RAPID REDUCTION OF NANO-SIZE IRON ORE PARTICLES IN AN IRON ORE/CARBON COMPOSITE

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Summary

Feeding an iron ore/carbon composite (IOC) in addition to conventional sintered ore and coke to the blast furnace is expected to be a method to decrease CO_2 emission by increasing the efficiency of iron making. The authors have recently found that the reduction rate of nano-size Fe_2O_3 particles in the composite of nano-size Fe_2O_3 particles and a kind of carbon is reduced at temperatures as low as 600°C. In this paper the reduction behavior of the nano-size Fe_2O_3 particles dispersed in the carbon matrix was examined to clarify the reduction mechanism and to estimate possible minimum reduction temperature.

Keywords

Sustainability, CO2 reduction, Iron ore/Carbon composite, Nano materials for iron making

Introduction

To increase the efficiency of blast furnace iron making is one of great issues for decreasing CO_2 emission in the steel industry of Japan. Feeding of an iron ore/carbon composite (IOC) in addition to conventional sintered ore and coke to the blast furnace is expected to be one of methods to increase the efficiency. In the blast furnace iron ore is reduced by the following reactions:

$$FeO_x + C \rightarrow FeO_{x-1} + CO \quad (1)$$

$$FeO_x + CO \rightarrow FeO_{x-1} + CO_2 \quad (2)$$

$$C + CO_2 \rightarrow 2CO \quad (3)$$

Reaction (1) is the reduction of FeO_x by carbon (direct reduction), reaction (2) is the reduction of FeO_x by CO (indirect reduction), and reaction (3) is the so called carbon loss reaction. These reactions are expected to be enhanced using the IOC composite, which reduces the operation temperature of blast furnace and hence increases the efficiency of ironmaking[1]. However, the mechanism of the rate enhancement is not completely clarified[2, 3, 4], and hence how low the operation temperature can be decreased is unknown.

The authors have recently found that the reduction rate of nano-size Fe_2O_3 particles in the composite of nano-size Fe_2O_3 particles and a kind of carbon is reduced at temperatures as low as 600°C[5]. In this paper the reduction behavior of the nano-size Fe_2O_3 particles dispersed in the carbon matrix was examined to clarify the reduction mechanism and to estimate the minimum reduction temperature.

Experimental

Sample preparation. IOC composite samples were prepared from reagent grade Fe_2O_3 particles (Sigma-Aldrich Co.) of 10-70 nm in diameter (abbreviated to Nano-Fe_2O_3)and 150-300 μm in diameter (Micro-Fe_2O_3) and an ion-exchange resin (Mitsubishi Chemicals Co. Ltd, DIAION WK11; abbreviated to Resin). The Fe_2O_3 particles mixed with the ion exchange resin by the weight ratio of 12 to 88 (abbreviated to Nano-Fe_2O_3/Resin and Micro-Fe_2O_3/Resin) were heated to 500°C in an inert atmosphere during which the resin softens, melts, and is carbonized to form an amorphous carbon. This treatment is expected to realize intimate contact of Fe_2O_3 particles and the amorphous carbon. For comparison purpose, the Fe_2O_3 particles mixed with the Resin precarbonized at 500°C (abbreviated to Coke) by the weight ratio of 58 to 42 were also prepared. They were abbreviated to Nano-Fe_2O_3/Coke and Micro-Fe_2O_3/Coke.

Reduction experiment. About 20 mg of the composite was heated at the rate of 10 K/min up to 1350 ºC in a helium atmosphere using a thermobalance (Shimadzu, TG-50H). The weight change was continuously measured by the thermobalance, and the product gas was analyzed for CO and CO_2 using a micro gas chromatograph (GL Science Co. Ltd, Micro GC CP 4900). The reduction rate of Fe_2O_3 (RR) was calculated from the amounts of CO and CO_2 formed.

***In-situ* XRD measurement and TEM observation.** To directly observe the progress of the reduction of the IOC composite samples, *in-situ* XRD measurements were performed using an X-ray diffractometer (RIGAKU Co. Ltd, Ultima IV) which can scan at the rate of 10 degree/min. The reduction behavior of Nano- Fe_2O_3/Resin and Fe_2O_3 particles of 10-70 nm were also analyzed in a CO atmosphere and an atmosphere containing CO and CO_2 by the ratio of 85 to 15. TEM observations were also made for the IOC composite samples in the process of reduction by a transmission electron microscope (JEOL Co. Ltd, JEM-1010).

Results and Discussion

Reduction behavior of IOC in an inert atmosphere. Fig.1 shows the RR profiles estimated by the reduction experiments for the four IOC composite samples prepared. The RR profiles were significantly different among the samples. Nano-Fe_2O_3/Resin was surprisingly completely reduced at as low as 550 - 650 ºC in a single step. This reduction temperature range is 400 - 500 ºC lower than the temperature range in conventional blast furnace. The ratio of the formation rates of CO to CO_2 was 85 to 15 at600 ºC at which the reduction rate reached a maximum. Nano-

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Fe_2O_3/Coke and Micro-Fe_2O_3/Resin were reduced in three steps ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$) as reported in the literature, but at much lower temperatures. The RR profile of Micro-Fe_2O_3/Coke shifted to higher temperature range than the other three composite samples. These results indicate that the RR profiles are affected by both the particle size of Fe_2O_3 and the contact state of Fe_2O_3 and carbon. It was clarified that the reduction temperature of iron ore can be decreased to as low as 650 ºC by minimizing the particle size of iron ore and by realizing intimate contact between iron ore particles and carbon.

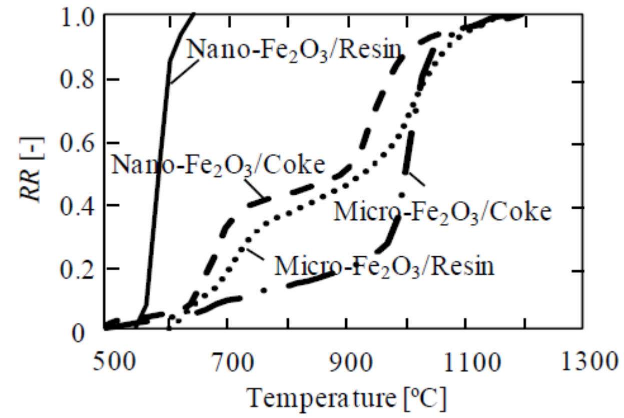

Fig. 1 Reduction profile of four IOC samples

***In-situ* XRD measurement and TEM observation.** *In-situ* XRD measurement during the reduction of Nano-Fe_2O_3/Resin in an inert atmosphere clearly and directly showed that the Fe_2O_3 particles in the composite are completely reduced to Fe at as low as 630 ºC, confirming the RR profile shown in Fig.2.

Fig. 2 shows the TEM photos at different stages of reduction for Nano-Fe_2O_3/Resin. It is clearly shown that Nano-Fe_2O_3 particles are completely and evenly covered by amorphous carbon layers of about 2 nm thick at 500 ºC at which the Fe_2O_3 particles are not reduced. At 580 ºC some of the nano size particles are still covered by the amorphous carbon layers but FeO_x particles larger than the original Fe_2O_3 particles and spherical hollow spaces that were presumed to be occupied by the nano Fe_2O_3 particles also exist. At 900 ºC at which the reduction is completed, the only large Fe particles formed by the reduction and agglomeration of the nano Fe_2O_3 particles exist.

Reduction behavior of Nano-Fe_2O_3/Resin and Nano-Fe_2O_3 in reducing gas atmosphere. The above results suggest that the rapid reduction of the Nano-Fe_2O_3 particles in Nano-Fe_2O_3/Resin is presumed to be realized by the enhancement of the direct reduction reaction (1). To examine the reduction mechanism in more detail, reduction behavior of Nano-Fe_2O_3/Resin and Nano-Fe_2O_3 particles were investigated by the *in-situ* XRD in a CO atmosphere and an atmosphere containing CO and CO_2 by the ratio of 85 to 15. **Table 1** summarizes the change of oxidation state of Fe_2O_3 particles in the samples with the increase of temperature. Fe_3C which is dissolving carbon inside is judged to be completely reduced state. In reducing gas atmospheres Nano-Fe_2O_3 particles them-selves were reduced at temperatures even lower than the Nano-Fe_2O_3 particles in Nano-Fe_2O_3/Resin were reduced, indicating that the rate of the indirect reduction reaction (2) is much faster than the direct reduction reaction (1). The reduction rate of Nano-Fe_2O_3 particles in Nano-Fe_2O_3/Resin was interestingly fastest in the inert atmosphere. This is because CO retards both reactions (1) and (3) both of which are carbon loss reactions. These results suggest that the reduction of the Nano-Fe_2O_3

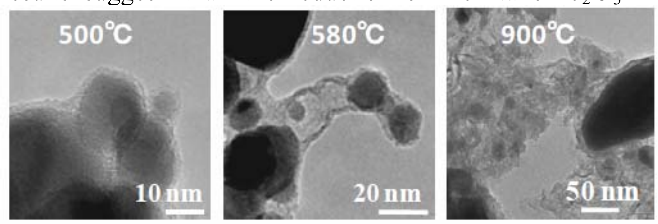

Fig. 2 Photos of at different stages of reduction for Nano-Fe_2O_3/Resin

Table 1 Change of oxidation state of Fe_2O_3 particles in the samples with the increase of temperature

Atmosphere	Sample	Temperature [ºC] 400	500	600	700	900
He	Nano-Fe_2O_3	Fe_3O_4	←		→	Fe_3O_4
	Fe_2O_3/Resin	Fe_3O_4	Fe_3O_4	Fe	Fe	Fe
CO 100 %	Nano-Fe_2O_3	Fe_3O_4	Fe_3C	Fe_3C	Fe_3C	Fe_3C
	Fe_2O_3/Resin	Fe_3O_4	FeO	Fe_3C	Fe_3C	Fe_3C
CO:85 % CO_2:15%	Nano-Fe_2O_3	Fe_3C	Fe_3C	Fe_3C	Fe_3C	Fe
	Fe_2O_3/Resin	Fe_3O_4	Fe_3O_4	FeO	Fe_3C	Fe_3C

particles in Nano-Fe_2O_3/Resin was mainly controlled by the carbon loss reactions. The carbon loss reaction is well known by the catalytic effect of nano size iron oxide particles when the particles are in good contact with carbon. Therefore, the Nano-Fe_2O_3 particles in Nano-Fe_2O_3/ Resin are judged to have acted as both catalyst and reactant. More detailed discussion separating the contributions of the direct reduction reaction (1) and the indirect reduction reaction (2) will be given in the full manuscript based on the kinetic measurements of the reduction reaction.

Conclusion

It was found that the reduction rate of Fe_2O_3 in the Fe_2O_3/carbon composite is significantly enhanced by minimizing the particle size of Fe_2O_3 and realizing an intimate contact between iron ore and carbon material. This enables to reduce the reduction temperature of iron ore to as low as 630 ºC, which is expected to increase the efficiency of iron making when the concept will be realized. The reduction rate enhancement of the Fe_2O_3 particles Nano-Fe_2O_3/Resin was mainly realized by the enhancement of the carbon loss reactions.

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