Reduction Kinetics of Hematite Powder Mechanically Milled with Graphite

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Reduction behavior of iron oxides mixed with graphite has been quantitatively investigated using a high temperature X-ray diffractometer. The mixture was mechanically milled using a vibration mill and heated under He gas flow from room temperature to 1550 K with the heating rate of 10 to 40 K/min. The diffraction pattern showed the sequential change of products by reduction from hematite to iron through magnetite and wustite. The temperature at which each reduced product sequentially appeared was decreased by several tens degrees with increasing mechanical milling time up to 160 min. The intensity change of diffraction profiles of constituents with temperature was in accordance with the chemical stoichiometry of reduction reactions. The reduction reactions were first order of reaction. The activation energy of reaction decreased and the frequency factor of reaction increased with increasing mechanical milling time. On the other hand, the mixture of milled graphite powder and non-milled hematite powder gave less effect to the activation energy and frequency factor than the milled mixture.

KEY WORDS: high temperature X-ray diffraction; milling; iron oxides; graphite; activation energy of reduction.

1. Introduction

Iron oxide pellet containing carbon can be reduced at lower temperature (1323–1423 K) in inert-gas atmosphere1–5) than that in a blast furnace. The decrease of temperature of the reduction of iron ore and the melt of carbonized iron as pig iron gives the benefit of the increase of energy efficiency and carbon utility as CO2. It has been reported that the mechanical milling of the mixture of hematite and graphite gives the effect to the decrease of reduction temperature.6–7) Otsuka et al.8) reported that the smaller diameter of iron oxide was, the lower reduction temperature was obtained, while the diameter of graphite was independent on the reduction rate of iron oxide. Khaki et al. investigated the kinetics of reduction of iron oxide milled with graphite using a thermo-gravimetric and differential thermal analysis method.6) They found that the milling of graphite effected to the decrease of reduction temperature rather than the milling of iron oxide. 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Then, the hematite particles were formed to be spherical with about 54 µm in diameter. Graphite powder was separately milled in dry. The diameter of graphite particles was controlled to be about 30, 25, 17, 12 µm corresponding to the milling time of 10, 30, 60 and 160 min, respectively. After then, the spherical hematite powder and the milled graphite powder were mixed.

Type C: The hematite particles prepared by spray-drying method were coated with carbon using a vapor-deposition in vacuum of 1.3 Pa (0.01 Torr). Coating with the coating rate of 0.3 s/coat were 100 times repeated and the position of particles was changed every coating so as to make a uniform carbon layer. The coated hematite particles were mixed with graphite powder milled in dry for 10 min.

2.2. Analysis of Reduction of Iron Oxides by X-ray Diffraction

Sample was set on a shallow flat vessel of alumina with 0.8 mm in depth, 17 mm in length and 9 mm in width. The vessel was horizontally set on the heating plate with Pt resistant heating wire in the center of furnace. The furnace was installed in the sample chamber of a high temperature X-ray diffractometer (RINT2000-TTR, Rigaku Denki Co.), which is explained elsewhere.16) X-ray beam passed through two windows of an outer film of polyimide for sealing up the sample chamber and an inner film of Ni for preventing from heat radiation. The generator of X-ray had the maximum power of 10 kW. The target of X-ray source was Co and Co-Kα line was employed. The optical system was a parallel beam method. The diffraction-scanning rate was 10 degree/min and the diffraction angle was between 46 and 51 degree in 2θ. The diffraction angle was calibrated by means of internal standard specimen method using pure silicon particles at room temperature. The temperature of samples was measured by a R-type thermocouple by the side of vessel and was calibrated with a thermocouple in the center of vessel. Gas was introduced in front of the vessel through a Pt tube with the inside diameter of 3.5 mm in the center of front door of the chamber. Gas was flowed out from the bottom of chamber.

After replacing air to He gas with 0.04 NL/min for 30 min in the chamber, the sample was analyzed using X-ray diffractometer with heating up from room temperature to 1 550 K under the constant heating rate of 10, 20 and 40 K/min, respectively.

3. Result

3.1. Intensities of X-ray for Iron Oxides during Reduction

The X-ray diffraction peaks of (113) plane of hematite, (400) plane of magnetite, (200) plane of wustite and (111) plane of γ-iron were detected. Figure 1 shows the peaks during scanning the diffraction angles between 46 and 51 degree in 2θ under the constant heating rate of 20 K/min for the sample Type A. These peaks moved to lower angles due to thermal expansion and rose and fell due to the reduction of iron oxides. The relation of the diffraction intensities of iron oxides to temperature is shown in Fig. 2 for the sample type A, in Fig. 3 for the sample type B and in Fig. 4 for the sample type C. The intensity of hematite did not change at lower temperatures than 900 K for all of the mixing conditions and fell over 1 200 to 1 300 K. Magnetite peak rose in according to the fall of hematite peak. When magnetite peak fell, wustite peak sequentially rose, following by falling wustite peak and rising γ-iron peak.
3.2. Temperatures at Start and End of Reduction of Iron Oxides

The temperatures at start and end of reaction are defined as half of maximum counts of each oxide during the rise and fall of peaks, respectively. As shown in Fig. 5, the temperatures for Type A and Type B decreased with increasing milling time. The temperature of the appearance of iron for Type A decreased by about 30 K during the milling time of 120 min. The decrease of temperatures for Type B with milling time was smaller than that for Type A. In case of Type C, the temperature for the reduction from hematite to magnetite decreased by about 200 K from that in the case of Type B and there was little effect to the temperature decrease for the reductions from magnetite to wustite and from wustite to iron. The reason is that carbon coated on hematite particles is consumed for reduction of hematite.

As shown in Fig. 6, the intensity is empirically represented as the quadratic of temperature such as $I=at^2+bt+c$, where $a$, $b$ and $c$ are constant and are listed in Table 1. $T$ is absolute temperature.

Fig. 3. Intensity changes of X-ray diffraction for reduction of iron oxides mixed with milled graphite (Type B) for different milling times during heating up with 20 K/min in He gas.

Fig. 4. Intensity changes of X-ray diffraction for reduction of carbon-coated iron oxides mixed with graphite (Type C) milled for 10 min during heating up with 20 K/min in He gas.

Fig. 5. The temperatures at the start and end of reduction of iron oxides as a function of mechanical milling time.

Fig. 6. Intensity changes of hematite and magnetite during reduction of the mixture of hematite and graphite milled for 10 min (Type A) under the constant heating rate of 20 K/min in He gas.
4. Discussion

4.1. Relation between the Intensity of X-ray Diffraction and the Mole of Constituents

Iron ore particles initially adhere with carbon by mechanical milling. After the reduction of iron ore starts, adhered carbon is consumed and separates from the surface of iron ore to make a gap. Then, iron ore particles are reduced by CO gas that is generated at the surface of carbon and transferred through the gap.

The reduction reaction of hematite to magnetite is expressed as

\[
3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2
\]

The reaction rates of reduction of hematite and production of magnetite is formulated as

\[
\frac{1}{3} \frac{dn_{\text{Fe}_2\text{O}_3}}{dt} = \frac{1}{2} \frac{dn_{\text{Fe}_3\text{O}_4}}{dt} \tag{2}
\]

where \(n_i\) is the mole fraction of constituents and \(t\) time.

For example, the intensities of hematite and magnetite were obtained from Table 1;

\[
\frac{dn}{dt}(at \ T_1) = \lim_{T_2 \to T_1} \left( \frac{(dn/dT)(dT/dt)_2}{(dn/dT)(dT/dt)_1} \right)_T \tag{3}
\]

The Eq. (2) is rewritten as follows,

\[
-(1/3)(\partial^2 n_{\text{Fe}_2\text{O}_3}/\partial T^2) = (1/2)(\partial^2 n_{\text{Fe}_3\text{O}_4}/\partial T^2) \tag{4}
\]

Both sides of the equation are divided by a constant heating rate, \((dT/dt)\). The following equation is obtained.

\[
-(1/3)(\partial^2 I_{\text{Fe}_2\text{O}_3}/\partial T^2) = (1/2)(\partial^2 I_{\text{Fe}_3\text{O}_4}/\partial T^2) \tag{5}
\]

If the intensity of X-ray diffraction is proportional to the mole fraction of constituents, the following equation is obtained,

\[
-(1/3)(\partial^2 I_{\text{Fe}_2\text{O}_3}/\partial T^2) = (1/2)(\partial^2 I_{\text{Fe}_3\text{O}_4}/\partial T^2) \tag{6}
\]

For example, the intensities of hematite and magnetite were obtained from Table 1;

\[
I_{\text{Fe}_2\text{O}_3} = -0.0407 T^2 + 90.10 T - 48970 \tag{7}
\]

\[
I_{\text{Fe}_3\text{O}_4} = 0.0277 T^2 - 58.76 T + c \tag{8}
\]

for the milled mixture for 10 min (Type A). The ratio of the slope of intensity changes \((dT/dT)^2)\) of hematite to magnetite against temperature is 1.47 and corresponds to 1.5 of the ratio of the chemical stoichiometry number for the Eq. (1).

The reduction reactions of magnetite to wustite and wustite to iron are expressed as

\[
\frac{\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2 \tag{9}}
\]

and

\[
\frac{\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2 \tag{10}}
\]

respectively. The ratios of \((dT/dT)^2)\) of iron oxide to the reduced iron oxide are summarized in Table 2. The ratios well agree the ratios of the chemical stoichiometry numbers of 3 : 2, 1 : 3 and 1 : 1 for the Eqs. (1), (9) and (10), respectively. From these results, it is realized that the intensity of X-ray diffraction is proportional to the mole fraction of constituents.
4.2. Effect of Milling Time on the Activation Energy and Frequency Factor of Reduction Reaction

Neglecting the reverse reaction of reduction, the reaction rate of n-th order is represented as follows;

\[-\frac{dC}{dt} = C^n k_0 \exp(-E/RT) \]  \( \ldots \ldots \ldots (11) \)

where \(E\) is activation energy and \(k_0\) frequency factor and \(R\) gas constant.

\[-dI/dT = \alpha^{-1}I^n k_0 \exp(-E/RT) \]  \( \ldots \ldots \ldots (12) \)

Figure 7 shows the relation between \(\ln(I^n \times dI/dT)\) \((n = 0, 2)\) and the inverse of absolute temperature for the reduction of iron oxides using the milled mixture for 10 min. (Type A). The best fitting of linear relation shows the first order of reaction \((n = 1)\). The activation energy and frequency factor of reaction are calculated from the following equation;

\[-d \ln I/dT = -m^{-1} \alpha^{-1} I^n k_0 \exp(-E/RT) \]  \( \ldots \ldots \ldots (13) \)

The slope of linear relation for the reduction of hematite to magnetite in Fig. 7 gives the activation energy of 72.94 J/mol and the intercept the frequency factor of \(3.63 \times 10^{-6} \text{s}^{-1}\). The other reduction reactions of iron oxides follow the first order reaction. Table 3 shows the activation energy and the frequency factor of reduction reaction of iron oxides, respectively.

The activation energy of the reduction from hematite to magnetite and magnetite to wustite decreases with increasing milling time, while that of the reduction from wustite to iron increases, as shown in Fig. 8. The frequency factor has

### Table 2. Ratio of \((dI^2/dT^2)\) of iron oxide to the reduced iron oxide.

| Mixture Type | Heating rate K/min | Milling time Min | \(3Fe_2O_3 + CO\) to \(Fe_3O_4 + CO_2\) | \(Fe_3O_4 + CO\) to \(FeO + CO_2\) | \(FeO + CO\) to \(Fe_2O_3\) |
|--------------|--------------------|-----------------|--------------------------------------|--------------------------------------|--------------------------------------|
| A            | 25                 | 0               | 1.55                                 | 0.345                                | -                                   |
|              | 20                 | 0               | 1.47                                 | 0.362                                | -                                   |
|              | 30                 | 1.55            | 0.335                                | -                                    | -                                   |
|              | 120                | 1.48            | 0.345                                | 0.970                                | -                                   |
| B            | 20                 | 0               | 1.27                                 | 0.305                                | -                                   |
|              | 10                 | 1.55            | 0.353                                | -                                    | -                                   |
|              | 30                 | 1.45            | 0.331                                | -                                    | -                                   |
|              | 60                 | 1.56            | 0.327                                | -                                    | -                                   |
|              | 160                | 1.52            | 0.323                                | 0.924                                | -                                   |
|              | 160                | 1.47            | 0.381                                | -                                    | -                                   |
|              | 160                | 1.79            | -                                    | -                                    | -                                   |
| C            | 20                 | 1.50            | 0.331                                | -                                    | -                                   |

**Theoretical ratio**: 1.5 0.333 1.0

### Table 3. Activation energies and frequency factors of iron oxides mixed with graphite powder.

| Mixture | Heating rate K/min | Milling time Min | \(Fe_2O_3\)/\(Fe_3O_4\) | \(Fe_3O_4\)/\(FeO\) | \(FeO\)/\(Fe\) |
|---------|--------------------|-----------------|------------------------|---------------------|----------------|
| Type A  |                    |                 |                        |                     |                |
| Milled mixture of \(Fe_2O_3\) and Gr (Type A) | 25 | 0 | 75.12 2.69x10^10 | 1100-1200 | 1167-1218 | 49 | 1480-1520 | 80.97 | 1.79x10^11 | 1165-1215 |
|         | 20 | 10 | 72.94 3.60x10^10 | 1100-1200 | 1167-1218 | 49 | 1353-1438 | 80.97 | 5.07x10^11 | 1145-1316 |
|         | 30 | 10 | 65.86 7.31x10^10 | 1100-1200 | 1167-1218 | 49 | 1375-1408 | 92.96 | 1.10x10^11 | 1140-1460 |
|         | 120 | 10 | 56.36 1.97x10^10 | 1100-1200 | 1136-1188 | 49 | 1328-1378 | 103.24 | 4.21x10^11 | 1140-1340 |
| Type B  |                    |                 |                        |                     |                |
| Mixture of \(Fe_3O_4\) and milled Gr (Type B) | 20 | 0 | 81.48 1.65x10^10 | 1283-1333 | 194.34 | 1.21x10^11 | 1421-1472 | - | - |
|         | 10 | 10 | 78.68 4.84x10^10 | 1249-1283 | 192.07 | 2.51x10^11 | 1440-1489 | - | - |
|         | 30 | 10 | 78.27 3.78x10^10 | 1240-1274 | 184.40 | 3.01x10^11 | 1432-1450 | - | - |
|         | 100 | 100 | 70.82 7.74x10^10 | 1197-1248 | 179.82 | 5.94x10^11 | 1421-1455 | - | - |
|         | 100 | 100 | 73.50 2.19x10^10 | 1198-1256 | 179.91 | 2.19x10^11 | 1385-1410 | 90.79 | 4.07x10^11 | 1400-1500 |
|         | 100 | 100 | 73.48 5.07x10^10 | 1210-1260 | 181.56 | 3.77x10^11 | 1433-1467 | 91.72 | 9.14x10^11 | 1530-1650 |
|         | 100 | 100 | 69.03 2.63x10^10 | 1235-1338 | 190.91 | 7.76x10^11 | 1418-1484 | - | - |

**Note**: \(1^\circ\) The target of X-ray was Mo and that for other conditions was Co. Type C is the mixture of carbon-coated hematite particles and milled graphite particles.
the opposite tendency from the activation energy, as shown in Fig. 9. The change of activation energy and frequency factor by milling time for Type A is larger than that for Type B. Type C has the remarkable decrease of activation energy of reduction from hematite to magnetite and little effect to the reduction from magnetite to wustite and wustite to iron.

The effect of heating rate on the activation energy and frequency factor is insignificant, as shown in Table 3. This means that the heat transfer through a mixture sample is fast and does not control the reaction rate.

4.3. Mechanisms of the Reduction of Iron Oxides Mixed with Graphite

Khaki et al.6) milled the mixture of hematite and graphite powder of about 20g using a planet-type alumina mill of 500 cc and 10 alumina balls of 20 mm diameter in the rotating speed of 200 rpm. Kasai et al.7) milled the mixture of 5g using a planet-type agate mill with 50 cc and 7 agate balls of 15 mm diameter in the rotating speed of 1350 rpm. Both of them obtained the temperature decrease of 150 to 200 K for the reduction of wustite to iron. Khaki et al. determined the activation energy of reduction reactions for the mixture of hematite and graphite powders which was mechanically milled for 6 to 100 h. The activation energy of reduction from hematite to magnetite was 98 to 166 kJ/mol, that from magnetite to wustite 249 to 358 kJ/mol and that from wustite to iron 831 to 3740 kJ/mol, corresponding to milling time. The last one was remarkably large. The frequency factors were also much larger than the present results. The activation energies and frequency factors decreased with the milling time of 6 and 24 h except the same value for the reduction of wustite and increased after 24 h. Kasai et al. reported that the activation energy of the reduction of wustite decreased from 226 to 19 kJ/mol and the order of reaction also decreased from 0.853 to 0.307 corresponding to the milling time of 0 and 60 min., respectively. The tendency of activation energy against milling time is opposite the present results. Sun et al.10) determined the activation energy of reduction from magnetite to wustite for the mixture of magnetite and carbon powders to be 65.7 kJ/mol and that from wustite to iron to be 69.5 kJ/mol. Murayama et al.12) reduced hematite powder to magnetite by CO–CO₂ gas and obtained the activation energy to be 100 kJ/mol. They have concluded that the controlling step of reduction is gas diffusion near the surface of iron oxide.

The effect of mechanical milling is the decrease of diameter of graphite particles, the strong contact of hematite with graphite and the distortion of atomic lattice of graphite.11) Graphite particles are crushed to be finer and adhere stronger to the surface of hematite particles by longer milling time. When the reduction of iron oxide proceeds, graphite covering iron oxide particles is consumed and the distance between graphite and iron oxide becomes large.

The reduction of iron oxides sequentially proceeds according to the Eqs. (1), (9) and (10) and a part of the product of CO₂ gas reacts with carbon to produce CO gas as follows;

\[ \text{CO}_2 + C \rightarrow 2\text{CO} \]

The reaction steps are composed of the reduction of iron oxide on its surface, the combustion of carbon by CO₂ on carbon surface and the interdiffusion of CO and CO₂ between both surfaces. The total activation energy of reduction is composed of the summation of these reaction steps. The distortion of atomic lattice of graphite by mechanical milling decreases the activation energy of reduction of iron oxides mixed with the graphite a little and less than the milled mixture of hematite and graphite. Thus, the decrease of activation energy due to milling is mainly caused by that graphite strongly adheres on the surface of iron oxide particles and the influence of gas diffusion to reaction rate becomes small.

The reaction rate of magnetite reduction is smaller and the effect of mechanical milling on the reaction rate is larger than that of hematite and wustite, as shown in Fig. 10. This is caused by that the magnetite reduction has the slowest rate of the reduction of iron oxides. Thus, the effect of adherence between iron oxide and graphite by mechanical milling appears clearly.

The activation energy and frequency factor of wustite reduction however tend to behave opposite those of hematite and magnetite reductions, though the reaction rate is same order as that of hematite reduction. As samples are the mixture of hematite and graphite, it is possible for the reduced...
iron to carbonize from graphite through their contact sites. The carbonization by CO gas is little possible because of high oxygen potential in equilibrium with iron and wustite. Then, the longer the milling time, the larger the contact area is and the more the carbonization of reduced iron proceeds. That is, the carbonization of reduced iron is added to the steps of wustite reduction and the activation energy additionally includes that of carbonization.

5. Conclusion

The reduction behavior of iron oxide powder mixed with graphite powder has been analyzed using a high temperature X-ray diffractometer. The start and end temperatures of reductions from hematite to magnetite, magnetite to wustite and wustite to iron decreased by 30 to 100 K with increasing mechanical milling time for the mixture of hematite and graphite. The activation energy of reduction remarkably decreased with increasing milling time for the milled mixture of hematite and graphite and a little for the mixture of hematite and milled graphite. The carbon coating on hematite particles was effective for the decrease of activation energy. The effect of mechanical milling on the reduction of iron oxides is concluded to make the adherence of graphite on iron oxide particles strong.

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