REDUCTION DISINTEGRATION MECHANISM OF IRON ORE SINTER UNDER HIGH H_2 AND H_2O CONDITION AT 773K[1]

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Abstract

Reduction of CO_2 emission is recognized as an urgent issue in the iron and steel industry. One feasible method may be the utilization of H_2 gas as a reducing agent in blast furnace (BF) ironmaking. In order to keep the BF condition stable under high H_2 operation, it is necessary to understand the effect of H_2 and H_2O gas on the disintegration behavior of iron ore sinter in the upper part of a BF. Therefore, the reduction disintegration mechanism of iron ore sinter at 773 K under N_2–CO–CO_2–H_2–H_2O gas was evaluated. Reduction experiments were carried out under N_2–20%CO–20%CO_2 (0% H_2) and N_2–12%CO–17.7%CO_2–8%H_2–2.3%H_2O (8% H_2) using a 25 g sinter sample, varying the reduction time between 1.8 and 7.2 ks. Reduction degree of the sinter was calculated in terms of the mass difference between before and after the reduction. A tumbling drum test was carried out for 1.8 ks to evaluate the strength of the reduced sinter. Reduction degree of the sinter by 8% H_2 gas steadily increased with time. On the other hand, it was retarded once when reduced under 0% H_2. At the same reduction time, the reduction degree obtained by 0% H_2 showed a lower value than that by 8% H_2. At the same reduction degree, however, the RDI value of the sinter reduced by 0% H_2 gas is higher than that by 8% H_2. This is because CO gas reduction proceeds mainly near the surface of the sinter particles, while H_2 gas reduction tends to proceed inside the particles.

Key words: Hematite; Magnetite; Disintegration; Reduction; Hydrogen; Crack density.

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1 INTRODUCTION

The iron and steel industry accounts for approximately 10% of anthropogenic CO_2 emissions in the world.[1] In Japan, this value is as high as 14%, because approximately 70% of steel products are produced by integrated steel mills. The mitigation of CO_2 emissions is an urgent necessity. One priority would be to improve energy efficiency, but this has already reached its saturation level in Japan. Therefore, drastic improvement would appear to be difficult. The utilization of H_2 gas as a reducing agent in blast furnaces (BF) may be a method for resolving this problem. One potential source of H_2 in a steel plant is coke oven gas (COG). Furthermore, increase in the utilization of pulverizing coal to tuyere in BF leads to greater concentration of H_2 gas. However, reduction of iron oxide by H_2 gas is an endothermic reaction. Thus, an increase in the contribution of H_2 gas to the reduction will lead to a drastic change in the temperature distribution in BF.[2]

In addition, permeability is a key factor for the stable operation of BF,[3] which is strongly affected by the disintegration behavior of the sinter in the low-temperature region of the BF. Therefore, research has long focused on the mechanism and suppression method of sinter disintegration.[4-5] It is well known that significant disintegration under CO gas reduction occurs at approximately 800 K. The main factor of the disintegration is volumetric expansion of the iron oxide phase due to reduction from hematite to magnetite.[4] In addition, sinter is composed of hematite with various phases, which have different effects on disintegration. Furthermore, as reported by Inazumi, Shinada and Kawabe, the value of the reduction disintegration index (RDI) for skeletal hematite can reach approximately 30%.[5]

ISO 4696 lists several methods for evaluating the RDI. For example, ISO 4696–2 conveniently uses a simple reducing gas system comprising N_2–30%CO and a shorter reducing time of 1.8 ks, and ISO 4696–1 simulates the gas composition in the upper part of the BF shaft, which is set at N_2–2%H_2–20%CO–20%CO_2. Even in this method, however, H_2O is not considered as a reducing gas component. In fact, H_2O concentration will strongly affect the reduction temperature and equilibrium gas concentration through reduction of iron oxide and the water-gas-shift reaction. The authors have reported the effects of a wide range of reducing gas compositions of the CO–CO_2–H_2–H_2O system on the reduction and disintegration behavior of sinter at 773 K.[6] Reduction by CO gas led to the formation of magnetite phases with not only thick and long but also fine cracks near the surface. In contrast, H_2 reduction did not lead to the formation of a significant number of fine cracks. The weight ratio of fine particles less than 0.25 mm in size decreased with an increase in H_2 concentration. This corresponds well with crack formation behavior in sinter particles. At the same reduction degree, the reduction reaction of hematite to magnetite accelerates with the addition of low concentration H_2 gas. However, a higher H_2 gas concentration results in a lower reduction rate. This result indicates that the change in gas concentration and temperature distribution in BF greatly affects the reduction disintegration behavior of sinter. Time dependence of reduction behavior is an especially important factor. Therefore, the objective in this study is to clarify the effect of CO–H_2 concentration and reduction time on the reduction disintegration behavior of sinter at 773 K.

2 EXPERIMENTAL

The sample was crushed and sieved to grain sizes of 6.7–9.5 mm before use and found to have an RDI value of 37.6, measured according to ISO 4696–2. The chemical composition of the sinter sample is listed in Table 1. Approximately 25 particles of the sinter sample, with a total weight of 25 ± 3 g, were randomly selected and charged in the furnace, as shown in Fig. 1. The sample was heated to 773 K in a N_2 gas stream with a flow rate of 21.5 Ncm^3/s and kept for 300 s. This gas rate of 3.0 × 10^{-2} Ncm/s matches the linear velocity defined in ISO 4696–2. The sample temperature was measured using a thermocouple inserted into the furnace from the top. Subsequently, the gas was changed to a reducing gas with the same flow rate, and the reduction experiment was carried out for 3.6 ks. The reducing gas compositions were N_2–20%CO–20%CO_2 (0% H_2) and N_2–12%CO–17.7%CO_2–8%H_2–2.3%H_2O (8% H_2). The composition of CO_2 and H_2O was determined by the equilibrium condition of the water-gas-shift reaction in eq. (1) at 773 K, after fixing the concentration of CO and H_2 gas.

$$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)} \qquad (1)$$

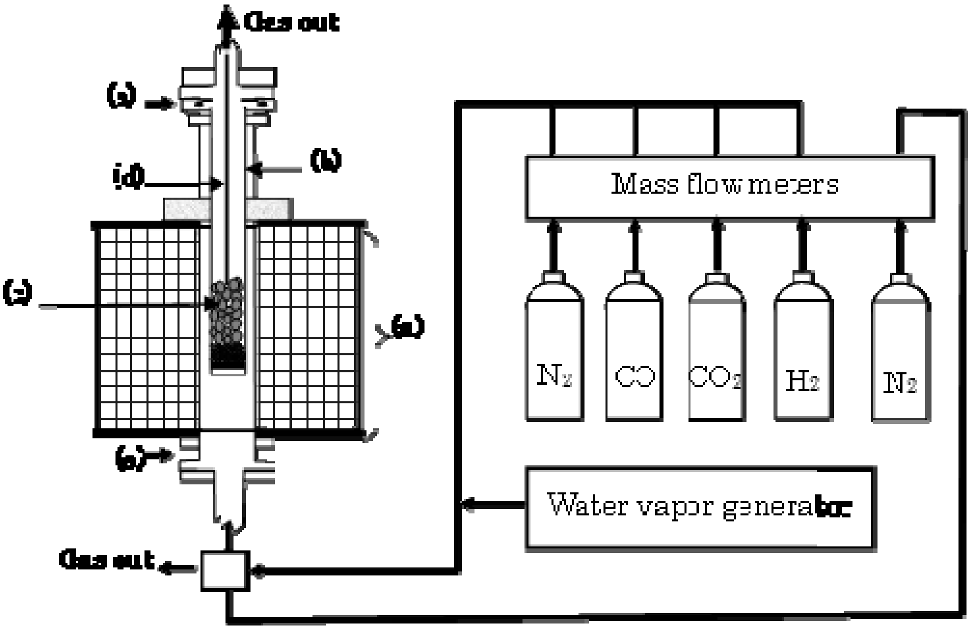

Figure 1. Schematics of experimental apparatus of reduction experiment. (a) electric furnace (b) sample holder (c) sample and alumina ball (d) thermocouple (e) cooling unit.

H_2O gas was generated by heating distilled water in the furnace at 573 K. After the reduction experiment, the gas was changed to N_2 again, and then, the reduced sample was cooled down to below 473 K. The reduction degree was then calculated from the change in weight before and after reduction.

Table 1. Chemical composition (mass%) of sinter sample

T-Fe	FeO	CaO	SiO_2	Al_2O_3	MgO	P	S	JIS-RDI
57.0	6.9	10.1	5.0	1.9	1.5	0.05	0.01	37.6

Disintegration test was conducted on the reduced samples on the basis of ISO 4696–2 using a tumbling drum with an inner diameter of 130 mm at a rotation speed of 30 rpm for 1.8 ks. Then, the sample was sieved with a 2.8 mm mesh to determine the weight of the sample with a particle size greater than 2.8 mm. The RDI value was calculated using the following equation:

$$RDI = 100 - W_1/W_0 \times 100 \qquad (2)$$

where W_0 is the weight of the sample after the reduction experiment, and W_1 is the weight of particles larger than 2.8 mm.

The particle size distribution of the sieved samples was measured. In addition, their microstructures before and after reduction were observed using an optical microscope. Quantitative analysis of phase ratio in the sinter before and after reduction was carried out by the internal standard method of X-ray diffraction (XRD) using NaF as standard material.

3 RESULTS AND DISCUSSION

3.1 Effects of H_2 Gas on Reduction and RDI

Figure 2 shows time dependence of reduction degree and RDI value of the sinter reduced by 0% H_2 and 8% H_2. The plots show the average values. Reduction degree increases with reduction time. For 0% H_2, but not for 8% H_2, increasing in the reduction reaction slows down from 30 min to 60 min. Therefore, the difference in reduction degree between 0% and 8% H_2 increases for 60 min. The reduction degree of 0% H_2 increases again from 60 min to 90 min and reaches the same value as that of 8% H_2. The RDI value of the sinter reduced under both conditions increases with reduction time. The value of 0% H_2 increases especially from 30 min to 60 min, though the reduction rate becomes slow. The RDI value of 0% H_2 is lower than that of 8% H_2, except for the reduction time of 90 min.

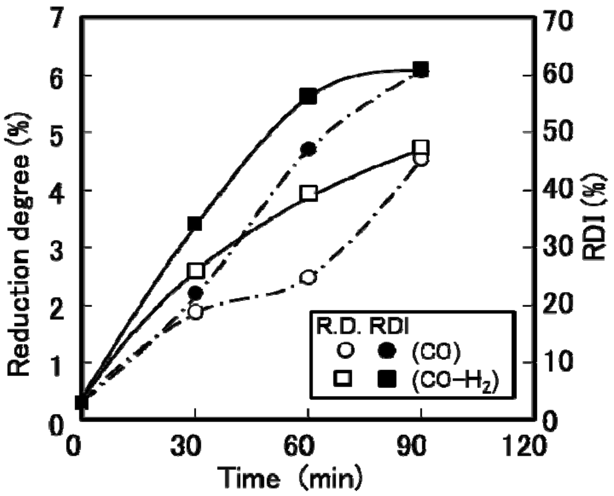

Figure 2. Effect of reduction time on reduction degree and RDI value of a sinter reduced by N_2–20% CO–20% CO_2 and N_2–8% H_2–2.3% H_2O–12% CO–17.7% CO_2.

3.2 Microstructure After Reduction and Size of the Formed Particles

Typical microstructures near the surface of the sinter after reduction with 0% H_2 and 8% H_2 for 30 min and 90 min are shown in Figure 3. The symbols “SH,” “FH,” “M,” and “CF” indicate the phases of skeletal hematite, fine hematite, magnetite, and multi-component calcium ferrite, respectively. M phases are observed around SH at all microstructures. This indicates that reduction of skeletal hematite occurs near the sinter surface under all conditions. For a 30 min reduction, a certain amount of crack is also observed. On the other hand, no progression of the reduction reaction was observed in the center of the sinter. The gas composition has little effect on the microstructure of the reduced sinter. For 60 min, the reduction reaction occurred not only at the surface but also in the center, most notably in the case of 8% H_2 reduction. This results from the fact that the reduction of skeletal hematite in the center part of the sinter, mainly by H_2, occurred because the interdiffusion coefficient of H_2/H_2O gas is three times higher than that of CO/CO_2 gas at 773K.[6] For 90 min, fine hematite was mainly reduced under both gas conditions. Reduction of fine hematite does not contribute poorly to reduction disintegration.[5] Therefore, it seems that the RDI value of 0% H_2 gradually increases, as the reduction degree rapidly increases.

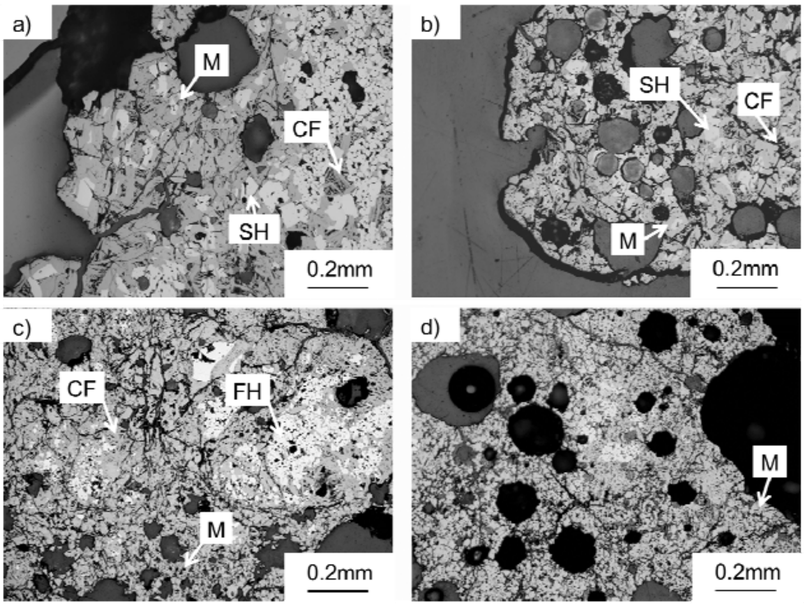

Figure 3. Microstructure of sinter reduced by N_2–20% CO–20% CO_2 and N_2–8% H_2–2.3% H_2O–12% CO–17.7% CO_2 for 1.8 and 5.4 ks. SH: Skeletal hematite, FH: Fine hematite, CF: Calcium ferrite, M: Magnetite. (a) 0% H_2 1.8 ks, (b) 8% H_2 1.8 ks, (c) 0% H_2 5.4 ks, and (d) 8% H_2 5.4 ks.

Figure 4 shows the reduction time dependence of the ratio (W/W_0) of the weight after the RDI test of the sinter sample reduced under both gas compositions to that of the sinter after reduction, for particles with sizes less than 0.25 mm, from 0.25 to 1.7 mm, and from 1.7 to 2.8 mm. Open and solid plots are the results of 0% H_2 and 8% H_2, respectively. With the reduction of 0% H_2 gas (CO–CO_2 gas system), there is no change in the particle size distribution with reduction time. On the other hand, the weight ratio of particles with sizes less than 0.25 mm decreases with reduction time, while that of particles with sizes from 0.27 to 1.7 mm increases. The reason is that few fine cracks formed in the sinter particles as a result of H_2 reduction.[6]

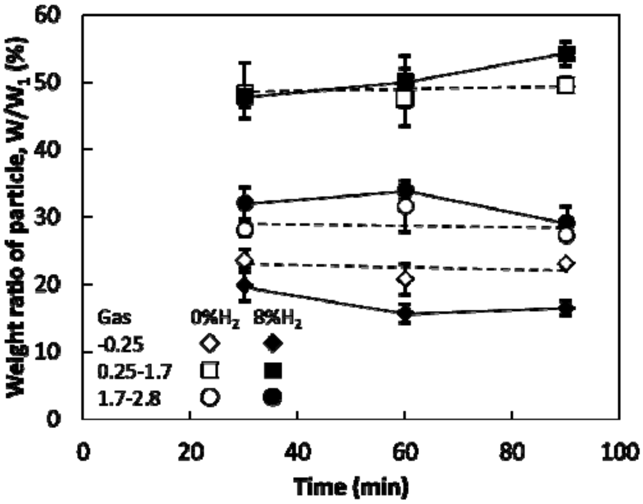

Figure 4. Change in weight ratio of particle after the RDI test of the sinter reduced by N_2–20% CO–20% CO_2 and N_2–8% H_2–2.3% H_2O–12% CO–17.7% CO_2 with reduction time.

3.3 Relation Between Disintegration and Stagnation of Reduction by 0% H_2

The RDI value increases with reduction time from 30 to 60 min, while the reduction rate slows down. After that, the reduction rate increases again. However, this trend was not found in the case of 8% H_2 reduction. To discuss the reason for this, the behavior of the formation of large cracks that reached to the center part of the sinter was estimated by microstructure observation of the cross section of the sinter sample. The large crack density was calculated from microstructural analysis using several images in each condition. The results are shown in Figure 5. The trend of change in thick crack density of the sinter reduced by 0% H_2 with time is the same as that by 8% H_2. The thick crack density increases with reduction time from 30 to 60 min, and further reduction keeps it constant. These results indicate that the crack penetrates into the center part of the sinter under each gas condition for 60 min. Consequently, the destruction of the sinter progresses for the time from 30 to 60 min, when the reduction rate by CO gas decreases, and then increases the RDI value.

The formation and growth of cracks should affect the morphology of the formed particles after the disintegration test. Figure 6 shows the change with reduction time in the ratio (W/W_0) of the weight after the RDI test of the sinter sample reduced under both gas compositions to that of the sinter after reduction, for particles with sizes less than 0.25 mm and from 1.7 to 2.8 mm. Open and solid plots are the results of 0% H_2 and 8% H_2, respectively. The weight ratio of particles with sizes from 1.7 to 2.8 mm increases with reduction time, and that obtained by 8% H_2 reduction is larger than that by 0% H_2. Furthermore, the weight of particles obtained by 8% H_2 reduction keeps constant from 60 to 90 min. This behavior is similar to that of the RDI value. The change in weight ratio of particles less than 0.25 mm with 8% H_2 reduction also shows similar behavior with that with sizes from 1.7 to 2.8 mm. With 0% H_2 reduction, on the other hand, the weight ratio of particles less than 0.25 mm increases with reduction time from 30 to 60 min, while the reduction rate lowers during this time period. This behavior can be explained in terms of the reduction of SH and the cracks formed from the stress caused by volume expansion.

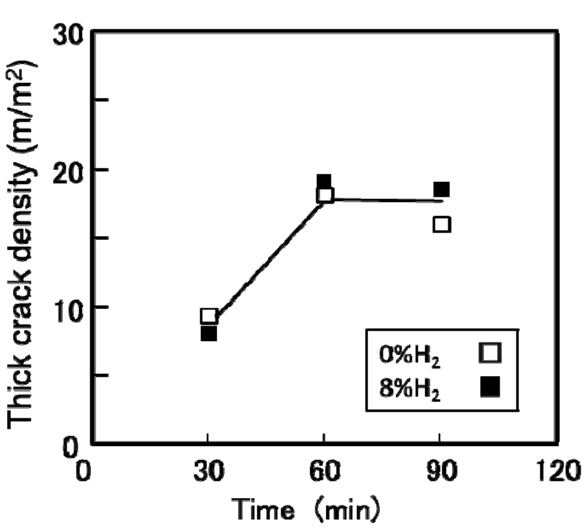

Figure 5. Change in thick crack density in the sinter reduced by N_2 - 20% CO - 20% CO_2 and N_2 - 8% H_2 - 2.3% H_2O - 12% CO - 17.7% CO_2 with reduction time.

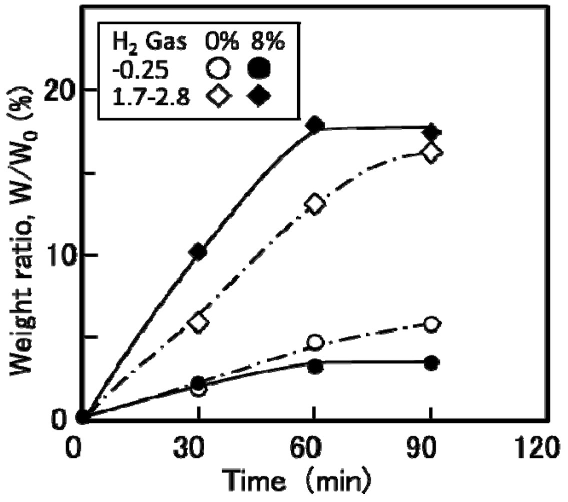

Figure 6. Effect of reduction time on the weight ratio (W/W_0) of particles after the RDI test of the sinter reduced by N_2–20% CO–20% CO_2 and N_2–8% H_2–2.3% H_2O–12% CO–17.7% CO_2.

4 CONCLUSIONS

The effect of CO–H_2 concentrations of the reducing gas and reduction time on the reduction disintegration behavior of iron ore sinter was examined. The results are summarized as follows:

- The reduction rate of sinter by CO gas without H_2 is once retarded during reduction, but even at such a stage RDI value continuously increases. This may be attributed to an increasing stress in secondary (skeletal) hematite phase, which causes the formation and growth of large cracks.
- As contrasted with CO gas reduction, reduction by H_2 proceeds not only near the surface of the sinter particles but also inside, without the formation of the fine cracks.
- The distribution of the particles formed from reduced sinter does not change with time when reduced by CO gas. When reduced by H_2 gas, on the contrary, the ratio of fine particles (- 0.25 mm) to the total weight of reduced sinter decreases but that between 0.25 and 1.7 mm increases with time.

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