Oxygen Exchange Reaction between CO$_2$–CO Gas and Molten Oxide Containing Iron Oxide

Xiaojun HU, Hiroyuki MATSUURA and Fumitaka TSUKIHASHI

1) Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083 China. 2) Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561 Japan.

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Oxygen exchange reaction rates between CO$_2$–CO gas and molten oxides containing iron oxide have been measured by isotope exchange technique with $^{18}$O at 1 773 K with $P_{CO_2}/P_{CO} = 1$. Measured results represent that the oxygen exchange reaction rates show the maximum values at the beginning of the reaction and sharply decrease within approximately 20 s, and then gradually decrease with the reaction time proceeds. These changes indicate that the rate-limiting step would change from the dissociative adsorption of oxygen on the surface of molten oxide in the initial stage of reaction to the mass transfer of oxide ion from the surface to the inside of molten oxide in the following stage. Based on the kinetic analysis of the oxygen exchange process, CO$_2$ dissociation rate constant, CO$_2$ re-formation rate constant and the mass transfer coefficient of oxide ion in molten oxides were calculated for the FeO$_x$–CaO and FeO$_x$–SiO$_2$ systems. Addition of CaO and SiO$_2$ to molten oxide increases and decreases the oxygen exchange reaction rate, respectively.

KEY WORDS: oxygen exchange reaction; kinetics; isotope exchange technique; CO$_2$ dissociation; CO$_2$ re-formation; mass transfer.

1. Introduction

It is well known that a real understanding to the overall reaction process of CO$_2$–CO gas and molten oxide containing iron oxide requires the knowledge of the interfacial reactions and transport phenomena in gas and molten oxide phases, simultaneously. However, due to the large difference between the chemical reaction rate and mass transfer rate in gas and in melts, it is difficult to give an accurate description with a whole kinetic equation for the overall reaction process. Usually, mass transfer coefficient and reaction rate constant are separately measured by the steady state approximation and various experimental techniques. Especially, the $^{14}$CO$_2$–CO and $^{13}$CO$_2$–CO isotope exchange technique has been utilized to measure the interfacial chemical reaction rate of CO$_2$ and CO gas on the surface of various molten oxide systems and many valuable results have been obtained.

In the field of catalyst, O$_2$, CO$_2$, H$_2$O and CO enriched $^{18}$O have been used to investigate the mechanisms of oxygen exchange reaction on the surface of solid metal and oxide as catalysts at lower temperature. Some researchers have noticed that the effect of oxygen diffusion in bulk of solid metal and oxide on the overall process became bigger with the increase of temperature and must be considered.

In the previous study, authors measured the oxygen exchange reaction rate between CO$_2$–CO gas containing $^{18}$O and molten iron oxide at 1 723 to 1 823 K with different $P_{CO_2}/P_{CO}$ ratios. The reaction rates were measured and the effects of temperature and $P_{CO_2}/P_{CO}$ ratio on the CO$_2$ dissociation rate constant, CO$_2$ re-formation rate constant and the mass transfer coefficient of oxide ion in the molten iron oxide were clarified.

In the present study, the oxygen exchange reaction rate between CO$_2$–CO gas and molten oxide containing iron oxide was measured by utilizing isotope exchange technique. The CO$_2$–CO gas containing $^{18}$O enriched CO$_2$ was used to clarify the oxygen exchange reaction process between gas and molten oxide. The experiments were carried out for the FeO$_x$–CaO and FeO$_x$–SiO$_2$ melts at 1 773 K with $P_{CO_2}/P_{CO} = 1$. To analyze the experimental results, a kinetic model considering the interfacial reaction and mass transfer of oxide ion in molten oxide was discussed. The CO$_2$ dissociation rate constant, the CO$_2$ re-formation rate constant and the mass transfer coefficient of oxide ion in molten oxide were calculated by this model. The effects of CaO and SiO$_2$ additions to molten oxide on the reaction rate constants were discussed.

2. Experimental

The experimental apparatus is similar to that used in previously reported works. The experimental arrangement is shown in Fig. 1. FeO was prepared by melting electrolytic iron powder and reagent grade Fe$_2$O$_3$ powder with 1 : 1 (mol ratio) in an iron crucible at 1 723 K for 30 min and rapidly cooling on an iron plate in argon atmosphere. CaO was prepared by calcining reagent grade CaCO$_3$ powder in a mullite crucible at 1 173 K for 24 h in air atmo-
sphere. Prepared FeO, CaO and reagent grade SiO₂ were preliminarily melted to prepare samples. About 5 g of pre-melted specimen were put in a platinum crucible (ID 16 mm, depth 8 mm and height 18.5 mm), whose up-edge was tightly connected to an alumina reaction tube (ID 16 mm, OD 21 mm). CO₂–CO–Ar gas mixture purified by passing through columns of H₂SO₄, Mg(ClO₄)₂ and, for CO gas, soda lime was blown through an alumina tube (ID 4 mm, OD 6 mm) to the surface of sample with flow rate of above 700 cm³/min STP. Flow rate was controlled and measured by using flowmeter calibrated by soap bubble flowmeter. Temperature was monitored by a dual wavelength pyrometer and controlled at 1 773 K.

In each experiment, C₁₆O₂–CO gas was blown into a reaction tube and then crucible was heated to the experimental temperature at first. Specimen was held at that temperature for about 30 min to ensure the equilibration with CO₂–CO gas, and then CO₂ gas was changed to ¹⁸O enriched CO₂ gas and Ar gas was added to increase the gas flow rate. The isotopic composition of the reaction gas was continuously measured by a quadrupole mass spectrometer. The content of ¹⁸O in the isotope enriched CO₂ gas was 4.0%. Experiments were conducted by using CO₂–CO gas which ratio is unity at 1 773 K for the FeO–CaO and FeOₓ–SiO₂ systems. After each experiment, the surface of the reacted sample was measured and the chemical composition was analyzed, by titration method with potassium dichromate for total iron and Fe⁡²⁺ contents, by ICP-AES for calcium content and by gravimetry for SiO₂ content, respectively.

3. Results and Discussion

3.1. Estimation of the Isotopic Composition of the Reaction Gas

It is necessary to clarify the isotopic composition of CO₂ gas enriched ¹⁸O (abundance 4.0%) in the reaction gas before experiments. Therefore, the isotopic composition of CO₂ gas was measured and compared with calculated composition assuming the isotopic equilibrium based on isotope relative ratios: ¹²C(0.9893), ¹³C(0.0107), ¹⁶O(0.9576), ¹⁷O(0.00036) and ¹⁸O(0.040). Blowing CO₂ gas into a blank reaction tube, the isotopic compositions of ingoing and outgoing gas were measured. The measured results represented no change of the isotopic composition between ingoing and outgoing CO₂. From the mass spectrometric results, the ratios of isotopic species were calculated, which results were shown in Table 1.

The measured and computed ratios of isotopic species are in accordance with each other as shown in Table 1 and the isotopic equilibrium in CO₂ gas was confirmed. The CO₂ gas contains 7.71% of ¹²C¹⁶O¹⁸O and 0.18% of ¹³C¹⁸O₂.

3.2. Calculation of Oxygen Exchange Rate

A typical result of ion current profiles of various isotopic species was shown in Fig. 2. From the measured mass spectrometric data, the following calculations were conducted to obtain the oxygen exchange rate.

The reaction exchange of oxygen between CO₂–CO gas and the molten oxide is expressed as Eqs. (1) to (3) and the reaction rates of each reaction could be represented as Eqs. (4) to (6), respectively.

\[
C^{18}O_2(g) = C^{18}O(g) +^{18}O(ad) \quad \text{(1)}
\]
\[
C^{16}O^{18}O(g) = C^{16}O(g) +^{18}O(ad) \quad \text{(2)}
\]
\[
C^{16}O^{16}O(g) = C^{18}O(g) +^{16}O(ad) \quad \text{(3)}
\]
Adsorbed $^{18}$O diffuses into the molten oxide as expressed by Eq. (7) and that rate is expressed as Eq. (8),

$$r_{(3)} = A \left( \frac{1}{2} k_3 P_{46} - k_2 P_{30} [^{16}\text{O}(\text{ad})] \right)$$

where, scripts (g) and (ad) represent species in gas and on the surface of melt, respectively. $k_1$ and $k_2$ represent the dissociation and the re-formation rate constants of CO$_2$. Dissociation rate of Eq. (2) was expressed by $1/2 k_2 P_{46}$ as described in Eq. (5) because the dissociation rate of Eq. (3) is considered to be the same as that of Eq. (2) assuming the isotopic effect is negligible. $k_3$ is the mass transfer coefficient of oxide ion in molten oxide. Subscripts represent the species (28: C$_{16}$O, 30: C$_{18}$O, 44: C$_{16}$O$_2$, 46: C$_{16}$O$^{18}$O and 48: C$_{16}$O$_{30}$), respectively. $P_i$ and $A$ are the partial pressure of species $i$ and reaction area, respectively. [$^{18}$O(ad)] and [$^{18}$O(b)] are the concentrations of $^{18}$O adsorbed on the surface of molten oxide and contained in molten oxide, respectively.

The oxygen exchange reaction rate was defined and calculated by Eq. (9) from the mass balance for $^{18}$O in the reaction system,\(^2\)

$$r = \frac{dn_{^{18}\text{O}}}{dt} = -\frac{\Delta(n_{30} + n_{46} + 2n_{48})}{\Delta t}$$

$$= -\frac{V}{RT} \frac{\Delta(P_{30} + P_{46} + 2P_{48})}{\Delta t}$$

$$= \frac{V}{RT} \left( (P_{30} + P_{46} + 2P_{48})^{in} - (P_{30} + P_{46} + 2P_{48})^{out} \right)$$

$$= \frac{P^o}{RT} \left[ \frac{I_{30}}{I_{44} + I_{46} + I_{48}} - \left( \frac{I_{46}}{I_{44} + I_{46} + I_{48}} \right)^{out} \right]$$

where $n_{^{18}\text{O}}$ is the number of mole of $^{18}$O transferred to melt. $t$ is time, $V$ and $T$ are volume and temperature of gas, and $R$ is gas constant. $n_i$ and $I_i$ are the number of mole and ion current measured by mass spectrometer for species $i$, respectively. $P^o (=1.01325 \times 10^5$ Pa) is the standard atmospheric pressure. $V$, $V_{CO}$, and $V_{CO}$ are the total flow rate of reaction gas, the flow rate of CO$_2$ and CO gases, respectively. Superscripts “in” and “out” represent the ingoing and outgoing gas, respectively.

In the present study, it is important to determine the starting point of the reaction ($t=0$). However, the change of the measured ion currents by mass spectrometer was observed about 10 s after the $^{18}$O-enriched CO$_2$ gas was introduced into the apparatus because of the dead volume in the gas introduction tubes. Since the oxygen exchange reaction rate would represent the maximum at the beginning of the reaction, the starting point of the reaction ($t=0$) was determined by the change of the calculated exchange reaction rate.

Figure 3 shows the oxygen exchange reaction rate between CO$_2$–CO gas ($P_{CO}/P_{CO}=1$) and the molten FeO$_x$–CaO at 1773 K. All measured results represent that the oxygen exchange reaction rates sharply decrease within approximately 20 s from the beginning of the measurement, and then gradually decrease with the reaction time proceeds. It can be considered that the rates of the forward reactions of Eqs. (1) and (2) are constant for particular compositions of molten oxide, however the rates of the inverse reactions in-
crease from 0 at the initial stage of reaction due to the increase of $^{18}$O concentration in molten oxide. The change of reaction rate indicates that the rate-limiting step would change from the dissociative adsorption of oxygen on the surface of molten oxide in the initial stage of reaction to the mass transfer of oxide ion from the surface to the inside of molten oxide in the following stage. Oxygen exchange reaction rates for the FeO$_x$–CaO system are larger than that for the FeO$_x$ system, though the effect of CaO content is not obviously measured.

Figure 4 shows the oxygen exchange reaction rate between CO$_2$–CO gas ($P_{CO_2}/P_{CO}=1$) and the molten FeO$_x$–SiO$_2$ at 1773 K. When the rate becomes small, the calculated data are scattered because the influence of fluctuations of measured data relatively swells. All measured results represent that the reaction rates are the largest at the beginning of the reaction and then decrease with time, that are the same as the cases of the FeO$_x$–CaO system. However, the reaction rate decreases with increasing SiO$_2$ content of molten oxides, which differs from the FeO$_x$–CaO system.

The experimental conditions and the results of chemical analyses are summarized in Table 2.

### 3.3. Kinetic Analysis for the Oxygen Exchange Process

To understand the oxygen exchange process between CO$_2$–CO gas and molten oxide, the kinetic analysis has been conducted considering the dissociation reaction of CO$_2$ on the surface of molten oxide and mass transfer of oxide ion in the bulk of molten oxide simultaneously.

The variation of the superficial concentration of $^{18}$O can be written as Eq. (10) from Eqs. (4), (5) and (8),

$$ A \delta \frac{d[^{18}O(ad)]}{dt} = \frac{A_k}{2} \left( \frac{P_{CO_2}^{in}}{P_{CO}} + \frac{P_{CO}^{in}}{P_{CO}} \right) $$

$$ - A_k \left( \frac{P_{CO_2}^{in} + P_{CO}^{in}}{2} \right) [^{18}O(ad)] - A_k \left[ [^{18}O(ad)] - [^{18}O(b)] \right] $$

On the other hand, Eq. (11) is obtained from the mass balance for $^{18}$O in molten oxide,

$$ V_i \frac{d[^{18}O(b)]}{dt} = A_k \left( [^{18}O(ad)] - [^{18}O(b)] \right) $$

where, $\delta$ represents a thickness of reaction layer on the surface of molten oxide where the reactions occur and the products accumulate. $V_i$ is the volume of molten oxide.

From Eq. (10), the following Eq. (12) can be obtained,

$$ [^{18}O(b)] = \frac{\delta}{k_3} \frac{d[^{18}O(ad)]}{dt} + k_2 \left( \frac{P_{CO_2}^{in} + P_{CO}^{in}}{2} \right) + k_3 [^{18}O(ad)] $$

$$ - \frac{k_1 \left( \frac{P_{CO_2}^{in} + P_{CO}^{in}}{2} \right)}{k_3} $$

Differentiation of Eq. (12) with time leads to Eq. (13),

$$ \frac{d[^{18}O(b)]}{dt} = \frac{\delta}{k_3} \frac{d^2[^{18}O(ad)]}{dt^2} $$

$$ + k_2 \left( \frac{P_{CO_2}^{in} + P_{CO}^{in}}{2} \right) + k_3 \frac{d[^{18}O(ad)]}{dt} $$

### Table 2. The experimental conditions and results.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>CO$_2$/CO</th>
<th>$\bar{V}_{CO_2}$</th>
<th>$\bar{V}_{CO}$</th>
<th>$\bar{P}_{CO}^{in}$</th>
<th>$\bar{P}_{CO_2}^{in}$</th>
<th>Reaction gas</th>
<th>Sample</th>
<th>$X_{CaO}$/$X_{SiO_2}$</th>
<th>CaO or SiO$_2$</th>
<th>$b$</th>
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<tbody>
<tr>
<td>F-0</td>
<td>1773</td>
<td>1.0</td>
<td>2.13</td>
<td>2.13</td>
<td>7.29</td>
<td>1.81</td>
<td>0.188</td>
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<td>5.0</td>
<td>6.6</td>
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<tr>
<td>FC-1</td>
<td>1773</td>
<td>0.91</td>
<td>2.23</td>
<td>2.46</td>
<td>7.32</td>
<td>2.00</td>
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<td>CaO: 4.11</td>
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<tr>
<td>FC-2</td>
<td>1773</td>
<td>1.0</td>
<td>2.15</td>
<td>2.15</td>
<td>7.29</td>
<td>1.81</td>
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<td>8.66</td>
<td>6.3</td>
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<td>FC-3</td>
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<td>2.15</td>
<td>2.15</td>
<td>7.29</td>
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<td>0.265</td>
<td>12.23</td>
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<tr>
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<td>2.17</td>
<td>2.17</td>
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<td>2.10</td>
<td>2.13</td>
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<td>0.230</td>
<td>SiO$_2$: 3.77</td>
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<tr>
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<td>2.05</td>
<td>7.14</td>
<td>1.74</td>
<td>0.165</td>
<td>8.62</td>
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<tr>
<td>FS-3</td>
<td>1773</td>
<td>0.99</td>
<td>2.11</td>
<td>2.15</td>
<td>7.16</td>
<td>1.80</td>
<td>0.238</td>
<td>13.32</td>
<td>4.7</td>
<td></td>
</tr>
</tbody>
</table>

* $\frac{1}{2} P_{CO_2}^{in} + P_{CO_2}^{in} = 0.0771 + 0.5 + 0.0018$ and $P_{CO_2}^{in} + P_{CO_2}^{in} = 0.0018$. $P_{CO_2}^{in}$ and $P_{CO_2}^{in}$ are calculated by flowrates of ingoing gases.
Substituting Eqs. (12) and (13) into Eq. (11), a second-order differential equation is obtained as Eq. (14),
\[
\frac{d^2[18O(ad)]}{dt^2} + \left[ k_2 \left( \frac{P_{28}^{in} + P_{30}^{in}}{\delta} \right) + Ak_3 \right] \frac{d[18O(ad)]}{dt} + \frac{Ak_2 k_3 (P_{28}^{in} + P_{30}^{in})}{V_1 \delta} [18O(ad)] = \frac{Ak_1 k_3 \left( \frac{P_{26}^{in} + P_{48}^{in}}{2} \right)}{V_1 \delta}
\]
Using the initial conditions \([18O(ad)]_{t=0} = 0\) and \(\frac{d[18O(ad)]}{dt}_{t=0} = \frac{k_1 (\frac{P_{46}^{in}}{2} + P_{48}^{in})}{k_2 (P_{28}^{in} + P_{30}^{in})}\), Eq. (15) is obtained,
\[
[18O(ad)] = \exp \left[ \lambda_1 t \right] \cdot \frac{k_1 (\frac{P_{46}^{in}}{2} + P_{48}^{in})}{k_2 (P_{28}^{in} + P_{30}^{in})} \left( 1 + \frac{k_2 (P_{28}^{in} + P_{30}^{in})}{\delta} + \frac{k_1 (P_{28}^{in} + P_{30}^{in})}{\lambda_2} + \frac{1}{\lambda_1 - \lambda_2} \right)
\]
where,
\[
\lambda_1 = \frac{e - k_1(V_e + A\delta)}{2V_1 \delta} \quad \lambda_2 = \frac{-e - k_1(V_v + A\delta)}{2V_1 \delta}
\]
\[
e = \sqrt{\left( k_1(V_e + A\delta) + V_1 k_2 (P_{28}^{in} + P_{30}^{in}) \right)^2 - 4AV_1 \delta k_1 k_3 (P_{28}^{in} + P_{30}^{in})}
\]
Hence, the \(^{18}\text{O}\) oxygen exchange reaction rate between CO\(_2\)-CO gas and molten oxide can be expressed as Eq. (19) from Eqs. (4), (5) and (15),
\[
r = A \left[ k_1 \left( \frac{P_{46}^{in}}{2} + P_{48}^{in} \right) - k_2 \left( \frac{P_{28}^{in} + P_{30}^{in}}{2} \right) [18O(ad)] \right]
\]
Using the initial conditions \([18O(ad)]_{t=0} = 0\) and \(\frac{d[18O(ad)]}{dt}_{t=0} = \frac{k_1 (\frac{P_{46}^{in}}{2} + P_{48}^{in})}{k_2 (P_{28}^{in} + P_{30}^{in})}\), Eq. (15) is obtained,
\[
[18O(ad)] = \exp \left[ \lambda_1 t \right] \cdot \frac{k_1 (\frac{P_{46}^{in}}{2} + P_{48}^{in})}{k_2 (P_{28}^{in} + P_{30}^{in})} \left( 1 + \frac{k_2 (P_{28}^{in} + P_{30}^{in})}{\delta} + \frac{k_1 (P_{28}^{in} + P_{30}^{in})}{\lambda_2} + \frac{1}{\lambda_1 - \lambda_2} \right)
\]
Since the oxygen exchange rate is expressed as \(r = C_1\) at \(t=0\) from Eq. (19), the parameter \(C_1\) was determined from the exchange rate at \(t=0\) for each experimental result. Then, regression analysis of each experimental result by Eq. (19) was conducted to determine other parameters \(C_2\), \(\lambda_1\) and \(\lambda_2\). Fitted curves by regression analysis for each experimental result are shown in Figs. 3 and 4, and obtained parameters were summarized in Table 3. Reaction rate constants, \(k_1\) to \(k_2\), can be calculated from obtained parameters by Eqs. (20) to (22), from the relationship between Eqs. (16) to (19).

\[
k_1 = \frac{C_1}{A \left( \frac{P_{46}^{in}}{2} + P_{48}^{in} \right)}
\]
\[
k_2 = \frac{V_1}{A \left( \frac{P_{28}^{in} + P_{30}^{in}}{2} \right)} \frac{-\lambda_1 \lambda_2 \left( C_2 \lambda_1 + (1-C_2) \lambda_2 \right)}{(\lambda_2 - \lambda_1)^2 (C_2 - 1)}
\]
\[
k_3 = \frac{V_1}{A \left( \frac{P_{28}^{in} + P_{30}^{in}}{2} \right)} \frac{-\lambda_1 \lambda_2}{C_2 \lambda_1 + (1-C_2) \lambda_2}
\]

3.4. Estimation of the Value of \(A\) and \(V_v\)

Since Eqs. (20) to (22) show that the surface area and the volume of molten oxide are the important parameters, therefore it is necessary to estimate the values of \(A\) and \(V_v\) of the sample for the accurate calculation of rate constants.

After each experiment, the sample was rapidly cooled to keep the shape of the surface of the reacted molten oxide and measured accurately. Solid circles shown in Fig. 5 shows an example of the measured shape of specimen surface after cooling. Considering the tangential relationship

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Parameters of Eq. (19)</th>
<th>Calculated reaction rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_1)\times10^8</td>
<td>C(_2) (m/s)</td>
<td>(\lambda_1) \times 10^4 (s(^{-1}))</td>
</tr>
<tr>
<td>F-0</td>
<td>7.65</td>
<td>0.621</td>
</tr>
<tr>
<td>FC-1</td>
<td>8.47</td>
<td>0.671</td>
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<td>FC-2</td>
<td>7.96</td>
<td>0.800</td>
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<td>FC-3</td>
<td>7.77</td>
<td>0.691</td>
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<td>FC-4</td>
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<td>0.645</td>
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<td>FS-1</td>
<td>8.07</td>
<td>0.579</td>
</tr>
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<td>FS-2</td>
<td>7.99</td>
<td>0.335</td>
</tr>
<tr>
<td>FS-3</td>
<td>8.05</td>
<td>0.221</td>
</tr>
</tbody>
</table>
between the top edge of the crucible and the bottom of the surface of sample, an ellipse equation was used to fit the measured data. The comparison of the fitted results by paraboloid, ball crown, ellipsoid and plane shows that the surface of molten oxide is reasonably represented as an ellipsoidal shape. Therefore, \( A \) and \( \frac{A}{V_s} \) can be accurately expressed as a function of the depth of meniscus, \( b \), by Eqs. (23) and (24), respectively.

\[
A = \pi r^2 \left[ 1 + \frac{b^2}{\sqrt{1 - \beta^2}} \ln \left( \frac{1 + \frac{1}{\beta} \sqrt{1 - \beta^2}}{\beta} \right) \right] \quad \left( \beta = \frac{b}{r} \right) \tag{23}
\]

\[
\frac{V_s}{A} = \frac{h - \frac{2}{3} b}{1 + \frac{b^2}{\sqrt{1 - \beta^2}} \ln \left( \frac{1 + \frac{1}{\beta} \sqrt{1 - \beta^2}}{\beta} \right)} \tag{24}
\]

where \( r \) and \( h \) are the inner radius and the depth of platinum crucible, respectively. The calculated results considering an ellipsoidal shape were shown in Table 3.

### 3.5. Effects of CaO and SiO \textsubscript{2} Additions

The ferric-ferrous ratio is plotted as a function of CaO or SiO \textsubscript{2} contents in Fig. 6 together with the results obtained by Mori \textit{et al.}\textsuperscript{89} for the FeO \textsubscript{2}–CaO system measured at 1 723 K. Takeda \textit{et al.}\textsuperscript{19} also measured the ferric-ferrous ratio of calcium ferrite slags equilibrated with CO\textsubscript{2}–CO gas at 1 473 K and 1 573 K, and reported that ratio as functions of CaO content and temperature. Calculated values at 1 773 K were shown in Fig. 6. Those previous results have shown that \( \log(X_{Fe^3}/X_{Fe^2}) \) has a linear relationship with CaO content for the FeO \textsubscript{2}–CaO system under a constant oxygen partial pressure and constant temperature. Our results also represent the linear relationship and indicate that the molten oxide was in chemical equilibrium with CO\textsubscript{2}–CO gas under the present conditions. On the contrary, the effect of SiO \textsubscript{2} addition on the ferric–ferrous ratio was not clearly observed. Authors\textsuperscript{8,9} previously measured that ratio for the FeO \textsubscript{2} and FeO \textsubscript{2}–SiO \textsubscript{2} systems containing 26 and 30 mass\% SiO \textsubscript{2} and the ferric–ferrous ratio slightly decreased with adding SiO \textsubscript{2}. The observed ferric–ferrous ratios in the present study were somewhat larger than those in the previous study.

Figure 7 shows the relationships between calculated CO\textsubscript{2} dissociation rate constants and CaO or SiO \textsubscript{2} contents. Observed rate constants were almost constant with changing CaO or SiO \textsubscript{2} concentration in molten oxide. In this figure, the CO\textsubscript{2} dissociation rate constants measured by isotope exchange technique with CO\textsubscript{2}–CO gas containing isotopic carbon (\textsuperscript{13}C or \textsuperscript{14}C) were also represented for comparison.\textsuperscript{3,4,6,8,9} The rate constants measured in the present study were approximately one order of magnitude larger than that measured in the previous studies. The previous results measured by many researchers including authors are mutually accordant and also correspond to those calculated from the oxidation or reduction rates of molten oxide.\textsuperscript{3,20,21} These facts indicate that the measured rate constants in previous researches are quite accurate. The reasons that present results were about one order of magnitude larger than previous ones are not clear at present.

Figure 8 shows the effects of CaO or SiO \textsubscript{2} addition on the CO\textsubscript{2} re-formation rate constant. Increasing CaO contents, the rate constants slightly decreased. On the other hand, the rate constants increased with adding SiO \textsubscript{2}, approximately tenfold with the increase of SiO \textsubscript{2} content to 13 mass\%. The CO\textsubscript{2} re-formation rate constant is considered to depend on the physical and chemical properties of the surface of molten oxide, however those effects on the rate constant are very complicated and the reaction mechanisms have not been clarified well.

Figure 9 shows the relationships between mass transfer coefficient of oxide ion in molten oxide and CaO or SiO \textsubscript{2} contents. The rate constant was unchanged with adding
CaO or SiO₂. It is well known that the addition of CaO increases the activity of the free oxide ion and vice versa for SiO₂, and CaO and SiO₂ play as a network modifier and network former in the molten oxide, 22,23) respectively. Accordingly, the mass transfer coefficient of oxide ion is expected to increase and decrease with the increase of CaO and SiO₂ content in melt, respectively. However, the expected effects by addition of these oxides were not shown in Figure 9.

4. Conclusions

The reaction rates of oxygen exchange reaction between CO₂–CO gas which ratio is unity and molten FeOₓ–CaO and FeOₓ–SiO₂ have been measured at 1 773 K by using ¹⁸O isotope exchange technique and the measured reaction rates represented the maximum at the beginning of the reaction and sharply decreased within 20 s, and then gradually decreased with the reaction time proceeds. The rate-limiting step of reaction is considered to change from the dissociative adsorption of oxygen on the surface of molten oxide in the initial stage of reaction to the mass transfer of oxide ion into the molten oxide in the latter stage. Addition of CaO and SiO₂ to molten oxide increased and decreased the oxygen exchange reaction rate between CO₂–CO gas and molten oxides, respectively.

REFERENCES