were conducted by using the scanning laser microscope mounted with the heating device. It was found that the main cause is the blockage of gas diffusion into the unreacted region of tablet due to the initial melt of oxide which occupies the micro pores in the tablet. The temperature of initial melt formation decreases and the amount of melt increases with increasing Al_2O_3 content. The deterioration of reducibility is thus explained by the formation of a molten oxide and its penetration to the micro pores in an unreacted region.

Key words: Iron ore agglomerate; Reducibility; FeO-CaO-SiO₂-Al₂O₃ system; Al₂O₃ content; Initial melt formation.

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Increasing reducibility of iron ore agglomerates is essential in order to reduce both the energy consumption and the CO_2 emission in the ironmaking process. However, in recent, the degradation in raw materials, especially the increase of Al_2O_3 content in iron ore, enormously deteriorates the reducibility of the agglomerates in the softening and melting zones, which is around 1100°C and above in a blast furnace (see Figure1).^[1,2] It is inferred that the increase in Al_2O_3 content promotes the formation of liquid oxide in the agglomerate to prevent the reduction of agglomerates.

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Present study undertakes to make the quantitative analysis on the effect of Al_2O_3 content of the iron ore agglomerates both on the reducibility of the agglomerates and on the initial melt formation by the reduction experiments and the in-situ observation with the scanning laser microscope.

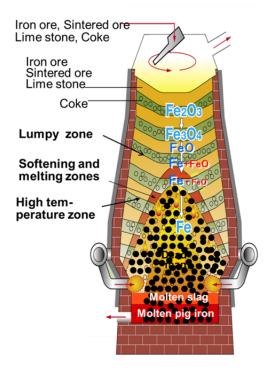


Figure 1. Cross-sectional layout of a blast furnace.

2 EXPERIMENTAL

A reagent grade of CaO, SiO₂, and Al₂O₃ powders were mixed together to be melted at 1600°C under Ar gas atmosphere. The average composition of the oxide is listed in Table 1. Solidified oxides was crushed into fine powder(50-100 μ m) which was then mixed with a reagent grade of Fe₂O₃ powder to be pressed with 100MPa for 3 minutes, finally sintered at 1050°C under the air as the iron ore agglomerates (tablet type sample, 14mm in diameter and 6mm in height, see Figure 2).

The arrangement of the reduction experimental apparatus is shown in Figure 3. After measuring the weight, the sample was hung with a platinum chain in the reduction furnace. Pre-reduction experiments from Fe_2O_3 to FeO were carried out at 900°C under 50vol%CO-50vol%CO₂, which corresponds to the higher temperature of lumpy zone in the blast furnace. After heated to 1000°C in N₂ gas atmosphere, reduction experiments from FeO to Fe were conducted under 30vol%CO-70vol%N₂



until 1200°C in the rate of 5°C/min. The heating hysteresis and the gas compositions are shown in Figure 4.

Table 1. Chemical composition of artificial iron ore sample (%Al₂O₃=0, 2, and 4)

Sample	Composition (mass%)			
	FeO	CaO	SiO ₂	Al ₂ O ₃
FCSA0	80	10	10	0
FCSA2	80	9	9	2
FCSA4	80	8	8	4

Mixture of CaO-SiO₂-Al₂O₃ reagent powders

Pre-melt at 1600°C under Ar atmosphere

·Crush pre-melt slag into powders of 50 \sim 100 μm

•Mixture of Fe₂O₃ reagent powders (80%FeO) and 20%Slag powders

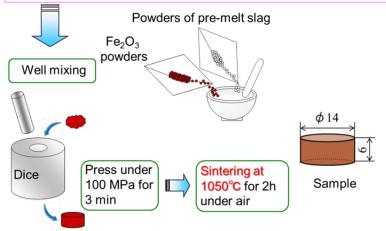


Figure 2. Making the artificial iron ore agglomerate (tablet type sample).

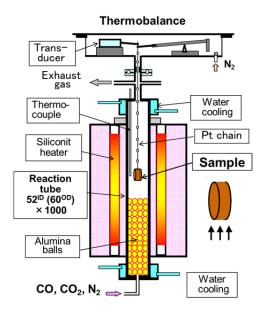
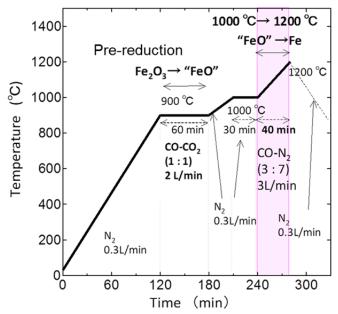


Figure 3. Schematic layout of the reduction furnace.



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Figure 4. Heating pattern of the iron ore agglomerate sample at the reduction experiment.

In-situ observation was performed from 1000 to 1350°C in the rate of 5°C/min under Ar gas atmosphere by using the scanning laser microscope equipped with the heating device as shown in Figure 5. The samples (4mm in diameter, 0.7mm in height), of which chemical compositions are listed in Table 1, were put on steel plate to prevent the reaction with alumina crucible.

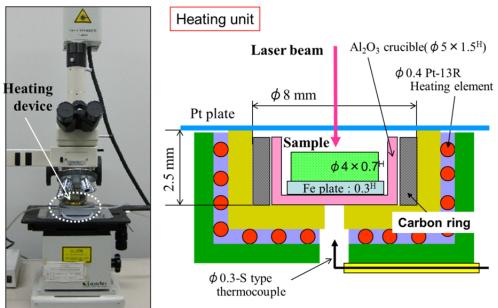


Figure 5. Scanning laser microscope equipped with the heating device.

3 RESULTS AND DISCUSSION

The effect of Al_2O_3 content on the reducibility of the iron ore agglomerates is shown in Figure 6. In case of FCSA0 ($(Al_2O_3=0)$) the reduction curve does not exhibit a saturated tendency up to 1200°C, while the reduction rates in cases of FCSA2 ($(Al_2O_3=2)$) and FCSA4 ($(Al_2O_3=4)$) tend to decelerate at higher temperature range

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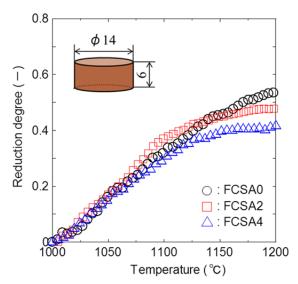


Figure 6. Effect of AI_2O_3 content on the reducibility of iron ore agglomerates.

Figure 7 shows the microstructure of the iron ore agglomerate observed by SEM after pre-reduction to FeO at 900°C under 50%CO-50%CO₂. Slag particles are seen in the wustite matrix. In a magnified picture, the many fine pores are observed in the wustite matrix. The porosity after pre-reduction is about 0.3. Figure 8 shows the microstructure of FCSA2 (%Al₂O₃=2) after reduction up to 1200°C under 30%CO-70%N₂. Reduction degree is 0.48 at 1200°C. Most of the micro pores between particles in (b) interface and (c) center (unreacted region) are filled with the initial melt. It is confirmed that reduction was prevented by initial melt formation in an unreacted region.

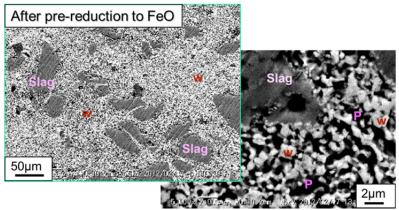
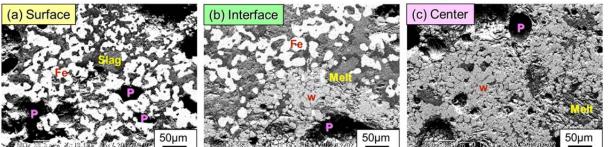


Figure 7. Microstructure of artificial iron ore agglomerate after pre-reduction to FeO at $900^{\circ}C$ under $50\%CO-50\%CO_2$.(FCSA4, w: wustite, P: pore)



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Figure 8. Microstructure of artificial iron ore agglomerate after reduction up to 1200°C under 30%CO-70%N₂ (FCSA2, w: wustite, P: pore)).

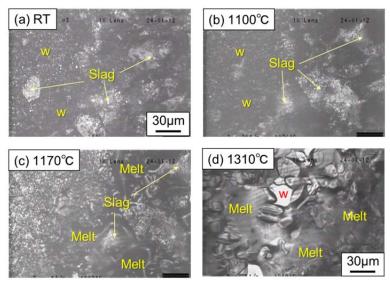


Figure 9. Real images of melt formation by in-situ observation (FCSA2, w: wustite)

The real images of melt formation taken at the in-situ observation with the scanning laser microscope are shown in Figure 9. Melt formation is clearly observed at 1170°C. The melt penetrates between oxide particles to fill the pores.

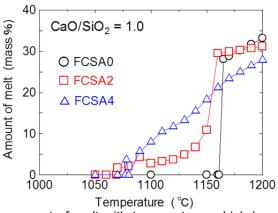


Figure 10. Change of the amount of melt with temperature, which is calculated with FactSage and confirmed by the in-situ observation.

The influence of Al_2O_3 content on the amount of melt formed during temperature rising is shown in Figure 10. The thermodynamic calculation results by FactSage,^[4] and the in-situ observation results are in consistent for the present experimental condition of FCSA4 system.^[5] In case of FCSA0 (%Al₂O₃=0), the melt forms at around

1160°C immediately. On the other hand, the temperature of initial melt decreases and the amount of melt increases with increasing AI_2O_3 content (FCSA2 and FCSA4).

Taking account of these results obtained, it is clear that the increasing in AI_2O_3 content of iron ore agglomerate promotes the oxide melt formation in the unreacted region which decreases the reducibility by penetrating into the micro pores of agglomerate to prevent the diffusion of reduction gas into the agglomerate.

4 CONCLUSIONS

The effect of AI_2O_3 content on the reducibility of the iron ore agglomerates was investigated by the reduction experiments and the in-situ observation with the scanning laser microscope.

It was found that (1) the reducibility of the agglomerates in high temperature region (>1100°C) deteriorates with increasing AI_2O_3 content, (2) temperature of initial melt formation decreases and the amount of melt increases as AI_2O_3 content of the agglomerates increases, and (3) the initial melt of oxide penetrates into the micro pores in the agglomerates to block the gas diffusion in the unreacted region of the sample.

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