Gaseous Reduction Behavior of Powdered Iron Ore Sinter and Analysis on the Basis of Rist Model for Fixed Bed

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For the analysis of a blast furnace process, it is necessary to investigate the reduction behavior of iron ore sinter, which is the main source of an iron oxide charged into the blast furnace. It is impossible to accurately analyze the reduction behavior of the iron ore sinter without considering the existence of a quaternary calcium ferrite (CF), which has another reduction equilibrium different from hematite. From this point of view, the gaseous reduction behavior of powdered iron ore sinter has been investigated mainly at 1 173 K and the analysis has been conducted on the basis of a model derived by modifying Rist model for a fixed bed in consideration of CF. The hydrogen reduction behavior is found to be in reasonable agreement with the reduction curve calculated from the derived model at temperatures ranging from 1 073 to 1 273 K. Subsequently, in order to confirm the validity of the derived model, the hydrogen reduction behavior of hematite, and a mixture of the CF and hematite was investigated. The trend was observed that the reduction behavior of hematite and the mixture of the CF and hematite is almost the same and that the reduction behavior of the single CF sample has a delay for the others, in reasonably accordance with the relationship derived from the model. Moreover, the reduction behavior can be almost explained by the derived model regardless of the mixture ratio of H2 and CO in the ingoing gas under the present experimental conditions; the reduction progress has a delay by the difference of the reduction equilibrium by replacing H2 with CO(–CO2).

KEY WORDS: iron ore sinter; gaseous reduction; calcium ferrite; Rist model; ironmaking.

1. Introduction

For the analysis of a blast furnace process, it is necessary to investigate the reduction behavior of iron ore sinter, which is the main source of an iron oxide charged into the blast furnace. In order to know the gaseous reduction behavior, the knowledge of the reducibility of hematite, magnetite, and a quaternary calcium ferrite (CF), which are reducible constituents of the iron ore sinter, is needed and many researches have been conducted.1,2) The quaternary calcium ferrite (CF) is included in the self-fluxed iron ore sinter at about 20 to 40 mass %.3,4) The reducibility of the iron ore sinter has not sufficiently been clarified, since the components and shape of the sinter are complicated and those factors are related to each other.5) Maeda et al.6–8) investigated the reducibility of CF using the synthesized samples and clarified that the reduction equilibrium of CF is different from that of an iron oxide. From this point of view, it is impossible to accurately analyze the reduction behavior of the iron ore sinter without considering the existence of CF. On the other hand, in the production of iron ore sinter, it is necessary to positively utilize low grade ore, of which SiO2 content is high, because good quality ore is decreasing and the use of powdered ore is increasing. As the result, it is important to know the gaseous reduction behavior of the iron ore sinter.

In analyzing the gaseous reduction behavior, Rist and Bonnivard9,10) reported theoretical researches of the gaseous reduction of an iron oxide packed bed under the assumption of the infinite reaction rate.11) In the first report,9,11) the gaseous reduction of an iron oxide packed bed is theoretically analyzed on the basis of the material balance and thermodynamics under the assumption that the chemical reactions proceed in a moment. It is advantageous that Rist model enables to analyze the reduction behavior by considering only the chemical equilibria of the reactions.

In the present study, these points are taken into consideration, and the gaseous reduction behavior of powdered iron ore sinter is investigated under the condition that the reduction behavior would not be limited by mass transfer and chemical reaction rates. Rist model for a fixed bed is applied to the analysis in consideration of the existence of CF, which has another reduction equilibrium different from hematite. Moreover, in order to confirm the validity of the application of Rist model to the powdered iron ore sinter, the gaseous reduction behavior of a powdered sample prepared by mixing pure hematite and CF synthesized from reagents is also investigated.
2. Application of Rist Model for Fixed Bed to Powdered Iron Ore Sinter

The fundamental details of Rist model for a fixed bed have been given elsewhere\(^9,11\). However, the important subjects particularly related to the present study are described here. The schematic cross section of an iron oxide packed bed, which shows the situation of the reduction progress of hematite with hydrogen at 1 173 K, is exemplified in Fig. 1. Here, hematite, magnetite, and wustite are displayed for an iron atom, namely FeO\(_{1.5}\), FeO\(_{1.33}\), and FeO\(_{1.05}\), respectively, in accordance with the representation in the literature\(^9,11\)....

To begin with, the reactions of hydrogen reduction are considered to proceed as shown in Fig. 1(a). From the assumption that the equilibrium is attained at the interfaces, the oxidized ratios of hydrogen, \(P_{H_2}/(P_{H_2}+P_{H_2O})\), at these interfaces can be calculated from the equilibrium constants for the hydrogen reductions. In these calculations, the following equations derived\(^9,11\) on the basis of the data in the literature\(^9,11\) are used:

\[
K_{H_2}^{(H_2)} = \exp(8.185 + 3364/T) \quad \text{(873 to 1 600 K) \ldots (1)}
\]

\[
K_{H_2}^{(H_2O)} = \exp(7.767 - 3 345/T) \quad \text{(873 to 1 273 K)} \ldots (2)
\]

\[
K_{H_2}^{(H_2O)} = \exp(0.9733 - 1 743/T) \quad \text{(873 to 1 600 K)} \ldots (3)
\]

The calculated oxidized ratios of hydrogen, \(x_1\), \(x_2\), and \(x_3\), are shown on the left side of the corresponding interfaces in Fig. 1(a).

Here, the oxygen balance per unit time can be written at each interface, \(i\), as follows:

\[
\frac{n_{O_i}}{n_g} = \frac{(\Delta x_i)}{(\Delta y_i)}
\]

where \((\Delta x_i)\) represents the mol number of oxygen transferred from solid phase to vapor phase per unit time at the interface, \(i\), \(n_{O_i}\) and \(n_g\) the mol numbers of iron and reducing gas which are associated with the reduction reaction per unit time at the interface, respectively, and \(x = (H_2O)/(H_2 + H_2O)\) and \(y = (O/Fe)\) the oxidized ratio of the ingoing hydrogen and the ratio of the number of oxygen atom to the number of iron atom in the solid, respectively. Then, \((\Delta x_i)\) and \((\Delta y_i)\), represent the variations of the \(x\) and \(y\) values with the passage of the reaction interface, \(i\). From Eq. (4), the following relationship is derived at each interface, \(i\):

\[
\frac{n_{O_i}}{n_g} = \frac{(\Delta x_i)}{(\Delta y_i)}
\]

where \((\Delta x_i)\) and \((\Delta y_i)\), denotes the ‘specific formation’ of the new phase, which is represented by the ratio of the mole number of iron to the mole number of the reducing gas at each interface, \(i\). Under the condition that the equilibrium is held at each interface, the value for \((\Delta x_i)/(\Delta y_i)\) can be calculated from the constant values for \((\Delta x_i)\) and \((\Delta y_i)\). For example, the \((\Delta x_i)/(\Delta y_i)\) value at FeO\(_{1.33}\)/FeO\(_{1.05}\) interface in Fig. 1(a) can be calculated as follows:

\[
\frac{n_{O_i}}{n_g} = \frac{(\Delta x_i)}{(\Delta y_i)} = \frac{(0.818 - 0.375)}{(1.33 - 1.05)} = 1.58 \ldots (6)
\]

In the same way, the calculated ‘specific formation’ at each interface is expressed by the length of the upward arrow in Fig. 1. The value is proportional to the progress rate of the interface. That is to say, the reduction reaction proceeds faster when the \((n_{O_i}/n_g)\) value is larger. It is possible to compare the progress rate of each interface from the value of ‘specific formation’. From this point of view, the value for ‘specific formation’ at FeO\(_{1.33}\)/FeO\(_{1.05}\) interface is larger than that at FeO\(_{1.5}/\text{FeO}_{1.33}\) interface; i.e., the FeO\(_{1.33}/\text{FeO}_{1.05}\) interface catches up with the FeO\(_{1.5}/\text{FeO}_{1.33}\) interface. In actual fact, the formed interface is, therefore, not FeO\(_{1.33}/\text{FeO}_{1.33}\) but FeO\(_{1.5}/\text{FeO}_{1.05}\); the hydrogen reduction of hematite proceeds according to Fig. 1(b) at 1 173 K.

Continuously, an application to the mixture of several oxides which have different reduction equilibria is considered in order to examine the hydrogen reduction behavior of powdered iron ore sinter at 1 173 K. It is composed of hematite, magnetite, and ‘FeO\(_{1.5}\)’, and the mol number ratios of iron are 5 : 2 : 3, respectively, where ‘FeO\(_{1.5}\)’ represents reducible iron oxide components in CF. The following equilibrium constants for the reduction reactions of CF with CO are submitted by Maeda et al.\(^9,11\):

\[
K_{CO}^{(H_2)} = \exp(2.624 - 2 161/T) \quad (1 090 to 1 323 K) \ldots (7)
\]

\[
K_{CO}^{(CO)} = \exp(-2.785 - 2 040/T) \quad (1 079 to 1 326 K) \ldots (8)
\]

where \(m\) and \(n\) are abbreviations for ‘FeO\(_{1.33}\)’ and ‘FeO\(_{1.05}\)’ which represent reduction reaction products from ‘FeO\(_{1.5}\)’. The reduction experiments mainly with H\(_2\) are carried out in the present study. Accordingly, the equilibrium constants for the reduction reactions of CF(‘FeO\(_{1.5}\)’→ ‘FeO\(_{1.33}\)’→ ‘FeO\(_{1.05}\)’→Fe) with \(H_2\) are necessary. The equilibrium constant for the water-gas-shift reaction at each reduction stage is calculated by combining Eqs. (2) and (3) with the equilibrium constant for the reduction reactions of an iron oxide with CO\(_2\) respectively, and is represented as follows:

\[
H_2O(g) + CO(g) = H_2(g) + CO_2(g) \ldots (9)
\]

\[
K_{9}^{(w/CO)} = 7^{3.973} \exp(-35.01 + 7.831/T) \ldots (10)
\]

\[
K_{9}^{(w/Fe)} = 7^{0.926} \exp(-11.05 + 4.961/T) \ldots (11)
\]

The equilibrium constants for the reduction reactions of CF with \(H_2\) can be derived by combining Eqs. (7) and (8) with Eqs. (10) and (11), respectively, and are expressed by

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The reduction progress of iron ore sinter in a fixed bed with H₂ at 1 173 K. (Fig. 2).

When the difference of the reduction equilibrium of CF given by Eqs. (12) and (13) is taken into account, the schematic cross section of the packed bed, which represents the situation of the reduction progress, is shown in Fig. 2. Here, the reduction equilibrium of CF at ‘FeO1.5’/‘FeO1.33’ interface can be considered to be the same as that of hematite at ‘FeO1.33’/‘FeO1.11’ interface at the present experimental temperature, 1 173 K. The iron ore sinter is described by being divided into three oxide phases: hematite (Fe₂O₃), magnetite (Fe₃O₄), and CF (FeO). The reduction lines based on Rist model are independent of the oxide ratio of ingoing reducing gas against total iron in the sample, which is related to the time from an experimental start in Sec. 4. From the above equations, the calculated reduction ratio of each reaction at C or D interface in Fig. 2(c) against the total amount of the reduction, f_C or f_D, can be calculated as follows:

\[ f_C = \frac{0.45 \times 0.8 + 0.28 \times 0.2}{1.5 \times 0.8 + 1.33 \times 0.2} = 0.284 \] ..............................(16)

\[ f_D = \frac{1.05}{1.5 \times 0.8 + 1.33 \times 0.2} = 0.716 \] ..............................(17)

The overall fractional reduction, F, can be calculated by the following equations:

\[ F = 0.284 \times \frac{n_{Fe} / n_{Fe}^0}{(n_{Fe} / n_{Fe}^0)c} + 0.716 \times \frac{n_{Fe} / n_{Fe}^0}{(n_{Fe} / n_{Fe}^0)d} \] ..............................(18)

\[ (0 \leq n_{Fe} / n_{Fe}^0) < (n_{Fe} / n_{Fe}^0)c \]

\[ F = 0.284 + 0.716 \times \frac{n_{Fe} / n_{Fe}^0}{(n_{Fe} / n_{Fe}^0)c} \] ..............................(19)

where \((n_{Fe} / n_{Fe}^0)c\) is the reciprocal of the ‘specific formation’ and is called ‘specific consumption’. The numerical value can be calculated as the reciprocal of the value of ‘specific formation’ at each interface, \(i \cdot n_{Fe} / n_{Fe}^0\), denotes the mol number ratio of ingoing reducing gas against total iron in the sample, which is related to the time from an experimental start in Sec. 4. From the above equations, the calculated reduction behavior for the powdered iron ore sinter is shown in Fig. 3 as well as that for hematite, magnetite, and CF. The reduction lines based on Rist model are independent of the content of iron oxide and the flow rate of reducing gas by taking the \(n_{Fe} / n_{Fe}^0\) value as the horizontal axis. In the case that CF independently exists, the reduction has a delay in comparison with the case of hematite because of the difference of the reduction equilibrium. In the iron ore sinter, ‘specific formation’ of the CF interfaces are larger, because
the CF content is smaller than hematite and the reduction behavior is only affected by the initial content of magnetite; it can be concluded that the reduction behavior of the iron ore sinter almost agrees with that of hematite. Similarly, the effect of the mixture ratio of H2 and CO on the reduction behavior of the iron ore sinter is calculated at 1 173 K and is shown in Fig. 4. The iron ore sinter is found to be more reducible with H2 as well as the case of hematite at 1 173 K.

3. Experimental

The schematic cross section of the experimental arrangement is shown in Fig. 5. The apparatus consisted of an SiC electric resistance furnace, which is connected to a PID controller with a Pt/6%Rh–Pt/30%Rh thermocouple. Temperature was controlled within ±2.5 K over a length of 5 cm in the furnace from 1 073 to 1 273 K. A mullite tube (21 mm O.D., 16 mm I.D., 600 mm long) was used as a reaction tube. Iron ore sinter was presented by Nippon Steel Corporation and the chemical analysis is shown in Table 1. The mineral composition of the sinter is estimated as hematite: 42.9, magnetite: 15.2, CF: 33.7, and slag: 8.2 (mass %) from Table 1. The proportion of ‘FeO1.5’ in CF is assumed to be 70%, namely ‘FeO1.5’ = 23.6 mass %. The assumption is validated by the measurement of the attainable final fractional reduction.19) The iron ore sinter powdered under 70 mesh (~210 μm) by being crushed and ground was used in the present work. The powdered sample weighing about 35 g was fixed in the reaction tube as shown in Fig. 5. The ceramic wool was put upside and underside adjacent to the sample. After the sample was heated up to an experimental temperature ranging from 1 073 to 1 273 K in an argon or a nitrogen, the experiment was carried out by introducing a hydrogen. The outgoing gas including a water vapor formed by the gaseous reduction was lead through a copper pipe wrapped by a ribbon heater kept over 383 K to a condenser and the condensed water was sampled in a tube meter. The amount of the condensed water was measured at 5 min intervals. The residual water vapor was trapped in a sulfuric acid. The fractional reduction, F, was calculated by

\[
F = \frac{w_{A,t} + w_{B,t}}{w_{\text{cal}}} \tag{20}
\]

where \(w_{A,t}\) and \(w_{B,t}\) denote the mass of water trapped in the tube meter and the sulfuric acid (g), respectively, and \(w_{\text{cal}}\) the mass of water calculated from the packed content of the iron ore sinter (g). In several experiments, (H2–)CO–CO2 mixtures were introduced instead of hydrogen and the outgoing components of the gas were analyzed by a quadrupole mass spectrometer.

Table 1. Chemical analysis of iron ore sinter.

|        | T. Fe | FeO | CaO | SiO2 | Al2O3 | MgO | Apparent density (kg/m³) |
|--------|-------|-----|-----|------|-------|-----|--------------------------|
| Mass % | 56.62 | 5.46 | 9.98 | 5.82 | 1.93  | 1.41 | 3.6 × 10³                 |

Fig. 3. The estimated reduction behavior of hematite, magnetite, ‘FeO1.5’ in CF, and iron ore sinter with H2 at 1 173 K.

Fig. 4. The estimated reduction behavior of iron ore sinter with several H2–CO mixtures at 1 173 K.

Fig. 5. Schematic cross section of the experimental apparatus and the packed bed of sample.
4. Results and Discussion

Figure 6 shows the fractional reduction of the powdered iron ore sinter as a function of $n_g/n_{Fe}^o$ for several gas flow rates at 1 173 K. The reduction line calculated by applying Rist model for a fixed bed to the powdered sinter is also described in Fig. 6. The $n_g/n_{Fe}^o$ value introduced in Sec. 2 is related to the time by the following equation:

$$\frac{n_g}{n_{Fe}^o} = \frac{PV - t}{RT} \frac{M_{Fe}}{w_{Fe}}$$  \hspace{1cm} (21)

where $M_{Fe}$ denotes the atomic weight of iron (g/mol), $P$ the partial pressure of reducing gas (atm), $R$ the gas constant \[582.1 \text{ cm}^3 \cdot \text{atm}/(\text{K} \cdot \text{mol})\], $T$ the temperature of gas (K), $t$ the time (s), $V$ the flow rate (cm$^3$/s), and $w_{Fe}$ mass of the iron in the solid (g). Namely, the variation of the $n_g/n_{Fe}^o$ value corresponds to the passage of time from the experimental start. Generally speaking, at lower flow rates, the assumption that the gas uniformly flows in the packed bed may not be satisfied by being constructed the preferred pathway of the gas. On the other hand, the assumption of the infinite reaction rate may not be satisfied at higher flow rates. Therefore, the measurements should be carried out at the appropriate gas flow rate, at which the two assumptions described above are satisfied. From Fig. 6, it is found that the reduction behavior at the flow rate of 80 and 113 cm$^3$/min (s.t.p.) considerably differs from the reduction line derived for the sinter on the basis of Rist model and that the reduction behavior at the flow rate of 185 cm$^3$/min (s.t.p.) reasonably agrees with the calculated reduction line.

Accordingly, the subsequent experiments were carried out at the flow rate of about 185 cm$^3$/min (s.t.p.); namely 160 to 205 cm$^3$/min (s.t.p.). Dependence of the hydrogen partial pressure on the reduction behavior of the powdered sinter is investigated by introducing the $H_2$-$N_2$ mixture at the fixed total flow rate. The variation of the fractional reduction with $n_g/n_{Fe}^o$ at several hydrogen partial pressures is shown in Fig. 7. The reduction behavior is in reasonable agreement with the reduction line calculated on the basis of Rist model at each hydrogen partial pressure. It can be concluded that the reduction behavior is independent of the hydrogen partial pressure of the ingoing gas from the results. The hydrogen reduction behavior of the powdered sinter measured at 1 073, 1 173, and 1 273 K is shown in Fig. 8. The reduction line calculated on the basis of Rist model at each temperature is also shown in Fig. 8. The three reduction lines are described in Fig. 8, because the reduction equilibrium is dependent on temperature; the reduction reaction with $H_2$ is endothermic and the iron oxide is more reducible at higher temperatures. The measured reduction curve is found to be in reasonable agreement with the reduction line calculated on the basis of Rist model at each temperature, which implies that the equilibrium is held at each interface during the progress of the reduction reaction, under the present experimental condition of $\bar{V}_{H_2} = 161$ to 188 cm$^3$/min (s.t.p.).

Subsequently, in order to confirm the validity of the derived model for the iron ore sinter on the basis of Rist model for a fixed bed, a quaternary calcium ferrite, CF, was synthesized by the method described in the literature, \cite{6, 7, 21}; the reagent grades of Fe$_2$O$_3$, CaCO$_3$, SiO$_2$, and Al$_2$O$_3$ were mixed at a fixed proportion shown in Table 2 and were kept...
for 1 h at 1 273 K, and then the mixed sample was crushed. After the foregoing operation was repeated 3 times, the sample was held for 60 h at 1 523 K. The synthesized sample was identified to be CF by an X-ray diffraction analysis. The hydrogen reduction behavior of the powdered CF was investigated using the synthesized sample at 1 173 K. In order to simulate iron ore sinter, hematite and the CF were mixed in the proportion of 1 to 1 and the mixed sample was also reduced with hydrogen at 1 173 K. The results are shown in Fig. 9 with the reduction behavior of hematite. It is found that the reduction progress for all three kinds of samples has a delay from the calculated line on the basis of Rist model. The reduction delay may be caused by a little smaller introducing gas flow rate of 160 cm³/min (s.t.p.). However, the trend can be observed that the reduction behavior of hematite and that of the mixture of CF and hematite are almost the same and that the reduction behavior of the single CF sample has a delay for the others, which reasonably accords with the relationship derived from the model and suggests the validity of the model.

Fig. 9. Hydrogen reduction behavior of hematite, a synthesized CF and their mixture at 1 173 K.

5. Conclusions

The gaseous reduction behavior of powdered iron ore sinter has been investigated mainly at 1 173 K and the analysis has been conducted on the basis of a model derived by modifying Rist model for a fixed bed in consideration of a quaternary calcium ferrite (CF), which has another reduction equilibrium different from hematite. The results are summarized as follows:

(1) Dependence of the hydrogen partial pressure was investigated and the reduction behavior is in reasonable agreement with the reduction line calculated from the derived model at each hydrogen partial pressure.

(2) The hydrogen reduction behavior is in reasonable agreement with the reduction line calculated from the derived model at temperatures ranging from 1 073 to 1 273 K under the present experimental condition of \( V_{H_2} = 161 \) to \( 188 \) cm³/min (s.t.p.).

(3) The hydrogen reduction behavior of a synthesized CF, hematite, and their mixture was investigated and the trend was observed that the reduction behavior of hematite and the mixture of hematite–CF is almost the same and that the reduction behavior of the single CF sample has a delay for the others, which reasonably accords with the relationship derived from the model and suggests the validity of the model.

(4) The reduction behavior can be almost explained by the derived model regardless of the mixing ratio of \( H_2 \) and CO under the present experimental conditions. The reduction progress is found to have a delay by the difference of the reduction equilibrium by replacing \( H_2 \) with CO(–CO₂); i.e., the gaseous reduction rate of the powdered sinter is large enough to follow the derived model and the reaction proceeds under the condition that the equilibrium is held at each interface.

Table 2. Chemical compositions of the mixed sample for synthesizing CF

|          | (mass%) |
|----------|---------|
| Fe₂O₃    | 70      |
| CaCO₃    | 16      |
| SiO₂     | 7.0     |
| Al₂O₃    | 7.0     |

Fig. 10. Reduction behavior of iron ore sinter with \( H_2 \), CO and a \( H_2 \)-CO mixture at 1 173 K.

Table 2. Chemical compositions of the mixed sample for synthesizing CF

|          | (mass%) |
|----------|---------|
| Fe₂O₃    | 70      |
| CaCO₃    | 16      |
| SiO₂     | 7.0     |
| Al₂O₃    | 7.0     |
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