Reduction Disintegration Behavior of Iron Ore Sinter under High $H_2$ and $H_2O$ Conditions

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(Received on January 13, 2012; accepted on March 6, 2012)

Reduction of CO$_2$ emissions is an important object for the iron and steel industry. One feasible method may be the utilization of $H_2$ gas as a reducing agent in the blast furnace (BF). However, for stable BF operation, it is first necessary to understand the effects of high $H_2$, and therefore high $H_2O$, concentrations in the reducing gas on the disintegration behavior of iron ore sinter, because it significantly affects the gas permeability of the upper part of the BF. In the present study, disintegration behavior of a sinter sample at 773 K for 3.6 ks under gas flow of $N_2$–CO–CO$_2$–$H_2$–$H_2O$ system was examined. The results showed a remarkable increase in the reduction degree and reduction-disintegration index (RDI) upon the addition of a small amount of $H_2$. However, further increase in the $H_2$ concentration caused these values to decrease gradually. 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 formation of a significant number of fine cracks. Image analysis of samples revealed that the crack length density showed the similar trend to RDI value. CO gas reduction mainly proceeds near the surface of sinter particles, while $H_2$ gas reduction tends to proceed inside the particles. Accordingly, reduction of $H_2$ gas gave lower RDI than CO gas to the sinter with same reduction degree.

KEY WORDS: hematite; magnetite; disintegration; reduction; hydrogen; crack density.

1. Introduction

The iron and steel industry accounts for approximately 10% of anthropogenic CO$_2$ emissions in the world. In Japan, this value is as high as 14% because approximately 70% of steel products are produced by integrated steel mills. Therefore, reduction of CO$_2$ emissions is an urgent requirement. One priority would be improvement of the energy efficiency, but it has already reached to a saturated level in Japan. Therefore, a drastic improvement seems to be difficult.

The utilization of $H_2$ gas as a reducing agent in the blast furnace (BF) may be one of the possible ways to overcome this problem. One potential source of $H_2$ in a steel plant is coke oven gas (COG). However, reduction of iron oxide by $H_2$ gas is an endothermic reaction. Thus, an increase in the contribution of $H_2$ to the reduction will lead to a drastic change in the temperature distribution in the BF.

In addition, permeability is a key factor for the stable operation of BF, which is strongly affected by the disintegration behavior of the sinter in the low-temperature region of the BF. Therefore, the mechanism and suppression method of disintegration of sinter have been the focus of research for a long time. It is well known that the disintegration under CO gas reduction occurs significantly at around 800 K. The main factor of the disintegration is volumetric expansion of the iron oxide phase due to the reduction from hematite to magnetite. In addition, sinter is composed of hematite with various phases, which have different effects on disintegration. Furthermore, as reported by Inazumi et al., the value of reduction-disintegration index (RDI) for skeletal hematite reached approximately 30%.

ISO 4696 lists several methods for evaluating the RDI. Among them, ISO 4696-2 is a convenient method that employs a simple reducing gas system comprising $N_2$–30%CO and a short reducing time of 1.8 ks. However, another method, 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 water-gas-shift reaction.

A few studies have made on the disintegration behavior under the condition of high $H_2$ concentration. For example, Shen et al. investigated the effects of the $H_2$ concentration on disintegration of sinter, although they did not consider the effect of $H_2O$. Compared to the large number of studies on the disintegration mechanism under CO reduction, little is known regarding the effects of $H_2$ gas reduction. Therefore, it is necessary to elucidate the disintegration behavior of sinter in a CO–CO$_2$–$H_2$–$H_2O$ atmosphere.

Kokubu et al. reported that the actual gas composition in the upper part of BF at a temperature range of 673–873 K is different from that estimated from the equilibrium of the water-gas-shift reaction. They found that the actual gas
composition was similar to that determined assuming equilibrium at a temperature of 873–1073 K. Further, with the addition of H₂, the temperature distribution in the BF may potentially change as described above. Therefore, it is required to examine the disintegration behavior of sinter across a wide range of gas compositions. Hence, the objective of the present study was to evaluate the effects of a wide range of reducing gas compositions of the CO–CO₂–H₂–H₂O system on the reduction and disintegration behavior of sinter at 773 K.

2. Experimental

The sinter sample used in this study was supplied by a Japanese steel mill and had the composition listed in Table 1. The sample was crushed and sieved to grain sizes of 6.7–9.5 mm before use, and the RDI value, measured according to ISO 4696-2, was 37.6. In the experiments, approximately 25 particles, with the total weight of 25 ± 3 g, were randomly picked up and charged in the furnace, as shown in Fig. 1.

The sample was heated to 773 K in a N₂ gas stream with a flow rate of 21.5 cm³/s and kept for 300 s. This gas rate of 3.0 × 10⁻² N cm/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. H₂O gas was generated by heating distilled water in the furnace at 573 K. The reducing gas composition listed in Table 2 was set as follows: In all cases, the concentration of (CO + H₂) and (CO₂ + H₂O) were 20%. In Cases 1, 2, and 3, the concentration of H₂O was 0%. In Cases 4, 5, 6, and 7, the concentrations of CO₂ and H₂O gas were determined by the equilibrium condition of the water-gas-shift reaction in Eq. (1) at 773 K, after fixing the concentration of CO and H₂ gas. The gas composition in Cases 8 and 9 was determined in a similar manner but by assuming equilibrium at 1073 K and 1273 K, respectively. Among these conditions, Case 1 was regarded as the base condition.

\[
\text{CO(g)} + \text{H}_2\text{O(g)} = \text{CO}_2(g) + \text{H}_2(g) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

After the reduction experiment, the gas was changed to N₂ 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.

Disintegration tests were 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. Then, the RDI value was calculated using the following equation:

\[
\text{RDI} = 100 - \frac{W_1}{W_0} \times 100 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

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 optical microscope.

3. Results

3.1. Effects of H₂ and H₂O Concentration on Reduction Degree and RDI

Figure 2 shows the effect of H₂ concentration in a reducing gas with the composition N₂–(20–x)%CO–x%H₂–(20–y)%CO₂–y%H₂O on the reduction degree of the sinter. The plots are the average values, and the error bars show both maximum and minimum values of reduction degree from multiple experiments. Although the presence of H₂O led to a small decrease in the reduction degree, the differences were not significant. And with regard to H₂, an increase in the concentration from 0% to 2% led to an increase in the reduction degree, but further increase in the H₂ concentration only led to a decrease in the reduction degree. Finally, the reduction degree at 12% H₂ was similar to that at 0% H₂.

Effect of H₂ concentration in the reducing gas on the RDI value is shown in Fig. 3. The addition of H₂O had little effect on the RDI value, as in the case of the reduction degree. And with regard to H₂, the RDI trend was similar to

| Case | H₂ (%) | CO (%) | CO₂ (%) | H₂ (%) | H₂O (%) |
|------|--------|--------|---------|--------|---------|
| 1    | 0      | 20     | 20      | 0      | 0       |
| 2    | 60     | 16     | 20      | 4      | 0       |
| 3    | 60     | 12     | 20      | 8      | 0       |
| 4    | 60     | 18     | 20      | 2      | 0.4     |
| 5    | 60     | 16     | 19.1    | 4      | 0.9     |
| 6    | 60     | 12     | 17.7    | 8      | 2.3     |
| 7    | 60     | 8      | 15.5    | 12     | 4.5     |
| 8    | 60     | 16     | 16.3    | 4      | 3.7     |
| 9    | 60     | 16     | 14.2    | 4      | 5.8     |

Table 2. Gas composition employed for the reduction of the sinter sample.
that seen in the reduction degree. However, the RDI value at 12% \(H_2\) was approximately 8% lower than that at 0% \(H_2\).

The effects of the \(H_2O\) concentration on the reduction degree and the RDI value at 4% \(H_2\) are shown in Fig. 4. At a constant \(H_2\) concentration, an increase in the \(H_2O\) concentration produced no change in the reduction degree but caused a decrease in the RDI value.

Figure 5 shows the relation between the RDI value and reduction degree under different reducing gas compositions together with the result of the drum test before reduction. The RDI value of the sample before reduction was 3. The RDI value shows an upward tendency with increasing reduction degree. At the same reduction degree, however, higher concentrations of \(H_2\) and \(H_2O\) led to lower RDI values, except the case of 2% \(H_2\). Further, it seems that the plots obtained with and without \(H_2\) have a different slope. The reason why the case of 2% \(H_2\) showed different trend from other gas concentration may be that the sample weight of 25 g is short to be fully disintegrated. The drum test of the sinter reduced by 2% \(H_2\) with alumina ball of 475 g with the particle size of 7 mm was carried out. Total weight of 500 g is same as that based on ISO 4696-2. The obtained RDI value was approximately 80%. Therefore, the reason is that the RDI value is upper limit obtained by this method of the drum test.

3.2. Structure Changes and Crack Formation on Sinter Reduction

Figure 6 shows the cross section of the sinter sample before reduction. The symbols “H,” “M,” and “CF” indicate the phases of hematite (Fe\(_2\)O\(_3\)), magnetite (Fe\(_3\)O\(_4\)), and multi-component calcium ferrite, respectively. White small square-shaped grains are skeletal secondary hematite, which crystallized from the melt during sintering. The gray matrix phase is multi-component calcium ferrite (CF). Magnetite phase is observed in CF phase at the upper part of Fig. 6(b). The black parts are pores, which are of two types: open pores connected to the outside of the particle and closed pores that are not. Further, a thick and long crack is observed, although this was not a reduced sample. It was assumed that this crack formed when the sinter was cooled down or crushed.

Figure 7 shows the microstructures near the surface of the sinter after reduction with a) 0%, b) 4%, c) 8%, and d) 12% \(H_2\). After reduction near the particle surface, the area of magnetite formed from hematite decreased with increasing \(H_2\) concentration. Further, the reduction of skeletal hematite to magnetite proceeds without \(H_2\). Many cracks are observed in not only the CF phase but also magnetite
Fig. 6. Microstructure of sinter before reduction. H: Hematite, M: Magnetite, CF: multi-component Calcium Ferrite.

Fig. 7. Microstructure of surface area of sinter reduced at 773 K for 3.6 ks under different gas concentrations. a: N₂–20%CO–20%CO₂, b: N₂–16%CO–19.1%CO₂–4%H₂–0.9%H₂O, c: N₂–12%CO–17.7%CO₂–8%H₂–2.3%H₂O, d: N₂–8%CO–15.5%CO₂–12%H₂–4.5%H₂O.

Fig. 8. Microstructure of center part of sinter reduced at 773 K for 3.6 ks under different gas concentrations. a: N₂–20%CO–20%CO₂, b: N₂–16%CO–19.1%CO₂–4%H₂–0.9%H₂O, c: N₂–12%CO–17.7%CO₂–8%H₂–2.3%H₂O, d: N₂–8%CO–15.5%CO₂–12%H₂–4.5%H₂O.
formed by reduction. At 4% H₂, there is no large difference in the microstructure from that at 0% H₂. However, the area of magnetite without cracks seems to increase with the H₂ concentration.

The microstructures at the center of the sinter particles after reduction with various reducing gas concentrations are shown in Fig. 8. Reduction from hematite to magnetite proceeds to a greater degree inside the sinter particles with increasing H₂ concentration. Compared with the case in which no H₂ was added, reduction seems to occur more significantly along the thick cracks formed in the sinter reduced with 12% H₂. Furthermore, although the reduction degree at 12% H₂ was similar to that at 0% H₂, the RDI value obtained under the former condition was 8% lower than that under the latter condition. This suggests that reduction inside the sinter particles proceed further under the former condition.

Figure 9 shows the relation between the crack density of the reduced sinter and the H₂ concentration in the reducing gas. The crack density was calculated by microstructural analysis over a region from the surface to a 3-mm depth using six pictures in each condition. The cracks with larger size than 2 μm were analyzed. The crack density initially increased with increasing H₂, and then abruptly decreased to a value much lower than that without H₂ at 12% H₂. This matches the trend seen in the RDI value, as shown in Fig. 3. It seems that crack formation near the surface leads to the formation of a larger number of fine particles, thus contributing to the RDI value. When many fine cracks are formed near the surface during reduction without H₂, it was deduced that a large amount of fine powder is formed. Therefore, the particle size distributions of the disintegrated sinter samples were measured and compared.

Figure 10 shows the particle size distribution after the RDI test of the sinter sample reduced under various gas compositions. The vertical axis indicates the weight ratio (W/W₂) of particles within a certain size range to that of particles smaller than 2.8 mm. The weight ratio of the particles between 0.25 and 1.7 mm in size shows a similar trend under each gas condition. However, the weight ratio of fine particles less than 0.25 mm in size decreases with increasing H₂: the weight ratio of such fine particles formed by CO reduction was 1.4 times larger than that with 12% H₂. By contrast, the weight ratio of the particles between 1.7 and 2.8 mm increases with increasing H₂ concentration. Taking into account the size of cracks formed in the sinter sample, as shown in Figs. 7 and 8, it is expected that many fine particles less than 0.25 mm in size are formed under CO reduction. This corresponds to the above-mentioned trend seen in the particle size distribution.

4. Discussion

4.1. Comparison of Reduction Behaviors of Sinter Reduced by CO and H₂

As indicated in the previous studies, CO gas reduction from hematite to magnetite tends to proceed from the surface of the sinter particles, and the stress generated by the volumetric expansion of iron oxide causes crack formation. Furthermore, Inazumi et al. reported that fine cracks are formed during reduction because of the formation of micropores. Figure 11 shows a schematic illustration of the reduction and crack formation behavior with CO and CO–H₂. It has been reported that there is no significant dif-
ference in the chemical reaction rate of the reduction from hematite to magnetite in a single particle ore between CO/CO₂ and H₂/H₂O atmospheres. The interdiffusion coefficient De of H₂/H₂O gas in the sinter particle is higher than that of CO/CO₂ at 773 K. It is three times higher for the former than the latter. Accordingly, it is estimated that the reduction of hematite mainly by H₂ proceeded along the cracks in the sinter particle.

Asada et al. found no cracks in the magnetite phase on reduction by H₂, even though phase transformation from hematite to magnetite completed. However, they also observed volumetric expansion of the magnetite phase and formation of many cracks in the multi-component CF phase near the magnetite phase, and concluded that the reason for the difference in the crack formation as follows: The strain level in the magnetite crystals formed by H₂ reduction was lower than that formed by CO reduction because of the relatively uniform reduction of hematite. Therefore, there was no stress concentration at the surface of the sinter, unlike during CO reduction. This also supports our mechanism of reduction disintegration.

4.2. Effect of H₂O Concentration on Reduction and Disintegration Mechanisms

The RDI value markedly decreased with increasing H₂O concentration in the reducing gas at constant H₂ and CO concentrations, although the reduction degree was almost constant, as shown in Fig 4. Figure 12 shows a comparison of the microstructures near the surface ((a-1) and (b-1)) and center part ((a-2) and (b-2)) of sinter samples reduced by 4%H₂–3.7%H₂O–16%CO–16.3%CO₂ (Case 8) and 4%H₂–5.8%H₂O–16%CO–14.2%CO₂ (Case 9). The reduction to magnetite proceeds under all conditions. However, with increasing H₂O concentration reduction inside the sinter particles also proceeds along the thick cracks and magnetite phases having no cracks are observed. It seems that cracks were formed near magnetite at upper or lower of the observed surface.

In Case 5 whose condition is same H₂ and CO concentration as Case 8 and 9, many fine cracks are observed near magnetite phases as shown in Fig. 7(b). However, an increase in the H₂O concentration led to the disappearance of fine cracks. The effect of H₂O concentration on the crack density after reduction is shown in Fig. 13. The crack density was calculated by same method of that shown in Fig. 9. It decreases with increasing H₂O concentration, which well corresponds to the result of microstructure observation and the trend of RDI. The effect of H₂O concentration on the crack formation is discussed.

The reducing gas compositions in Cases 2, 8, and 9 are not at equilibrium conditions of the water-gas-shift reaction in Eq. (1) at 773 K. However, there is a possibility that the gas composition moved to the equilibrium condition during
the reaction. To examine it, the concentrations of H₂, CO, CO₂, H₂O, and N₂ were measured by gas-chromatography. In this case, only Al₂O₃ balls of 3 mm in diameter were set in the holder, and the gases with the compositions for Cases 2, 8, and 9 were flowed into the furnace. The gas composition measured was almost same as that supplied. Further, the retention time of the gas in the preheating bed (height, 20 mm) of the Al₂O₃ balls was only approximately 0.1 s at 773 K, assuming that the void fraction of this bed was 50%. Such a short retention time suggests that the preheating bed does not significantly affect the gas composition.

A further possibility is that the composition of the gas which penetrates into the pores of the sinter particles is not the same as that supplied. In Cases 8 and 9, the reaction proceeds toward the right side of Eq. (1), and therefore the H₂ concentration increases and the CO concentration decreases. In Case 2, the reaction proceeds toward the left side, and the H₂ concentration decreases and the CO concentration increases. Accordingly, an increase in the H₂O concentration leads to an increase in the H₂ concentration of the gas in the pores and cracks in the sinter, and it will causes a decrease in the CO concentration. The behavior of the RDI value and reduction degree in Fig. 4 was similar to that around 4%H₂ in Figs. 2 and 3. This may indicate a change in the H₂ concentration at the reaction interface in Cases 2, 8, and 9.

5. Conclusions

The effect of H₂ and H₂O concentrations of the reducing gas on the reduction disintegration behavior of iron ore sinter was examined for a wide range of gas compositions of the CO–CO₂–H₂–H₂O system. The obtained results are summarized as follows:

1) The reduction degree and RDI value increase with the addition of small amount of H₂. Further increase in the H₂ concentration leads to decreases of these values. This is because, H₂ reduction proceeds not only near the surface of the sinter particles but also inside without the formation of fine cracks unlike CO reduction.

2) The weight ratio of fine particles (less than 0.25 mm in size) decreases with an increase in the H₂ concentration. This well corresponds to the crack formation behavior in sinter particles.

3) The RDI value decreases with increasing H₂O concentration at constant H₂ and CO concentrations, whereas the reduction degree is almost constant.

Acknowledgment

This study was mainly carried out as a part of the research project “Environmentally Harmonized Steelmaking Process Technology Development.” Financial support from the New Energy and Industrial Technology Development Organization (NEDO) is gratefully acknowledged.

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