Reduction Kinetics of Natural Ilmenite Ore with Carbon Monoxide *

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In order to elucidate the reduction kinetics and mechanism of natural ilmenite ore with carbon monoxide, reduction experiments have been carried out using thermogravimetric technique in the temperature range between 1173 and 1323 K with three kinds of natural ilmenite ores from Australia, Malaysia and China. The reduction rate was analyzed in terms of the mixed-control kinetics by applying a shrinking unreacted-core model, on the basis of the observation of cross section of partially reduced ilmenite and X-ray diffraction patterns. The determined reaction rate constant $k_c$ and effective diffusivity $D_e$ are expressed in the temperature range between 1173 and 1323 K by the following equations:

$$k_c/\text{m} \cdot \text{s}^{-1} = \exp[-113 \times 10^3/(RT) + 5.03] \quad \text{(Australian)}$$

$$k_c/\text{m} \cdot \text{s}^{-1} = \exp[-47.0 \times 10^3/(RT) - 3.04] \quad \text{(Malaysian)}$$

$$k_c/\text{m} \cdot \text{s}^{-1} = \exp[-71.6 \times 10^3/(RT) + 0.554] \quad \text{(Chinese)}$$

$$D_e/\text{m}^2 \cdot \text{s}^{-1} = \exp[-4250/(T - 7.54)] \quad \text{(Australian)}$$

$$D_e/\text{m}^2 \cdot \text{s}^{-1} = \exp[-3860/(T - 7.94)] \quad \text{(Chinese)}$$

where $R$: gas constant (J · mol$^{-1}$ · K$^{-1}$), $T$: temperature (K). The activation energy of the reaction is 113, 47.0, 71.6 kJ mol$^{-1}$ for Australian, Malaysian and Chinese natural ilmenite ore, respectively. The calculated reduction curves using the rate parameters reproduced the experimental data well. The reduction rate increases with increasing reduction temperature. With respect to the rate-determining step for Australian and Chinese ilmenite ores, the relative contribution of resistance of a mass transfer step through gas film is smaller than that for synthetic ilmenite, while the relative contribution of resistance of a diffusion step of carbon monoxide through pores of the product layer is larger than that for synthetic ilmenite. As for Malaysian ilmenite ore, the overall rate is mainly controlled by a chemical reaction step.

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Keywords: reduction kinetics, natural ilmenite ore, upgrading, titanium, shrinking unreacted-core model, mixed-control kinetics, rate-determining step

1. Introduction

Since the available resources of high content natural rutile for a raw materials in the extractive metallurgy of titanium are diminishing, upgrading ilmenite occurred in abundant world wide to a rutile substitute and supplying it to titanium industries is in great demand. A number of processes has been proposed for upgrading ilmenite to a rutile substitute. One of these processes is the reduction of ilmenite ore with carbon monoxide to separate metallic iron and rutile. The objective of the present work is to analyze the reduction kinetics of natural ilmenite ore with carbon monoxide. However, the chemical composition, constituents and other properties in each natural ilmenite ore are different due to the difference of history such as weathering, preoxidation and so on. Therefore, with respect to an understanding the kinetics and mechanism in reduction of natural ilmenite ore, it is significantly difficult to put together the results for each ilmenite ore. From the above-mentioned view point, one of the present authors previously prepared a stoichiometric ilmenite, that is, synthesized FeTiO$_3$, and then carried out the reduction experiments by using the synthetic ilmenite with carbon monoxide to clarify the kinetics and mechanism in reduction.1)

In the present work the reduction experiments by using three kinds of natural ilmenite ores from Australia, Malaysia and China were conducted with carbon monoxide in the temperature range between 1173 and 1323 K, on the basis of the results of the synthetic ilmenite.

2. Experimental

2.1 Materials

Australian, Malaysian and Chinese natural ilmenite ores were used for the reduction experiments. Their chemical compositions are shown in Table 1. All the three kinds of natural ilmenite ores mainly consist of TiO$_2$, FeO and Fe$_2$O$_3$. The chemical compositions of these ores were then converted to the TiO$_2$–FeO–Fe$_2$O$_3$ system and illustrated in the phase diagram of titanium-iron-oxygen ternary system$^{2,3}$ as shown in Fig. 1. The oxygen content of each natural ilmenite ore is found to be higher than that of synthetic ilmenite. It was sup-

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Table 1 Chemical compositions of natural ilmenite ore.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Australian (mass%)</th>
<th>Malaysian (mass%)</th>
<th>Chinese (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>52.21</td>
<td>55.05</td>
<td>51.13</td>
</tr>
<tr>
<td>FeO</td>
<td>26.14</td>
<td>30.63</td>
<td>34.69</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>16.71</td>
<td>7.93</td>
<td>7.91</td>
</tr>
<tr>
<td>MnO</td>
<td>1.73</td>
<td>2.90</td>
<td>2.11</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.52</td>
<td>1.73</td>
<td>2.51</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.00</td>
<td>1.16</td>
<td>0.98</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.005</td>
<td>0.075</td>
<td>0.052</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.02</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0.12</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>0.40</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>
posed that the natural ilmenite ores were oxidized by weathering.

The mineral composition of each natural ilmenite ore was identified by X-ray diffraction technique and found to be principally FeTiO₃. The true density was 4.59 × 10³, 4.50 × 10³ and 4.71 × 10³ kg·m⁻³ for Australian, Malaysian and Chinese ilmenite ore, respectively. The particle diameters of these ores were observed under 10μm by means of scanning electron microscopy. These ilmenite ores were ground by using an agate mortar followed by pressuring to the 10 mm diam., 2.5 g briquette under about 400 MPa. The briquette sample has thickness of approximately 10 mm. The porosity of the briquette was 25–27%, regardless of a kind of the ilmenite ore. Assuming the briquette is regarded as sphere, the radius calculated from the volume of the briquette is 5.5–5.6 mm.

2.2 Apparatus and procedure

A thermogravimetric method was used to determine the reduction rate. The briquette sample was suspended from an electronic balance described elsewhere¹) into a quartz reaction tube of internal diameter 28.3 or 29.0 mm by a piece of Pt wire to measure the sample mass change. The temperatures examined were 1173, 1223, 1273 and 1323 K. While the sample was being heated to the experimental temperature, the reaction tube was purged with argon gas. When the temperature of the sample had reached the desired temperature, the inert argon gas was switched to CO–CO₂ gas mixture with the same flow rate as that of argon, and then the measurement of the mass change was commenced. After some definite time the CO–CO₂ gas mixture was switched to argon, the sample was cooled to room temperature and then weighed. The reduction ratio was calculated from the mass loss which corresponded to the oxygen content reduced with carbon monoxide during the experiment. Incidentally, the composition of CO–CO₂ gas mixture was adjusted to be 97%CO so as to prevent carbon deposition and cementite formation. The phases in the reduced product were identified by X-ray diffraction technique.

3. Analytical Method

Figure 2 shows an example of X-ray diffraction pattern of the reduction products for Australian ore. The X-ray diffraction patterns for Malaysian and Chinese ores were almost the same as that for Australian ore. Therefore, the main reaction in reduction of natural ilmenite ore with carbon monoxide is given by eq. (1).

\[
\text{FeTiO}_3(s) + \text{CO(g)} = \text{Fe(s)} + \text{TiO}_2(s) + \text{CO}_2(g)
\]  

(1)

The cross sections of partially reduced natural ilmenite ores are shown in Fig. 3. Although the reaction interface was clearly observed for the synthetic ilmenite,¹) it was not sharply observed for all the natural ilmenite ores. However, there appeared that the reduction reaction proceeded topochemically under the experimental conditions. The outer side was product layer composed of Fe and TiO₂, while the inner side was unreacted-core of FeTiO₃. Thus in this study, the reduction rate was analyzed in terms of the mixed-control kinetics by applying a shrinking unreacted-core model,⁴,⁵ similarly applied for the synthetic ilmenite.¹)

Considering the following three steps: the mass transfer of CO and CO₂ gas through gas film, then the diffusion of CO and CO₂ gas through pores of the product layer formed (Fe + TiO₂), and the chemical reaction at the reaction interface, the rate equation is derived as eq. (2).⁴,⁵

\[
\frac{C_b - C_e}{r_0 d_0} \left( \frac{t}{F} \right) = \frac{3 - 3F + F^2}{3k_\ell} + \frac{1}{k_e(1 + 1/K)}
\]  

(2)

Therefore, by plotting the left-hand side of eq. (2) against 3F–2F², the effective diffusivity of CO and CO₂ through the product layer Dₑ and the rate constant of the chemical reaction kₑ can be calculated from the slope and the intercept of eq. (2), respectively. The mass transfer coefficient through gas film kₖ can be estimated according to Ranz-Marshall’s equation.⁶ Incidentally, isothermal condition was assumed in the model, since the reaction heat in the reduction of ilmenite with CO–CO₂ gas mixture is relatively small. In fact the temperature change of the sample was not observed during the experiment. Moreover, neither swelling nor shrinking was observed in the briquette sample, and thus no change in size of the sample before and after the reduction was assumed in the model.
4. Results and Discussion

4.1 Effect of gas flow rate on reduction rate

Figure 4 shows an example of the effect of CO–CO$_2$ gas flow rate on reduction rate of ilmenite with carbon monoxide for Chinese ore under the experimental condition of 1273 K, CO97%. The reduction ratio of ilmenite was calculated from the mass loss which corresponded to the oxygen content reduced with carbon monoxide during the experiment. Then the reduction ratio $f$ is zero at $t = 0$. The difference of the reduction rate between the case of $V = 25.1 \times 10^{-6}$ m$^3$(STP) s$^{-1}$ and that of $V = 16.7 \times 10^{-6}$ m$^3$(STP) s$^{-1}$ is not significantly observed. This suggests that the relative contribution of resistance of mass transfer of gaseous species through gas film is relatively small. Similarly, the above-mentioned observation was found for the other ilmenite ores. Then the experimental data with the case of $V = 25.1 \times 10^{-6}$ m$^3$(STP) s$^{-1}$ was adopted to analyze the reduction kinetics.

4.2 Determination of rate parameters

Figures 5, 6 and 7 show the mixed-control plots based on eq. (2) for the representative data of the natural ilmenite ores. The mass transfer coefficient through gas film $k_f$ was estimated according to Ranz-Marshall’s equation$^6$ in the same manner as the synthetic ilmenite.$^1$ Table 2 shows the calcu-
lated values of mass transfer coefficient \( k_I \) through gas film at the various temperatures in the reduction with carbon monoxide for the natural ilmenite ores.

For both Australian and Chinese ores, the linear relationship with about the same slope is observed except for both the initial and final stages of the reaction. The straight lines are the regression results by the method of least squares. The rate constant of the chemical reaction \( k_c \) and the effective diffusivity of \( \text{CO} - \text{CO}_2 \) \( D_e \) through the product layer were determined from the intercept and the slope of the lines, respectively. However, as for Malaysian ore, almost the horizontal linear relationship was observed except for the initial stage of the reaction as shown in Fig. 7. This suggests that the chemical reaction step controls the overall reaction rate compared with the gas diffusion step through pores of the product layer. Figure 8 shows the plots of the experimental data under the presumption of chemical reaction control. The plots for Malaysian ore exhibit a good linear relationship, where the straight lines are the regression results by the method of least squares. Therefore, the rate constant of the chemical reaction \( k_c \) for Malaysian ore was determined from the slope of the lines. Incidentally, the straight lines in Fig. 7 correspond to those in Fig. 8.

With the values of the rate constant and the effective diffusivity obtained, their temperature dependence is shown in Fig. 9, together with those of the synthetic ilmenite. The effective diffusivities \( D_e \) for Australian and Chinese ilmenite ores are smaller than that for the synthetic ilmenite. This indicates that the resistance of the diffusion of gaseous species
through pores of the product layer for these ores is larger than that for the synthetic ilmenite. The rate constant $k_c$ decreases in the sequence of the synthetic, Australian, Chinese, Malaysian samples. This is caused by the FeTiO$_3$ activity of less than unity for natural ilmenite ores. Especially the rate constant $k_c$ for Malaysian ore is considerably small.

This suggests that the resistance of the chemical reaction for Malaysian ore is much larger than those for the other samples.

The temperature dependence of the rate constant and the effective diffusivity obtained is given in terms of Arrhenius equation as eqs. (3)–(9),

$$
k_c / m \cdot s^{-1} = \exp[-130 \times 10^3/(RT) + 7.15](1173–1373 \text{ K}) \quad \text{(synthetic)}^{1}
$$

$$
D_c / m^2 \cdot s^{-1} = \exp(-4330/T - 6.16)(1173–1373 \text{ K}) \quad \text{(synthetic)}^{1}
$$

$$
k_c / m \cdot s^{-1} = \exp[-113 \times 10^3/(RT) + 5.03](1173–1323 \text{ K}) \quad \text{(Australian)}
$$

$$
D_c / m^2 \cdot s^{-1} = \exp(-4250/T - 7.54)(1173–1323 \text{ K}) \quad \text{(Australian)}
$$

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**Table 2** Calculated values of mass transfer coefficient through gas film at the various temperatures in the reduction of ilmenite with carbon monoxide for Australian, Chinese, Malaysian ilmenite ores. A: Australian, C: Chinese, M: Malaysian

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$D_{CO-CO_2}$ (m$^2$ s$^{-1}$)</th>
<th>$\mu$ (kg m$^{-1}$ s$^{-1}$)</th>
<th>$\rho$ (kg m$^{-3}$)</th>
<th>$Sc$ (-)</th>
<th>$\rho_0$ (kg m$^{-3}$)</th>
<th>$Re$ (-)</th>
<th>$Sh$ (-)</th>
<th>$k_c$ (m s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1173</td>
<td>$2.23 \times 10^{-4}$</td>
<td>$4.94 \times 10^{-5}$</td>
<td>$2.96 \times 10^{-1}$</td>
<td>0.681</td>
<td>A</td>
<td>$16.4 \times 10^{-2}$</td>
<td>12.1</td>
<td>3.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>$16.3 \times 10^{-2}$</td>
<td>11.9</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>$16.6 \times 10^{-2}$</td>
<td>12.2</td>
<td>3.85</td>
</tr>
<tr>
<td>1223</td>
<td>$2.41 \times 10^{-4}$</td>
<td>$4.60 \times 10^{-5}$</td>
<td>$2.84 \times 10^{-1}$</td>
<td>0.674</td>
<td>A</td>
<td>$17.1 \times 10^{-2}$</td>
<td>11.8</td>
<td>3.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>$17.0 \times 10^{-2}$</td>
<td>11.6</td>
<td>3.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>$17.3 \times 10^{-2}$</td>
<td>12.0</td>
<td>3.82</td>
</tr>
<tr>
<td>1273</td>
<td>$2.59 \times 10^{-4}$</td>
<td>$4.71 \times 10^{-5}$</td>
<td>$2.73 \times 10^{-1}$</td>
<td>0.667</td>
<td>A</td>
<td>$18.7 \times 10^{-2}$</td>
<td>12.1</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>$17.7 \times 10^{-2}$</td>
<td>11.3</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>$18.0 \times 10^{-2}$</td>
<td>11.7</td>
<td>3.79</td>
</tr>
<tr>
<td>1323</td>
<td>$2.78 \times 10^{-4}$</td>
<td>$4.82 \times 10^{-5}$</td>
<td>$2.62 \times 10^{-1}$</td>
<td>0.661</td>
<td>A</td>
<td>$18.5 \times 10^{-2}$</td>
<td>11.3</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
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<td>C</td>
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<td>11.1</td>
<td>3.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>$18.7 \times 10^{-2}$</td>
<td>11.4</td>
<td>3.77</td>
</tr>
</tbody>
</table>

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Fig. 8 Plots of experimental data under the presumption of chemical reaction control for Malaysian ilmenite ore.

Fig. 9 Temperature dependence of the reaction rate constants $k_c$ and the effective diffusivities $D_c$. S: Synthetic, A: Australian, C: Chinese, M: Malaysian.
Table 3 The rate parameters and equilibrium constant used in calculation of the reduction curves of ilmenite with carbon monoxide.

<table>
<thead>
<tr>
<th></th>
<th>Australian</th>
<th>Chinese</th>
<th>Malaysian</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>$D_c$ (m$^2$·s$^{-1}$)</td>
<td>$k_c$ (m·s$^{-1}$)</td>
<td>$D_c$ (m$^2$·s$^{-1}$)</td>
</tr>
<tr>
<td>1173</td>
<td>$1.41 \times 10^{-5}$</td>
<td>$1.44 \times 10^{-3}$</td>
<td>$1.33 \times 10^{-3}$</td>
</tr>
<tr>
<td>1223</td>
<td>$1.64 \times 10^{-5}$</td>
<td>$2.31 \times 10^{-3}$</td>
<td>$1.52 \times 10^{-3}$</td>
</tr>
<tr>
<td>1273</td>
<td>$1.88 \times 10^{-5}$</td>
<td>$3.57 \times 10^{-3}$</td>
<td>$1.73 \times 10^{-3}$</td>
</tr>
<tr>
<td>1323</td>
<td>$2.13 \times 10^{-5}$</td>
<td>$5.34 \times 10^{-3}$</td>
<td>$1.93 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

where $R$ is gas constant (8.3144 J·mol$^{-1}$·K$^{-1}$), $T$: temperature (K). The activation energy of the reaction for the synthetic, Australian, Chinese and Malaysian samples is obtained to be 130, 113, 71.6 and 47.0 kJ·mol$^{-1}$ from eqs. (3), (5), (7) and (9), respectively. The values of the activation energy of the reaction for all the natural ilmenite ores are smaller than that for the synthetic ilmenite. This is supposed to be due to the FeTiO$_3$ activity of less than unity for natural ilmenite ores. On the other hand, the temperature dependence of $D_c$ is small compared with that of $k_c$. The apparent activation energy of the diffusion for Australian and Chinese ores is calculated as 35.3 and 32.1 kJ·mol$^{-1}$ from eqs. (6) and (8), respectively, similarly obtained as 36.0 kJ·mol$^{-1}$ from eq. (4) for the synthetic ilmenite. These values were about the same. Table 3 shows the rate parameters obtained and equilibrium constant $k$. \(^{1)}

4.3 Comparison of experimental data with calculated reduction curves

The comparison of the experimental data with the calculated reduction curves based on eq. (2) are shown in Figs. 10, 11 and 12 for Australian, Chinese and Malaysian ores, respectively. In these figures, the symbols and the solid lines correspond to the representative experimental data and the calculated reduction curves, respectively. The calculated reduction curves using the rate parameters reproduce the experimental data well, except for early stage of reaction where they exhibit delays as compared with the experimental data. This

\[
k_c/m \cdot s^{-1} = \exp(-71.6 \times 10^{3}/(RT) + 0.554)(1173-1323 K) \quad \text{(Chinese)} \]

\[
D_c/m^2 \cdot s^{-1} = \exp(-3860/T - 7.94)(1173-1323 K) \quad \text{(Chinese)}
\]

\[
k_c/m \cdot s^{-1} = \exp(-47.0 \times 10^{3}/(RT) - 3.04)(1173-1323 K) \quad \text{(Malaysian)}
\]
is because the reduction reaction of the following equation, which proceeds much faster than the main reaction of eq. (1), also occurs.

$$\text{Fe}_2\text{TiO}_3(s) + \text{TiO}_2(s) + \text{CO}(g) = 2\text{FeTiO}_3(s) + \text{CO}_2(g)$$

(10)

As it can be noted, the reduction rate increases with increasing the reduction temperature. However, the effect of the temperature on reduction rate was not so large. Incidentally, the rate parameters used in calculation are given for $k_1$ in Table 2, for $D_\varepsilon$ and $k_\varepsilon$ in Table 3.

In Fig. 13, the reduction curves of ilmenite with carbon monoxide for the synthetic, Australian, Chines and Malaysian samples are summarized. The reduction of all the natural ilmenite ores proceeds considerably slower than that of the synthetic ilmenite. This is because the relative contribution of resistance of the diffusion of gaseous species through pores of the product layer for Australian and Chinese ores and that of resistance of the chemical reaction for Malaysian ore is much larger than that of the synthetic ilmenite, as described next.

4.4 Relative contributions of resistance to the overall resistance

In the shrinking unreacted-core model, three steps are considered as described by eq. (2). The overall resistance $\lambda$ is expressed as the sum of three terms in right-hand side of eq. (11), which pertains to the resistance of mass transfer of gaseous species through gas film, the diffusion of gaseous species through pores of the product layer, and the chemical reaction at the interface $1,4,5$.

$$\lambda = \frac{1}{k_f} + \frac{r_0}{D_\varepsilon} \left\{ (1 - f)^{-1/3} - 1 \right\} + \frac{(1 - f)^{-2/3}}{k_\varepsilon (1 + 1/K)}$$

(11)

Figure 14 summarizes the relative contributions of resistance to the overall resistance. For Australian and Chinese ores, the fractional resistance of the mass transfer through gas film $\eta_1$ is smaller than that for the synthetic ilmenite, while the fractional resistance of the diffusion through pores of the product layer $\eta_2$ is larger than that for the synthetic ilmenite. As for Malaysian ore, the fractional resistance of the chemical reaction is much larger than that for the synthetic ilmenite.

With respect to the effect of the temperature on fractional resistance, at the lower temperature the fractional resistance of the chemical reaction $\eta_2$ for Australian and Chinese ores is relatively large, similarly observed for the synthetic ilmenite. It follows that both the fractional resistance of the mass transfer through gas film $\eta_1$ and the diffusion through pores of the product layer $\eta_2$ increase with increasing the temperature. As for Malaysian ore, the effect of the temperature on fractional resistance was not significantly observed.

Consequently, in the initial stage of the reaction for Australian and Chinese ores, the overall rate is controlled by both the mass transfer step through gas film and the chemical reaction step, while in the final stage both the diffusion step through pores of the product layer and the chemical reaction

![Image of graphs showing reduction curves of ilmenite with carbon monoxide for different temperatures and samples.](image-url)
step determine the overall reaction rate, similarly observed for the synthetic ilmenite. Concerning Malaysian ore, the overall rate is mainly controlled by the chemical reaction step.

5. Conclusions

Reduction experiments of three kinds of natural ilmenite ores with carbon monoxide have been carried out in the temperature range between 1173 and 1323 K to clarify the kinetics and mechanism in reduction. The reduction rate was analyzed in terms of the mixed-control kinetics by applying the isothermal shrinking unreacted-core model, on the basis of the observation of cross section of partially reduced ilmenite and X-ray diffraction patterns. The results are summarized as follows:

The reduction rate increases with increasing reduction temperature. The reaction rate constant $k_c$ and the effective diffusivity $D_e$ determined are expressed in the temperature range between 1173 and 1323 K by the following equations for Australian, Malaysian and Chinese ilmenite ores:

\[
k_c/m \cdot s^{-1} = \exp[-113 \times 10^3/(RT) + 5.03]\]  
(Australian)

\[
k_c/m \cdot s^{-1} = \exp[-47.0 \times 10^3/(RT) - 3.04]\]  
(Malaysian)

\[
k_c/m \cdot s^{-1} = \exp[-71.6 \times 10^3/(RT) + 0.554]\]  
(Chinese)

\[
D_e/m^2 \cdot s^{-1} = \exp(-4250/T - 7.54)\]  
(Australian)

\[
D_e/m^2 \cdot s^{-1} = \exp(-3860/T - 7.94)\]  
(Chinese)

where $R$: gas constant (J-mol$^{-1}$-K$^{-1}$), $T$: temperature (K). The activation energy of the reaction is 113, 47.0, 71.6 kJ-mol$^{-1}$ for Australian, Malaysian and Chinese ilmenite ores, respectively. The calculated reduction curves using the rate parameters finely reproduced the experimental data.

With respect to the rate-determining step for Australian and Chinese ores, in the initial stage of the reaction the overall rate is controlled by both the mass transfer step through gas film and the chemical reaction step, while in the final stage both the diffusion step through pores of the product layer and the chemical reaction step determine the overall reaction rate, similarly observed for the synthetic ilmenite. As for Malaysian ilmenite ore, the overall rate is mainly controlled by the chemical reaction step.
Acknowledgments

The authors wish to thank Miss S. Takano and Messrs. K. Mugishima, H. Utsumi and T. Kikuya for their assistance in the experiments.

Nomenclature

\( C_b \): CO gas concentration in bulk of gas (molCO \cdot m^{-3})
\( C_e \): CO gas concentration at equilibrium (molCO \cdot m^{-3})
\( D_{CO-CO_2} \): gas diffusivity of CO–CO_2 (m^2 \cdot s^{-1})
\( D_{e} \): effective diffusivity in product layer (m^2 \cdot s^{-1})
\( F \): relative thickness of product layer \( F = 1 - r_i/r_0 = 1 - (1 - f)^{1/3} \)
\( K \): equilibrium constant of reaction, FeTiO_3(s) + CO(g) = Fe(s) + TiO_2(s) + CO_2(g)
\( R \): gas constant 8.3144 J \cdot mol^{-1} \cdot K^{-1}
\( Re \): Reynolds number \( = 2r_0u_d\rho/\mu \)
\( Sc \): Schmidt number \( = \mu/(\rho D_{CO-CO_2}) \)
\( Sh \): Sherwood number \( = 2r_0k_i/D_{CO-CO_2} \)
\( T \): temperature (K)
\( V \): gas flow rate (m^3(STP) \cdot s^{-1})
\( dO \): apparent oxygen concentration (mol \cdot m^{-3})
\( f \): reduction ratio of ilmenite (—)
\( k_i \): rate constant of chemical reaction at the reaction interface (m \cdot s^{-1})
\( k_t \): mass transfer coefficient through gas film (m \cdot s^{-1})
\( r_i \): initial radius (m)
\( r_o \): radius of unreacted-core (m)
\( r \): time (s)
\( u \): gas velocity (m \cdot s^{-1})
\( \eta_i \) (i = c, d, f): fractional resistance of chemical reaction, gaseous diffusion through pores of product layer and mass transfer through gas film, respectively (—)
\( \lambda \): overall resistance of reaction (s \cdot m^{-1})
\( \mu \): viscosity of gas mixture (kg \cdot m^{-1} \cdot s^{-1})
\( \rho \): density of gas mixture (kg \cdot m^{-3})

REFERENCES