Dissolution Behavior of Mg and Ca from Dolomite Refractory into Al-killed Molten Steel

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(Received on April 20, 2020; accepted on June 25, 2020; J-STAGE Advance published date: March 25, 2021)

Dolomite refractories are widely used in the refining process of clean steel and are considered potential sources of Mg and Ca that form MgO·Al2O3 spinel and CaO-containing inclusions. In this study, dolomite refractories were immersed into Al-killed molten steel with either 0.05% Al or 0.25% Al. The dissolution behavior of Mg and Ca from the dolomite refractory was studied, and the inclusion transformation behavior was observed. The results revealed that MgO in the dolomite refractory was reduced by Al in the molten steel, and the Mg content depended on the Al content. On the contrary, CaO barely dissolved into the molten steel even though the Al content increased. After immersion in both the low Al (0.05% Al) and high Al (0.25% Al) steels, an interfacial layer consisting of solid MgO and liquid phase CaO–Al2O3–MgO was formed on the surface of the rods. The initial Al2O3 inclusions gradually changed into Al2O3 saturated MgO–Al2O3 spinel after 60 min in low-Al steel; but were quickly transformed into MgO-saturated MgO–Al2O3 spinel in high Al steel. No CaO-containing inclusions were detected in the molten steel regardless of the immersion time and Al content.

KEY WORDS: Mg dissolution; Ca dissolution; dolomite refractory; spinel; inclusion; Al-killed steel.

1. Introduction

Non-metallic inclusions have a significant influence on steel performance.1,2) For instance, MgO–Al2O3 spinel inclusion may lead to steel defects and clogging of nozzles during the continuous casting process because of its high melting temperature and high hardness.3,4) Since magnesia is rarely added to molten steel, MgO from slag and MgO-based refractory materials are considered the main sources of the magnesium that generates spinel inclusions.5) On the other hand, the CaO-containing inclusions can hardly lead to the clogging of nozzles due to its low melting temperature. However, liquid CaO-containing inclusions normally show a large size, and large linear defects are sometimes found in steel products after the rolling process because of their good deformability. Therefore, CaO in inclusions should be avoided in certain Si–Mn–killed steels as well as in ultra-low oxygen steels.6) The calcium in ferroalloy and slag are considered to be the main sources of the calcium that forms CaO-containing inclusions in steel. However, the CaO in refractory materials should not be ignored. Currently, MgO-based refractories, such as MgO–C, MgO–Cr2O3, and MgO–CaO, are widely used in the secondary refining process because of their high resistance to erosion and thermal shock.7,12) Owing to clean steel production requirements, the effects of refractories on the transformation of inclusions have recently drawn much attention in addition to refining slags. Several mechanisms for the reduction of MgO-based refractories by Al-killed steel have been proposed, such as reduction by either the dissolved Al in steel13,14) or by the carbon contained in the refractory.15) However, the dissolution or reduction of CaO from refractory materials to molten steel has not been reported. Additionally, thermodynamic equilibria have been studied for decades to understand the relations between oxides and molten steel, including those of Al–Al2O3, Mg–MgO, and Ca–CaO systems.16)
of Mg from MgO–C and MgO–Cr₂O₃ refractories into Al-killed molten steel has been investigated in detail. The MgO–C refractories with various carbon contents were immersed into Al-killed molten steel with varying Al concentrations.¹⁷) The Al dissolved in molten steel and the C in the refractory reduced MgO and supplied Mg to the molten steel. After the reaction, an MgO–Al₂O₃ spinel layer was found discontinuously attached at the refractory/steel interface. The inclusions changed from Al₂O₃ to the MgO–Al₂O₃ spinel. Conversely, the Mg content in molten steel was lower than that of the MgO–C refractory after reacting the MgO–Cr₂O₃ refractory with Al-killed steels, and the inclusions did not transform but remained as Al₂O₃.¹⁸) A thick MgO–Al₂O₃ spinel layer was generated continuously at the refractory/steel interface. As this layer was saturated with Al₂O₃, there was insufficient driving force for the transformation of inclusions. From these studies, it was clarified that dissolution behaviors such as the dissolution of Mg and the transformation behavior of inclusions are strongly affected by the refractory materials.

Dolomite refractories are widely used as lining materials for steel refining processes, and their reaction behaviors with refining slag have been studied.¹⁹–²¹) However, only a few studies have been conducted on their reactions with molten steel.²²) Furthermore, there are no reported effects of dolomite on the change of composition of inclusions. Therefore, in this study, laboratory experiments were conducted to investigate the reactions between dolomite refractory materials and Al-killed molten steel; and the transformation behaviors of inclusions were observed.

2. Experimental

2.1. Raw Materials

Commercial dolomite refractory rods employed in this study were supplied by the Kurosaki-Harima Corporation. The rods were of a square shape and had a width, length, and height of 10 mm, 10 mm, and 100 mm, respectively. The chemical composition and physical properties of the refractory material are summarized in Table 1. Part of the dolomite rod was cut out and crushed into fine powder, and its chemical composition was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). All the compositions in the current study are given in mass percentage, unless otherwise specified.

The structure of the refractory material was analyzed using X-ray diffraction (XRD) and an electron probe microanalyzer (EPMA). As shown in Fig. 1. The main crystalline peaks were confirmed to be CaO and MgO; a few peaks representing MgCO₃, CaCO₃, and Ca(OH)₂ were also found. Although the refractory rods were kept in a dry environment, there was still a slight moisture adsorption and Ca(OH)₂ was formed. However, as the rods would be dried at a high temperature for several hours before immersion into molten steel as described in later sections, the effects of the adsorbed moisture on the experimental results were ignored. Figure 2 shows the compositions of the CaO and MgO phases in the dolomite refractory. In these analyses, carbon was not measured considering the accuracy of EPMA analysis. Although the CaO–MgO phase diagram²³) showed the solubility of each component to CaO or MgO, the analyzed MgO content in CaO was low, and the MgO barely contained CaO. Low contents of other impurities such as Fe, Si, Al, and Mn were also observed. Therefore, the dolomite refractory used in this study mainly consisted of single phases of either CaO or MgO; alongside small amounts of CaCO₃ and MgCO₃.

Steels containing approximately 11% Cr were used because the formation of spinel inclusions in stainless steel had been previously studied.¹⁶,¹⁷,²⁴,²⁵) In order to investigate the effects of the dissolved Al in molten steel, steels with low and high Al contents were prepared. The low Al steel

<table>
<thead>
<tr>
<th>Chemical composition (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>39.10</td>
</tr>
</tbody>
</table>

Fig. 1. Mineralogical phases in dolomite refractory observed by XRD.

Fig. 2. Mineralogical structure of the dolomite refractory observed by EPMA.
containing 0.06% Al was selected considering its near similarity with normal Al-killed steel, while the high Al steel with 0.28% Al was chosen to enhance the reaction between the refractory and molten steel and for comparison with the results of previous studies. To prepare these steels, electrolytic Fe, high-purity Cr (99.9%), and high-purity Al (99.999%) metals were melted in an argon-arc furnace, followed by cooling within the vacuum chamber of the arc furnace. After preparation, the steel compositions were confirmed using ICP-AES analysis.

2.2. Experimental Procedure

The experimental setup is shown in Fig. 3, and the experimental conditions are given in Table 2. All experiments were conducted using an induction furnace. Prior to heating, 200 g of the prepared steel was loaded into a dense Al$_2$O$_3$ crucible (OD: 38 mm; ID: 32 mm; H: 1 000 mm). Subsequently, the furnace chamber was subjected to vacuum conditions and then purged with purified argon (99.999%, O<0.1 ppm) using Mg chips at 573 K. This process was repeated three times. After the purification of the atmosphere, the crucible with steel was heated to 1 873 K, and the temperature was measured and controlled by immersing a thermocouple into the molten steel. The thermocouple was covered with a dense Al$_2$O$_3$ protective tube. Then, Al–Al$_2$O$_3$ equilibrium between the molten steel and crucible was established to simulate the Al-killed steel. During heating, a dolomite rod was hung about 5 cm above the molten steel for drying. Because heating and temperature stabilization requires more than 3 h, it was assumed that the moisture in the dolomite rod was completely removed.

After the temperature stabilized at 1 873 K, the dolomite rod was slowly immersed into the molten steel to a depth of 20 mm, and the exact time of immersion was recorded as the starting time of the experiment. The dolomite rod was kept immersed for 5, 30, 60, or 120 min, and then removed and cooled in air. The molten steel was rapidly taken out with the crucible and quenched by water.

2.3. Analysis

The steels before and after reacting with dolomite rods were cut into two parts for the chemical analysis and for inclusion observation. The dissolved Al and Mg content in steel were analyzed using ICP-AES. The Ca content of steel was analyzed using glow discharge mass spectrometry (GDMS) because the Ca content in steel was extremely low. The accuracy of GDMS on Ca analysis was proven by a previous study. The total oxygen was analyzed using an infrared X-ray absorption method. The inclusions were observed using automatic SEM/EDS inclusion analysis (P-SEM, ASPEX Corporation). The scan area for each sample was larger than 20 mm$^2$, and the minimum size of detected inclusions was set as 1.0 $\mu$m. After analysis, the analyzed values of Mg, Ca and Al were converted to their oxides, and the analyzed values of Fe and Cr were not considered as inclusion components.

To investigate the formation of the reaction layer on the surface of the dolomite rod after immersion, the air-cooled dolomite rod was embedded in resin and then cut. A cross-section of the part that had been immersed into the molten steel was polished and observed by EPMA.

3. Results

Figure 4 shows the changes in the Al, Mg, Ca, and T.O. contents of molten steels with immersion time at 1 873 K. As shown in Fig. 4(a), the Al content decreased within 5 min, and then changed slightly after prolonging the immersion period. The decrease in the Al content within 5 min was about 500 ppm, and this decrease was independent of the Al content. According to Fig. 4(b), in low Al steel, the Mg content changed little from 0.7 ppm throughout the immersion period. In the case of high Al steel, the Mg content gradually increased up to 60 min, reaching approximately 5.5 ppm. The increase in the Mg content was due to the reduction of MgO from the dolomite rod by the Al in molten steel. However, the increase in the Mg content was much smaller in magnitude compared to the decrease in the Al content. Therefore, the rapid decrease in Al might be caused by the oxidation reaction of Al with CO$_2$, which was formed during the decomposition of CaCO$_3$ and MgCO$_3$ in the refractory.

The Ca content of molten steel is shown in Fig. 4(c). The Ca content was roughly 1 ppm for low Al steel and 0.5 ppm for high Al steel, and it did not change during the immersion period. Therefore, the CaO in the dolomite refractory was hardly reduced by Al in the molten steel under the present experimental conditions. The concentration of Ca in high Al steel was very similar to that observed in the reaction of CaO-saturated slag with steel of a similar Al content, as shown in a previous paper. However, the Ca content of low Al steel was high and the reason behind the high content should be clarified in future research.

![Fig. 3. Schematic of the experimental setup for studying the dissolution behavior of the dolomite refractory.](image)

**Table 2. Experimental conditions.**

<table>
<thead>
<tr>
<th>Mark</th>
<th>Target steel composition</th>
<th>Time (Min)</th>
<th>Temperature (K)</th>
<th>Crucible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Al</td>
<td>Fe–11% Cr–0.05% Al</td>
<td>5, 30, 60, 120</td>
<td>1 873</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>High Al</td>
<td>Fe–11% Cr–0.25% Al</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4(d) shows the change in the T.O. content in steel as a function of the immersion time. The T.O. content decreased gradually with immersion time for low Al steel, and finally reached approximately 20 ppm after 60 min. The decrease in the T.O. content resulted in the inclusions in molten steel floating up to the surface of molten steel or adhering to the surface of the Al$_2$O$_3$ crucible and dolomite rod.

Figure 5 shows the change in the average compositions of inclusions with immersion time. As equilibrium was established between molten steel and the Al$_2$O$_3$ crucible, before immersing the dolomite rod, the initial inclusions were pure Al$_2$O$_3$. For low Al steel, the average MgO content of the inclusions gradually increased to about 20% until 60 min, and the deviation of the inclusion composition was small. From the MgO–Al$_2$O$_3$ phase diagram, the average composition is in the two-phase coexisting region except for the content observed at 60 min. Thus, in these cases, both Al$_2$O$_3$ and MgO–Al$_2$O$_3$ spinel were observed, as shown in Fig. 6. At 60 min, most of the observed inclusions were Al$_2$O$_3$ saturated spinel, as shown in Fig. 6.

For high Al steel, the average MgO content of the inclusions increased to 30% or more after 5 min, and remained constant until 60 min. The deviation in the inclusion composition was small. The average composition was located close to the boundary line of the MgO-saturated spinel; thus, MgO-saturated spinel was observed, as shown in Fig. 6. A higher Al content of steel led to a higher MgO content of the inclusion, which indicated that a rise in Al content increased the reduction rate of Mg from the dolomite refractory. Compared with the increasing behavior of the Mg content in molten steel shown in Fig. 4(b), the average composition of inclusions did not change after 5 min. This meant that the reduced Mg at 5 min was sufficient to transform Al$_2$O$_3$ into MgO-saturated spinel. In addition, like the low Al steel, the MgO content of the inclusion decreased and that of Al$_2$O$_3$ increased after 60 min, and the deviation of the average inclusion composition also increased.

Both steels contained less than 1 ppm of Ca content, and the CaO-containing inclusions were detected neither in the low Al nor in the high Al steels despite the immersion time. This indicated that the Ca in the steel, which was supplied by the reduction of CaO from the dolomite refractory by dissolved Al in molten steel, was not in sufficient volumes.
to change the composition of the inclusion.

Figure 7 shows the changes in the number density and average diameter of inclusions. The number density was similar across both steels and started to decrease from 30 min. Because the flotation and adhesion by the crucible decreased the number density of inclusions, the chemical reactions primarily controlled the inclusion composition. The average diameter of inclusions in both steels increased slightly with reaction time, indicating the removal or coalescence of small inclusions in molten steel. In addition, the average diameter of inclusions between two steels was not compared, because there are no significant differences according to the standard deviations as shown in Fig. 7.

Figure 8 shows the elemental mapping of the interfaces between the dolomite refractory rod and the low Al steel with varying durations of immersion. The element mapping images of Al, O, Ca, and Mg are listed. Within 30 min of immersion, a thin layer containing $\text{Al}_2\text{O}_3$, CaO, and MgO formed at the interface and coexisted with MgO particles. After 60 min, the layer grew thick, and two phases were clearly observed. One comprised of MgO particles with particle sizes larger than those observed in the dolomite matrix. The second phase contained $\text{Al}_2\text{O}_3$, CaO, and MgO, which were observed as threads within the dolomite matrix.

Figure 9 shows the elemental mapping of the interface of the high Al steel. After 5 min, a thick layer consisting of MgO particles and an $\text{Al}_2\text{O}_3$–CaO–MgO phase was observed, and its thickness was close to that formed after immersion for 60 min in the low Al steel. With prolonged immersion periods, the layer grew thick, and the MgO particles became larger and more densely distributed compared to those in the dolomite matrix.

To understand the effects of the above layer, especially the $\text{Al}_2\text{O}_3$–CaO–MgO phase, on both the dolomite dissolution and the inclusion transformation, the composition of the $\text{Al}_2\text{O}_3$–CaO–MgO phase was analyzed by EPMA. The analyzed points are marked in the images of Figs. 8 and 9, and the results are summarized in Fig. 10. For both steels, most of the compositions were located near or within the liquid phase area. Therefore, the $\text{Al}_2\text{O}_3$–CaO–MgO phase observed in the layer at the dolomite surface was considered to be a liquid phase. However, it must be noted that the results are scattered, especially for low Al steel. There are probably two reasons for such scattering. One is that the liquid oxide has a small area, and the MgO particle may affect the
accuracy of point analysis which has a spot size about 1–3 microns. Another is probably because of the inhomogeneity of the Al₂O₃–CaO–MgO liquid phase; as the reaction between previously existing MgO particles became larger in size comparing to those in the bulk of refractory. This was probably because the MgO particles was small and had a high interfacial energy when the surroundings became liquid oxide. Then, the particles might move and coalesce to grow larger to decrease the interfacial energy. However, since the growth of MgO particles inside the interfacial oxide layer is unlikely to affect the transformation of inclusions, this phenomenon will be studied in future.

4. Discussion

Based on the results shown in Figs. 8, 9, and 10, the dissolution mechanism of the dolomite refractory is first discussed. Initially, the dolomite rods consisted of MgO and CaO particles, and the reduction of these particles by Al in molten steel are listed in Eqs. (1) and (2).

\[
3 \text{MgO}(s) + 2[\text{Al}] = 3[\text{Mg}] + \text{Al}_2\text{O}_3(s) \quad \text{(1)}
\]

\[
3 \text{CaO}(s) + 2[\text{Al}] = 3[\text{Ca}] + \text{Al}_2\text{O}_3(s) \quad \text{(2)}
\]

The equilibrium constants of these reactions are widely varied depending on the combination of the reported values, as summarized in a previous paper. However, the Mg content at equilibrium is greater than that of Ca, and reaction (1) occurs prior to reaction (2). Then, the dissolution of Mg into the molten steel and the formation of Al₂O₃ occur at the interface. As a result, the interfacial area is changed from a binary system of MgO and CaO to a ternary system containing Al₂O₃. In this system, a liquid phase is formed as shown in Fig. 10. The solubility of MgO in this liquid is much lower than that of CaO. Therefore, only solid MgO particles coexisted with the liquid. This would be a reason for the formation of the CaO–Al₂O₃–MgO phase with MgO particles at the interface. This liquid phase contacts directly with both CaO and MgO, and is saturated with them; however, it cannot be saturated with Al₂O₃ according to isothermal diagrams as shown in Fig. 10. Meanwhile, the molten steel remains under Al–Al₂O₃ equilibrium as it is contained in an Al₂O₃ crucible. Therefore, it can be deduced that the difference in the Al₂O₃ activity sustains the formation of the liquid phase, and the thickness of the layer increases with time.

Next, the changing behavior of the inclusion composition is discussed. To understand the relationship between the steel composition and the inclusion transformation, the stable oxides were evaluated by thermodynamic calculations. The Al–Al₂O₃ and Mg–MgO equilibrium equations are expressed by Eqs. (3), and (4). Since high Al has been investigated in this experiment, the equilibrium constant of Eq. (3) reported by H. Ito et al. is used instead of the value recommended by JSPS. Additionally, there is no recommended value for the equilibrium constant of Eq. (4), and thus two well-used values, which are listed as \( K_{\text{Mg}}(1) \) and \( K_{\text{Mg}}(2) \), are chosen for this calculation. Using these basic reactions, the transformation reaction of inclusions is expressed as Eq. (5). Its equilibrium constant (\( \log K_{\text{sp}} \)) was then obtained as 7.83 at 1873 K using \( K_{\text{Mg}}(1) \) and 11.01 using \( K_{\text{Mg}}(2) \). To calculate the boundary line for...

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**Fig. 9.** Element mapping of the interface between the dolomite refractory and molten Fe–0.25% (high Al) steel. (a) after 5 min of immersion, (b) 30 min, (c) 60 min, and (d) 120 min. (Online version in color.)

**Fig. 10.** Composition of the CaO–Al₂O₃–MgO phase observed in Figs. 8 and 9.
the MgO-saturated spinel, the MgO and Al2O3 activities were set to unity and 0.034, respectively.29) To calculate the boundary line of the Al2O3 saturated spinel, the activities of MgO and Al2O3 were set to 0.004 and unity, respectively.29) To calculate the transformation of Al2O3 inclusions to spinel saturated MgO-saturated spinel, the MgO and Al2O3 activities were set to 0.004 and unity, respectively. 29) To calculate the boundary line of the Al2O3 saturated spinel, the activities of MgO and Al2O3 were set to 0.004 and unity, respectively.

\[
\log K_{AI} = 11.62 - 45.300 / T \quad \text{(3)}
\]

\[
\log K_{Mg} = -4.28 - 4700 / T \quad \text{(4)}
\]

\[
\log K_{Mg} = 12.45 - 38.059 / T \quad \text{(5)}
\]

To investigate the effects of oxygen dissolved in steel on the activity coefficients of Al and Mg, the oxygen content was determined using the Al–Al2O3 equilibrium, as shown in Eq. (3). Moreover, the effects of Cr on the activity coefficients of solute elements in molten steel have been considered because the steel used in this study contained 11% Cr. The interaction parameters used for the calculation are summarized in Table 3.16,22,26,27,30,31) All parameters without a notation are from M. Hino and K. Ito.16)

The calculated results as well as the measured values of the Al and Mg contents of molten steel are shown in Fig. 11. Despite the initial Al content of steel, the steel compositions are located in the stable region of the MgO–Al2O3 spinel in Fig. 11(a), and are distributed mainly in the MgO stable region close to the boundary line of the MgO–Al2O3 spinel. The Mg content reached over 30 ppm, which was much larger than that of dolomite, and the inclusions gradually transformed from Al2O3 to MgO-Al2O3 spinel and then to MgO, as shown in Table 4. The differences in the kinetic conditions of the reactions between the liquid phase and the molten steel probably caused the difference in the Mg dissolution. The liquid phase formed at the surface of dolomite was thin and sandwiched between solid MgO particles. As a result, the fluidity of the liquid oxide would be very low, which would cause a low mass transfer rate; and the contact area with molten steel was small. Therefore, the reduction rate of MgO from the slag was much larger than that from the dolomite refractory. The Ca content was low after reducing slag, and was close to the Ca content following dolomite reduction, which was also low. Since Ca-containing inclusions were found in neither of the cases, such low concentrations of Ca in molten steel would not be sufficient for the transformation of spinel to CaO–Al2O3 type inclusions. In addition, there are several studies focusing on the inclusion chemistry after slag/metal reduction and without Ca treatment.32–35) They are not compared here because of the differences on the experimental conditions.

### Table 3. Interaction parameters used for calculating Fig. 9.

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>O</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0</td>
<td>-0.27</td>
<td>-3</td>
<td>0.02</td>
</tr>
<tr>
<td>Al</td>
<td>-0.3</td>
<td>0.0429</td>
<td>-1.98</td>
<td>0.0122</td>
</tr>
<tr>
<td>O</td>
<td>-1.98</td>
<td>-1.17</td>
<td>-0.174</td>
<td>-0.052</td>
</tr>
</tbody>
</table>

\[
\gamma_{Al}^{O} = 39.82; \gamma_{Al}^{Mg} = -0.02836; \gamma_{Al}^{O} = 0.02222; \gamma_{Al}^{Mg} = -260; \gamma_{Al}^{O} = 350; \gamma_{Al}^{O} = -60; \gamma_{Al}^{O} = -230; \gamma_{Al}^{O} = -0.01; \gamma_{Al}^{O} = -302.046; \gamma_{Al}^{O} = -0.000576; \gamma_{Al}^{O} = 462.000; \gamma_{Al}^{O} = -20000; \gamma_{Al}^{O} = 462.000; \gamma_{Al}^{O} = -230; \gamma_{Al}^{O} = -0.01; \gamma_{Al}^{O} = -302.046; \gamma_{Al}^{O} = -0.000576; \gamma_{Al}^{O} = 462.000; \gamma_{Al}^{O} = -20000;
\]

![Fig. 11. Mg and Al content on the stability diagram of the MgO–MgO-Al2O3–Al2O3 system calculated using $K_{Mg}$(1) and (b) $K_{Mg}$(2), respectively.](Image)
Table 4. Comparison of the reactions between different refractories with molten steel.

<table>
<thead>
<tr>
<th>Refractory type or slag and their composition</th>
<th>Before reaction</th>
<th>After reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral phases</td>
<td>MgO, CaO</td>
<td>MgO and graphite</td>
</tr>
<tr>
<td>Al content in molten steel</td>
<td>0.28%</td>
<td>0.30%</td>
</tr>
<tr>
<td>Initial inclusions</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Interfacial layer of refractory</td>
<td>Al₂O₃–MgO(sat.)–Al₂O₃ liquid phase</td>
<td>Partially covered by MgO(sat.)–Al₂O₃ phase</td>
</tr>
<tr>
<td>Maximum contents of Mg and Ca</td>
<td>[Mg]: 5.5 ppm</td>
<td>[Mg]: 3.5 ppm</td>
</tr>
<tr>
<td></td>
<td>[Ca]: 0.5 ppm</td>
<td>[Ca]: 0.3 ppm</td>
</tr>
<tr>
<td>Reduction rate of MgO</td>
<td>Smaller than slag and larger than MgO–C</td>
<td>largest</td>
</tr>
<tr>
<td>Change of inclusions</td>
<td>Al₂O₃→MgO(sat.)–Al₂O₃</td>
<td>Al₂O₃→MgO(sat.)–Al₂O₃</td>
</tr>
<tr>
<td>Reaction mechanism</td>
<td>MgO of the refractory reacted with Al in steel and generated Al₂O₃ to form the liquid phase. This liquid phase reacted with molten steel to release Mg but Ca barely dissolved. In comparison to that of slag, the reaction rate was small because the liquid phase was sandwiched by MgO particles. Inclusions changed into MgO(sat.)–Al₂O₃, Mg quickly dissolved from liquid slag but Ca was barely dissolved by the reaction between liquid slag and molten steel. Inclusions changed to MgO–sat. spinel and then to MgO. CaO-containing inclusions were only generated when the Al content of steel was extremely high (&gt; 0.75%). Mg was continuously dissolved by the direct contact between solid MgO of the refractory and molten steel, and by the reduction with carbon in the refractory. Inclusions transformed to MgO–sat. spinel. MgO–Cr₂O₃ of refractory was easily reduced by Al in steel and a dense spinel layer was formed. The layer in contact with steel was saturated with Al, and thus inclusions remained as Al₂O₃.</td>
<td></td>
</tr>
</tbody>
</table>

5. Conclusion

In this study, a dolomite refractory rod was immersed in Al-killed molten steel with low and high Al contents. The dissolution behavior of Mg and Ca from the dolomite refractory in molten steel was measured, and the transforming behaviors of inclusions were observed. The following conclusions were drawn:

(1) Both MgO and CaO from the dolomite refractory were reduced by the dissolved Al in the molten steel, but different dissolution behaviors were observed. For low Al steel, both the Mg and Ca contents of molten steel changed little with immersion time, which were approximately 0.7 ppm and 1 ppm, respectively. For high Al steel, the Mg content in steel gradually increased to approximately 5.5 ppm until 60 min and then a little scattering occurred, while the Ca content barely changed from 0.5 ppm.

(2) After immersing the dolomite refractory, a layer that mainly consisted of solid MgO and a CaO–Al₂O₃–MgO liquid phase formed on the interface between the dolomite rod and molten steel. The thickness of this layer increased with immersion time, and the MgO particles inside this layer aggregated and grew larger than the MgO particles in the dolomite matrix.

(3) The inclusions in both the low and high Al steels transformed from Al₂O₃ to MgO–Al₂O₃ spinel after reacting with the dolomite refractory. For the low steel, the inclusions
transformed gradually, and Al₂O₃-saturated spinel inclusions were found at 60 min. For the high Al steel, the inclusions transformed quickly and MgO-saturated inclusions were observed after 5 min. In addition, CaO-containing inclusions were not detected in the molten steel.

Acknowledgements
The authors appreciate the Kurosaki-Harima Corporation for supplying the dolomite refractory rods. We would like to thank the Program for International Scientific and Technological Cooperation supported by the Beijing Science and Technology Ministry for giving one of the authors (Y. Ren) an opportunity to stay at Tohoku University when conducting this research. Co-authors (Y. Ren and L. Zhang) acknowledge the financial support for the P-SEM analysis from the National Natural Science Foundation of China (Grant No. U1860206, No. 51725402).