Influence of P_2O_5 on Dissolution Behavior of Lime in Molten Slag

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Dissolution of lime into molten slag is an important phenomenon in hot-metal dephosphorization treatment and should be suitably promoted in order to obtain an effective refining reaction and to recycle slag as some environmental resources. A lot of research has been conducted on the phenomenon, but the influence of P_2O_5 on the dissolution behavior of lime has never been studied despite the presence of P_2O_5 in the slag obtained during actual operation.

In this study, the dissolution behavior of lime in CaO–SiO_2–FeO or CaO-SiO_2-FeO-5.2 mass% P_2O_5 molten slag was investigated via a high-temperature laser microscope, an optical microscope, and a scanning electron microscope/energy dispersive spectroscopy (SEM/EDS) in order to clarify the influence of P_2O_5 on the dissolution behavior of lime. We conclude that the addition of P_2O_5 to the slag accelerates the dissolution of lime in the molten slag mainly by increasing the CaO equilibrium content in the liquid slag saturated with 2CaO·SiO_2.

P_2O_5 is a product of the dephosphorization reaction, and basically, its content is preferred to maintain low content for dephosphorization based on equilibrium theory. However, the experimental results obtained in this study clarify that the presence of P_2O_5 in molten slag is effective for the promotion of the dephosphorization reaction when the reaction is limited by the dissolution of lime.

KEY WORDS: hot-metal dephosphorization; dephosphorization slag; lime; dissolution; 2CaO·SiO_2; P_2O_5; confocal laser-scanning microscope; high-temperature laser microscope.

1. Introduction

In hot-metal dephosphorization treatment, fast dissolution of lime into molten slag is an important subject because dephosphorization treatment is performed at relatively low temperatures of approximately 1,573 K, which is the thermodynamically preferred temperature for the dephosphorization reaction. Fluorite is well-known as a useful solvent that promotes the dissolution of lime into molten slag. However, the use of fluorite is not preferable from the viewpoint that fluorine-containing slag comes to be saturated with 2CaO·SiO_2.

As described above, many researchers have been using P_2O_5-free and CaO-SiO_2-FeO-based slag. However, the dissolution behavior of lime in molten slag has been some influence on the dissolution behavior of lime in molten slag. Moreover, it is well-known that P_2O_5 in molten slag has not been studied yet.

P_2O_5, characterized as a strong acidic oxide, has the potential of promoting the ionic dissociation of CaO in molten slag. Moreover, it is well-known that P_2O_5 in molten slag dissolves into 2CaO·SiO_2 formed at the interface as 3CaO·P_2O_5. This shows that P_2O_5 in molten slag has some influence on the dissolution behavior of lime in molten slag.

The purpose of our work is to clarify the influence of P_2O_5 on the dissolution behavior of lime in molten slag. The
dissolution behavior of lime in the molten slag comprising CaO–SiO₂–FeO or CaO–SiO₂–FeO–P₂O₅ was observed via a confocal laser-scanning microscope, which has been widely used to observe various phenomena in high-temperature processes; moreover, the chemical composition of the observed specimens was analyzed using a scanning electron microscope/energy dispersive spectroscopy (SEM/EDS). On the basis of obtained results, the effect of P₂O₅ on the dissolution behavior of lime is discussed.

2. Experiments

The dissolution behavior of lime in the CaO–SiO₂–FeO or CaO–SiO₂–FeO–P₂O₅ molten slag was examined using two experimental techniques. First, in situ observations were made using a confocal laser-scanning microscope. Second, the microstructures around the lime in the slag were observed using an optical microscope, and the chemical compositions of the mineral phases around the lime and bulk slag were analyzed via SEM/EDS.

2.1. Specimens

The specimen for the observations was made of lime and pre-melt slag. Lime was made from quick lime confirmed to the JIS R 9001 standard. Quick lime was processed into particles using a hammer and scriber. The particle was 2.0–2.5 mm wide, 2.0–2.5 mm long, and 1.0–1.5 mm thick, and this weight was 10 mg. The pre-melt slag was made from reagent-grade CaO, SiO₂, FeO, or P₂O₅. A mixture of these reagents was dried for 15 hours at 503 K in a drying oven. Then, the mixture was placed on an iron crucible in a high-frequency induction furnace and heated from room temperature to 1 623 K; this temperature was higher than the melting point of slag in this study. The mixture was then cooled to room temperature in the furnace under an argon atmosphere. Subsequently, the produced slag was collected from the iron crucible and crushed to a powder with a particle size ≤0.16 mm.

Table 1 shows the chemical compositions of two types of pre-melt slag. The contents of each component were evaluated via chemical analyses of the actual pre-melt slag. The mass ratios of CaO to SiO₂ in each pre-melt slag were identical (0.92) and the P₂O₅ contents were different. Slag 1 was P₂O₅-free slag and Slag 2 was 5.2 mass% P₂O₅-containing slag.

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Figure 1 shows the schematic of the preparation procedure of the specimen. The pre-melt slag was measured at 54 ± 1 mg, placed on a platinum crucible whose height and inner diameter were both 5 mm, and then compressed from the top. Subsequently, lime particle was compressed at the center of the pre-melt slag to prevent them from moving out of the scope during the observation. The total composition of the mixture of lime and pre-melt slag exists in the two-phase coexistence region of 2CaO·SiO₂ and the liquid on the CaO–SiO₂–FeO phase diagram at 1 623 K, and the mass ratios of CaO to SiO₂ in each specimen were constant values of 1.45.

2.2. Laser Microscope Observations

The high-temperature laser microscope used for the observation was a confocal laser-scanning microscope combined with an image furnace (VL2000DX-SVF-17DP) developed by Yonekura Corporation.

The specimen was heated and cooled in the image furnace, and the temperature of the specimen was controlled using a platinum–rhodium thermocouple located just below the platinum crucible. The temperature difference between the thermocouple and specimen was corrected using the calibration curve by measuring the melting point of the standard samples (Zn, Al, Ag, Au, Ni) in advance and controlled within ±1 K at 1 623 K.

The atmosphere in the furnace was argon. The specimen in the furnace was heated from room temperature at a rate of 200 K/min to 1 623 K and held for a predetermined duration; it was cooled at a rate of 500 K/min to 373 K under the condition of argon flow at a rate of 200 ml/min. The holding time (t) was defined as the time from the end of slag melting to the start of cooling, and the condition of t was set to approximately 0.3, 4, 7, 16, 32, 50, 75, and 100 min.

2.3. SEM/EDS Analyses

After laser microscope observations, the specimen was...
mounted with resin, and the section was polished and observed via SEM/EDS and an optical microscope.

Figure 2 shows an image observed on a section of the specimen. The chemical composition of the bulk slag, whose area is indicated in this figure, and that of the mineral phases around lime in the specimen were analyzed via SEM/EDS. Furthermore, the microstructures around lime were observed via an optical microscope.

3. Results

3.1. Laser Microscope Observations

The pre-melt slag in the specimen started to melt during heating, and lime reacted with molten slag after the end of slag melting under all experimental conditions. Figure 3 shows the photos of the observation results obtained after the end of slag melting; (a) and (b) in the figure represent the typical results for the cases of Slag 1 and Slag 2, respectively.

In Fig. 3, slag infiltrated into lime from the interfaces between lime and the molten slag during 0.2–3.3 min in the case of Slag 1 and during 0.2–1.7 min in the case of Slag 2. The infiltration rate of the slag in the case of Slag 2 was observed to be larger than that in the case of Slag 1. Moreover, lime in the case of Slag 2 was observed to fluidify and sink into the molten slag after 1.7 min, whereas that in the case of Slag 1 was observed not to fluidify and stay at the observation site after 3.3 min.

Comparing the results obtained for both cases, we inferred that $P_2O_5$ in molten slag promotes the infiltration of molten slag into lime and the dissolution of lime into molten slag.

Table 2 shows the temperatures of slag melting in each pre-melt slag; $T_s$ and $T_e$ represent the temperature at the start of slag melting and that at the end, respectively. The $T_s$ and the $T_e$ in the case of Slag 2 were lower than those in the case of Slag 1.

3.2. SEM/EDS Analyses

Figure 4 shows the relationship between the chemical composition of bulk slag and the holding time; (a) and (b)
in the figure indicate the results for the cases of Slag 1 and Slag 2, respectively. In each case, the changes in the contents of FeO and CaO were larger than those observed for the other oxides. However, the chemical composition and mass ratios of CaO to SiO2 were constant on and after approximately 75 min.

The changes in $\Delta(\%\text{FeO})$ and $\Delta(\%\text{CaO})$ of bulk slag in each case are presented in Fig. 5. $\Delta(\%\text{FeO})$ is the difference between the FeO content in bulk slag at each holding time ($t$) and that in pre-melt slag which converted Fe2O3 in Table 1 into FeO. Note that $\Delta(\%\text{CaO})$ was calculated in the same manner as $\Delta(\%\text{FeO})$. Comparing the results obtained for both cases, we inferred that P2O5 in molten slag increases the decreasing rates of $\Delta(\%\text{FeO})$ and the increasing rates of $\Delta(\%\text{CaO})$; moreover, it increases the attainment $\Delta(\%\text{CaO})$ and decreases the attainment $\Delta(\%\text{FeO})$ at approximately 75 min.

Figure 6 indicates that the microstructures of the mineral phases around lime and the chemical composition of the positions in the CaO–SiO2–FeOx phase diagram at 1 623 K13) in the cases of Slag 1 at 4 min and 16 min approximately. Moreover, Fig. 7 indicates the results of the same condition in the case of Slag 2. Each composition in the phase diagram corresponds to the plot on the photos in each figure. Table 3 lists the positions shown in Figs. 6 or 7; the phases and states, which are identified in the results obtained from these figures; and the chemical composition of each position. The phases are classified as “CaO,” “FeO–CaO,” “2CaO·SiO2–2FeO·SiO2,” and “2CaO·SiO2–3CaO·P2O5.” The state of FeO–CaO is classified as liquid at 1 623 K, and there are two types of phases wherein the FeO content was high and low.

The FeO–CaO liquid slag phase (the positions 1c, 2e, 3d, and 4e) existed around CaO particles (1d, 2f, 3e). The 2CaO·SiO2–2FeO·SiO2 phase (1a, 1e, 2a, 2b, and 2c) coexisted with a few amount of the FeO-rich FeO–CaO liquid slag phase (1b, 2d). The 2CaO·SiO2–3CaO·P2O5 phase (3a, 3b, 4a, and 4c) coexisted with some amount of the FeO-rich FeO–CaO liquid slag phase (3c, 4b, 4d). Moreover, the FeO content in the 2CaO·SiO2–FeO·SiO2 phase and that in the 2CaO·SiO2–3CaO·P2O5 phase increased as positions got close to the area indicated as “Slag” in the figures.

In Figs. 6 and 7, the thicknesses of the FeO–CaO layers, which did not contain CaO particles, were observed to be large if the holding time was large; the same was observed for the thicknesses of the 2CaO·SiO2 phases, which mainly contained 2CaO·SiO2. Figure 8 shows the relationship between the thickness of the FeO–CaO layer and the square root of the holding time ($\sqrt{t}$), and Fig. 9 shows the
Table 3. Results of SEM/EDS analyses and the classifications of the phase and state at 1623 K.

<table>
<thead>
<tr>
<th>Position</th>
<th>Phase</th>
<th>State at 1623 K</th>
<th>Composition (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2CaO·SiO₂-2FeO·SiO₂</td>
<td>Solid</td>
<td>CaO 51.5, SiO₂ 35.3, FeO 13.1, P₂O₅ 0.0</td>
</tr>
<tr>
<td>1b</td>
<td>(FeO-rich) FeO–CaO</td>
<td>Liquid</td>
<td>CaO 18.6, SiO₂ 3.0, FeO 78.4, P₂O₅ 0.0</td>
</tr>
<tr>
<td>1c</td>
<td>FeO–CaO</td>
<td>Liquid</td>
<td>CaO 43.1, SiO₂ 1.5, FeO 55.4, P₂O₅ 0.0</td>
</tr>
<tr>
<td>1d</td>
<td>CaO</td>
<td>Solid</td>
<td>CaO 95.8, SiO₂ 0.0, FeO 4.2, P₂O₅ 0.0</td>
</tr>
<tr>
<td>1e</td>
<td>2CaO·SiO₂-2FeO·SiO₂</td>
<td>Solid</td>
<td>CaO 62.6, SiO₂ 34.3, FeO 3.1, P₂O₅ 0.0</td>
</tr>
</tbody>
</table>

| 2a       | 2CaO·SiO₂-2FeO·SiO₂ | Solid | CaO 56.2, SiO₂ 34.8, FeO 9.1, P₂O₅ 0.0 |
| 2b       | 2CaO·SiO₂-2FeO·SiO₂ | Solid | CaO 58.1, SiO₂ 33.0, FeO 8.9, P₂O₅ 0.0 |
| 2c       | 2CaO·SiO₂-2FeO·SiO₂ | Solid | CaO 62.6, SiO₂ 34.3, FeO 3.1, P₂O₅ 0.0 |
| 2d       | (FeO-rich) FeO–CaO | Liquid | CaO 32.0, SiO₂ 1.1, FeO 66.9, P₂O₅ 0.0 |
| 2e       | FeO–CaO | Liquid | CaO 43.4, SiO₂ 1.9, FeO 54.7, P₂O₅ 0.0 |
| 2f       | CaO | Solid | CaO 95.7, SiO₂ 0.0, FeO 4.3, P₂O₅ 0.0 |

| 3a       | 2CaO·SiO₂-3CaO·P₂O₅ | Solid | CaO 67.7, SiO₂ 29.4, FeO 2.9, P₂O₅ 15.5 |
| 3b       | 2CaO·SiO₂-3CaO·P₂O₅ | Solid | CaO 68.4, SiO₂ 30.8, FeO 0.8, P₂O₅ 11.6 |
| 3c       | (FeO-rich) FeO–CaO | Liquid | CaO 24.0, SiO₂ 0.7, FeO 75.3, P₂O₅ 0.0 |
| 3d       | FeO–CaO | Liquid | CaO 43.7, SiO₂ 2.0, FeO 54.3, P₂O₅ 0.0 |
| 3e       | CaO | Solid | CaO 94.2, SiO₂ 0.0, FeO 5.8, P₂O₅ 0.0 |

| 4a       | 2CaO·SiO₂-3CaO·P₂O₅ | Solid | CaO 63.5, SiO₂ 30.5, FeO 6.0, P₂O₅ 8.3 |
| 4b       | (FeO-rich) FeO–CaO | Liquid | CaO 7.8, SiO₂ 0.4, FeO 91.9, P₂O₅ 0.0 |
| 4c       | 2CaO·SiO₂-3CaO·P₂O₅ | Solid | CaO 66.2, SiO₂ 32.8, FeO 1.0, P₂O₅ 7.7 |
| 4d       | (FeO-rich) FeO–CaO | Liquid | CaO 29.5, SiO₂ 5.3, FeO 65.2, P₂O₅ 1.6 |
| 4e       | FeO–CaO | Liquid | CaO 43.3, SiO₂ 3.8, FeO 52.9, P₂O₅ 0.5 |
relationship between the thickness of the 2CaO·SiO2 phase and \( \sqrt{t} \). These thicknesses were the average thickness of five places in the specimens at which the holding time was approximately 50 min or under because the shape of the reacted lime changed significantly after approximately 50 min. A linear relationship between the thickness of FeO–CaO layer and \( \sqrt{t} \) was confirmed in addition to the relationship between the thickness of the 2CaO·SiO2 phase and \( \sqrt{t} \). These mean that the growth rates of the FeO–CaO layer and that of the 2CaO·SiO2 phase were related.

Comparing the results for both cases, we found that \( \text{P}_2\text{O}_5 \) in molten slag increases the growth rate of the thicknesses of the FeO–CaO layer and that of the 2CaO·SiO2 phase. Table 4 shows the content of 2FeO·SiO2 in the 2CaO·SiO2-2FeO·SiO2 phase and that of 3CaO·P2O5 in the 2CaO·SiO2-3CaO·P2O5 phase at each position shown in Table 3, which are calculated using Eqs. (1) and (2).

\[
\text{mass}\% 2\text{FeO} \cdot \text{SiO}_2 = \text{mass}\% \text{FeO} \cdot \frac{M_{2\text{FeO} \cdot \text{SiO}_2}}{2 \cdot M_{\text{FeO}}}
\]

\[
\text{mass}\% 3\text{CaO} \cdot \text{P}_2\text{O}_5 = \text{mass}\% \text{P}_2\text{O}_5 \cdot \frac{M_{3\text{CaO} \cdot \text{P}_2\text{O}_5}}{M_{\text{P}_2\text{O}_5}}
\]

where \( M_i \) indicates the molar weight of component \( i \), and the values \( M_{2\text{FeO} \cdot \text{SiO}_2}, M_{\text{FeO}}, M_{3\text{CaO} \cdot \text{P}_2\text{O}_5}, \) and \( M_{\text{P}_2\text{O}_5} \) were 204, 72, 310, and 142, respectively.

As for 1a, 1e, 2a, 2b, and 2c shown in Table 4, the content of 2FeO·SiO2 in the 2CaO·SiO2-2FeO·SiO2 phase ranged from 4 to 18, and the position closer to the “Slag” area tended to exhibit higher values, as shown in Fig. 6. As for 3a, 3b, 4a, and 4c shown in the table, the content of 3CaO·P2O5 in the 2CaO·SiO2-3CaO·P2O5 phase ranged from 15 to 30, and the distribution of the contents did not show a clear tendency in the phase.

### Table 4

Content of 2FeO·SiO2 in 2CaO·SiO2-2FeO·SiO2 and that of 3CaO·P2O5 in 2CaO·SiO2-3CaO·P2O5 at each position shown in Table 3.

<table>
<thead>
<tr>
<th>Position</th>
<th>2FeO·SiO2 in 2CaO·SiO2-2FeO·SiO2 (mass%)</th>
<th>3CaO·P2O5 in 2CaO·SiO2-3CaO·P2O5 (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>18.4</td>
<td>–</td>
</tr>
<tr>
<td>1e</td>
<td>4.4</td>
<td>–</td>
</tr>
<tr>
<td>2a</td>
<td>12.8</td>
<td>–</td>
</tr>
<tr>
<td>2b</td>
<td>12.7</td>
<td>–</td>
</tr>
<tr>
<td>2c</td>
<td>4.4</td>
<td>–</td>
</tr>
<tr>
<td>3a</td>
<td>–</td>
<td>29.3</td>
</tr>
<tr>
<td>3b</td>
<td>–</td>
<td>22.8</td>
</tr>
<tr>
<td>4a</td>
<td>–</td>
<td>16.7</td>
</tr>
<tr>
<td>4c</td>
<td>–</td>
<td>15.6</td>
</tr>
</tbody>
</table>

#### 4. Discussion

On the basis of the experimental results obtained from laser microscope observations and SEM/EDS analyses, the dissolution mechanism of lime in molten slag and the effect of \( \text{P}_2\text{O}_5 \) are discussed.

### 4.1. Dissolution Mechanism of Lime in Molten Slag

Hamano et al. reported the dissolution mechanism of lime in molten slag as follows: when 2CaO·SiO2 is formed in molten slag, FeO-rich slag is formed around 2CaO·SiO2, and a part of \( \text{Fe}^{2+} \) diffuses from the FeO-rich slag to lime. Next, a FeO–CaO layer is formed beside lime, and \( \text{Ca}^{2+} \) diffuses from the FeO–CaO layer into the bulk slag through the FeO-rich slag.

The experimental results obtained for the cases of Slag 1 and Slag 2 suggest that slag infiltrated into lime from the interfaces between lime and the molten slag. Moreover, the growth rates of the FeO–CaO layer and that of the 2CaO·SiO2 phase were controlled by the diffusion of the substance. Additionally, the FeO content in bulk slag decreased with time, whereas the CaO content increased.

These results suggest that \( \text{Ca}^{2+} \) diffuses from lime to the bulk slag and that \( \text{Fe}^{2+} \) diffuses from the bulk slag to lime. The dissolution mechanism of lime in the molten slag in this study can be explained using Hamano’s theory.

The presence of \( \text{P}_2\text{O}_5 \) in the molten slag increased the growth rates of the FeO–CaO layer and the 2CaO·SiO2 phase. This result suggests that \( \text{P}_2\text{O}_5 \) in the molten slag accelerates the diffusion of \( \text{Fe}^{2+} \) and \( \text{Ca}^{2+} \) from the dissolution mechanism. This can explain the results that \( \text{P}_2\text{O}_5 \) in the molten slag increased the increasing rates of the CaO content in bulk slag and the decreasing rates of the FeO content; moreover, using a high-temperature laser microscope, lime in \( \text{P}_2\text{O}_5 \)-containing slag was observed to fluidify. These results indicate that the addition of \( \text{P}_2\text{O}_5 \) to slag promotes the dissolution of lime into molten slag.

In the case of Slag 2, the amount of the FeO-rich FeO–CaO liquid slag was observed to be larger than that in the case of Slag 1 probably owing to the decreasing FeO content in 2CaO·SiO2 as indicated in Table 3, because \( \text{P}_2\text{O}_5 \) in the molten slag changed the dissolved compound in 2CaO·SiO2 from 2FeO·SiO2 to 3CaO·P2O5.

In the cases of Slag 1 and Slag 2, the FeO content in 2CaO·SiO2 phase increased as positions got close to the “Slag” area. This is probably because a part of \( \text{Fe}^{2+} \) diffused from the FeO-rich slag to the bulk slag in the 2CaO·SiO2 phase, as described in Hamano’s report. Therefore, the increased FeO content around the interfaces between the 2CaO·SiO2 phase and the molten slag promotes the dissolution of 2FeO·SiO2 into 2CaO·SiO2 in the case of Slag 1.

#### 4.2. Effect of \( \text{P}_2\text{O}_5 \)

Matsushima et al. investigated the dissolution rates of CaO in the CaO–SiO2–FeO molten slag by measuring the decrease in the diameter of a rotating CaO cylinder dipped in the slag. They pointed out that the dissolution rates of CaO depended on the mass transfer coefficient of liquid slag and the difference in the CaO content between liquid slag saturated with 2CaO·SiO2 in a CaO–SiO2–FeO ternary system and the bulk slag in the same system.
On the basis of the abovementioned study, we focus on the changes in the CaO content in the bulk slag and evaluate the effect of P2O5 on the dissolution rate of lime by using Eq. (3).

\[
\frac{d(\% \text{CaO})_b}{dt} = K((\% \text{CaO})_b - (\% \text{CaO})_e), \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3)
\]

where \( K \) indicates the mass transfer capacity coefficient (1/min); \((\% \text{CaO})_b \) and \((\% \text{CaO})_e \) are the CaO contents in the bulk slag in the CaO–SiO2–FeO ternary system (mass%) and in the liquid slag saturated with 2CaO·SiO2 in the same system (mass%), respectively; and \((\% \text{CaO})_e - (\% \text{CaO})_b \) represents the driving force. From the result of the changes in the chemical composition of the bulk slag shown in Fig. 4, the \((\% \text{CaO})_e \) value of each specimen condition is regarded as the \((\% \text{CaO})_e \) at approximately 75 min because the chemical composition of the bulk slag is considered to be saturated at this condition. The effect of P2O5 on the driving force and \( K \) are discussed below.

**Figure 10** shows the chemical composition of the bulk slag at 0 min and approximately 75 min on the CaO–SiO2–FeO ternary phase diagram at 1623 K.13) The chemical composition of the bulk slag at 0 min is indicated in Table 1. The figures in the parentheses beside each plot are \((\% \text{CaO})_b \). A bold curve in the figure represents the liquidus curve saturated with 2CaO·SiO2. Additionally, the liquidus curve saturated with 2CaO·SiO2–3CaO·P2O5 in the CaO–SiO2–FeO ternary system (mass% FeO–5 mass% P2O5 system shown in the CaO–SiO2–30 mass% FeO–5 mass% P2O5 phase diagram14) is illustrated as a broken curve, assuming almost the same profile as that of the bold curve.

In the case of Slag 1 at approximately 75 min, the chemical composition exists upon the liquidus curve saturated with 2CaO·SiO2. Moreover, in the case of Slag 2 at approximately 75 min, the chemical composition exists upon the liquidus curve of 2CaO·SiO2–3CaO·P2O5. This means that the chemical composition in each bulk slag at approximately 75 min is saturated. Furthermore, P2O5 in the molten slag promotes the driving force, as described in Eq. (3), owing to the increasing CaO content in the liquid slag saturated with 2CaO·SiO2. In this study, P2O5 in the molten slag increases 3.4 mass% of \((\% \text{CaO})_b \) from the CaO content illustrated in Fig. 10. Additionally, as per the laser microscope observations, \( T_s \) and \( T_r \) in the case of Slag 2 were lower than that in the case of Slag 1. These results imply that the addition of P2O5 to slag shifts a solidus curve to be lower as well as a liquidus curve.

The integration of Eq. (3) yields Eq. (4).

\[
Lt \left( \frac{(\% \text{CaO})_e - (\% \text{CaO})_b}{(\% \text{CaO})_b - (\% \text{CaO})_e} \right) = K \cdot t. \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4)
\]

Note that \((\% \text{CaO})_b \) is written as the CaO content in the bulk slag in the CaO–SiO2–FeO ternary system (mass%) at 0 min. By using \((\% \text{CaO})_b \) and \((\% \text{CaO})_e \), which is indicated in the parentheses in Fig. 10, and \((\% \text{CaO})_e \), the \( K \) of each experimental condition is calculated.

**Figure 11** shows the changes in \( K \). Equations (5) and (6) in this figure represent the approximate curves of \( K \) in the cases of Slag 1 and Slag 2. The \( K \) in the cases of Slag 1 and Slag 2 decreases with time. This result shows that dissolution rate of lime cannot be explained as a first-order reaction rate. In addition, the \( K \) in the cases of Slag 1 and Slag 2 are similar at approximately 0.3 min, whereas the \( K \) in the case of Slag 2 is larger than that in the case of Slag 1 after approximately 0.3 min.

The decrease in \( K \) with time is probably because the 2CaO·SiO2 phase prevents the dissolution of lime.1–3) One of the reasons why the \( K \) after 0.3 min in the case of Slag 2 is larger than that in the case of Slag 1 can be the increase in the reaction area, according to the result that suggests that lime in the case of Slag 2 was observed to sink into the molten slag in laser microscope observations. Additionally, the reason why lime sunk is that the density of lime became larger than that of the molten slag because P2O5 in the molten slag accelerates the diffusion of Fe2+ from the molten slag to lime.

In this study, it was difficult to experimentally estimate the reaction area. Therefore, \( \Delta(\% \text{CaO})_b \), defined as the difference between \((\% \text{CaO})_b \) and \((\% \text{CaO})_e \), was calculated via Eq. (3), and the functions of \( K \) are represented in Eqs. (5) and (6) for clarifying the effect of P2O5.

**Figure 12** shows the changes in the calculated and observed \( \Delta(\% \text{CaO})_b \). The equations and values for each calculation are shown in this figure. The curves of Calc. 1 and Calc. 2 indicate the results of the calculations for the
$K$ of the reasons for the increase in the reaction area owing to the sinking of lime into the molten slag. Thus, the effect of an increase in reaction area in the actual cases of Slag 1 and Slag 2; the obtained values are approximately equal to the observed values. The curve of Calc. 3 is calculated using the $K$ of Slag 1 (= Eq. (5)) and the ($\%$CaO)$_s$ of Slag 2. The differences in the curves of Calc. 3 and Calc. 1, and that in the curves of Calc. 2 and Calc. 3 are represented by $\alpha$ and $\beta$ in Fig. 12, and they indicate the effect of the increase in the driving force and that of $K$ due to the addition of $P_2O_5$ to slag, respectively.

Figure 13 shows the change in the value of $\alpha/(\alpha + \beta)$ on and after approximately 4 min. The values of $\alpha/(\alpha + \beta)$ range from 0.6 to 0.7. This result suggests that the main effect of $P_2O_5$ on the increase in the driving force. The addition of $P_2O_5$ to slag increases the dissolution rate of lime mainly by increasing the CaO content in the liquid slag saturated with $2CaO\cdotSiO_2$.

The values of $\beta/(\alpha + \beta)$ range from 0.3 to 0.4. This is the effect of $P_2O_5$ on the increase of $K$. As described above, one of the reasons for the increase in $K$ is an increase in the reaction area owing to the sinking of lime into the molten slag. However, in actual hot-metal dephosphorization treatment, lime gets involved in molten slag with strong agitation. Thus, the effect of an increase in reaction area in the actual treatment probably becomes smaller than that of this study.

In this study, we conclude that the addition of $P_2O_5$ to slag promotes the dissolution of lime into molten slag mainly because of an increase in the CaO content in the liquid slag saturated with $2CaO\cdotSiO_2$. This result suggests that the dissolution rate of lime changes according to the $P_2O_5$ content in molten slag in hot-metal dephosphorization treatment.

$P_2O_5$ is the product of the dephosphorization reaction. It is preferable to maintain a low-$P_2O_5$ content for the dephosphorization reaction according to the viewpoint of equilibrium theory. However, when the dephosphorization rate is controlled by the dissolution rate of lime, the presence of $P_2O_5$ in molten slag is effective for the promotion of the dephosphorization reaction because $P_2O_5$ in molten slag accelerates the dissolution of lime.

5. Conclusions

The dissolution behavior of lime in the CaO–SiO$_2$–FeO or CaO–SiO$_2$–FeO–$5.2$ mass% $P_2O_5$ molten slag was observed using a laser microscope; moreover, the chemical composition of the observed specimens was analyzed via SEM/EDS. On the basis of the obtained results, the effect of $P_2O_5$ on the dissolution rate of lime was discussed. The results are as follows:

(1) The addition of $P_2O_5$ to the CaO–SiO$_2$–FeO slag promotes the infiltration of slag into lime, and the lime is dissolved. The infiltrating slag is FeO. Therefore, the FeO content in the bulk slag decreases with time, and the CaO content in the bulk slag increases with time.

(2) FeO–CaO layers and $2CaO\cdotSiO_2$ phases exist beside the interface between lime and the molten slag. The thicknesses of the FeO–CaO layer and that of the $2CaO\cdotSiO_2$ phase are correlated; both of these are larger when the slag contains $P_2O_5$. This is because the addition of $P_2O_5$ to the slag accelerates the diffusion of Ca$^{2+}$ from lime to the bulk slag, and the diffusion of Fe$^{2+}$ from the bulk slag to lime is promoted accordingly.

(3) The addition of $P_2O_5$ to the slag promotes the dissolution of lime mainly by increasing the CaO content in the liquid slag saturated with $2CaO\cdotSiO_2$.

(4) $P_2O_5$ is the product of the dephosphorization reaction. It is preferable to maintain a low-$P_2O_5$ content for the dephosphorization reaction according to the viewpoint of equilibrium theory. However, when the dephosphorization rate is controlled by the dissolution rate of lime, the presence of $P_2O_5$ in molten slag is effective for the promotion of the dephosphorization reaction because $P_2O_5$ in molten slag accelerates the dissolution of lime.

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