Effect of Silica in Slag on Inclusion Compositions in 304 Stainless Steel Deoxidized with Aluminum

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Experiments were carried out to determine the effect of silica in the slag of CaO–SiO₂–Al₂O₃–MgO–F system on the formation of MgO·Al₂O₃ spinel inclusion in 304 stainless steel deoxidized with Al. Immediately after the addition of Al into the molten steel, alumina clusters formed. Simultaneously, reduction of MgO in the slag occurred to raise Mg content in the steel. This resulted in the change in inclusion composition to MgO·Al₂O₃ spinel which did not further change. In the previous experiments with CaO–Al₂O₃–MgO–F slag, however, spinel inclusions changed to MgO or liquid CaO–Al₂O₃–MgO system. The difference in behavior was caused by the existence of silica in the slag. Silica in the slag was considered to prevent the extensive reduction of MgO or CaO in the slag by Al to supply soluble Mg or Ca into the molten steel. A stability diagram of inclusions corresponding to Mg and Al contents in the steel was calculated employing available thermodynamic data. The inclusion compositions experimentally obtained well agreed with the diagram. This implies that spinel inclusions were the most stable in the molten 304 stainless steel deoxidized with Al under the presence of 10 mass% silica in the slag. As a result, it was concluded that silica in the slag enhanced the formation of spinel inclusions.

KEY WORDS: spinel; magnesia; alumina; aluminum; deoxidation; stainless steel; inclusion; silica; slag.

1. Introduction

Recently, austenitic stainless steels are widely employed for the various usage including electronic materials which are typified by some parts of computer units or CRT. A slight defect may deteriorate their required properties. Therefore, the requirement to improve cleanliness in the steels is particularly increasing in this field. In surface defects in stainless steels, a large number of MgO·Al₂O₃ spinel inclusions of several microns are typically observed.¹,²,³ So, spinel inclusions are recognized to be harmful. One of the authors has previously reported that spinel inclusions tend to accumulate on the inner wall of a submerged entry nozzle of a continuous casting machine.³,⁴ As the accretion grows to certain thickness, it may occasionally detach from the nozzle wall at some moment and flow down to the mold with the molten steel.³,⁴ It is entrapped by solidified shell, it may cause a sliver defect appearing on a strip surface. This is why spinel inclusions must be avoided to prevent the defects.

A number of investigations have been so far reported on clarifying how spinel inclusions form in liquid iron and steels. In iron, extensive work has been made to create the stability diagrams of oxide inclusions corresponding to Mg and Al contents using the thermodynamic data experimentally obtained.⁶,⁷ It has been proved that very small amounts of Mg and Al enable the formation of spinel. Problems with spinel are rather associated with stainless steels than with carbon steels. This reason may be attributed to the fact that MgO-based refractory such as dolomite, MgO–C and MgO–chromite bricks are commonly employed for refining molten stainless steels using AOD and/or VOD converters.⁵ Nishi and Shimme⁹ studied spinel formation in Fe–18mass%Cr–8mass%Ni stainless steel deoxidized by Al. They described that the inclusion compositions changed from alumina to spinel with time when the slag basicity was higher. Okuyama et al.¹⁰ also studied the effect of slag basicity on spinel formation in Fe–16mass%Cr stainless steel deoxidized by Al. Their result showed the same tendency as that of Nishi and Shimme.⁹ They further showed that the rate controlling step of spinel formation was the reaction to reduce MgO in the slag by Al to supply soluble Mg into the molten steel. In both studies,⁹,¹⁰ spinel was formed with Mg content in the steels as low as about 1 ppm supplied from MgO in the slag. Jo et al.¹¹ most recently reported a stability diagram of oxides in Fe–18mass%Cr–Al–Mg system taking it into account that MgO·Al₂O₃ would form solid solution with Cr substituting the site of Al.

A series of experiments have been performed by the authors to clear the formation mechanism of spinel in Fe–18mass%Cr–8mass%Ni stainless steels deoxidized with ferrosilicon alloys³,⁴ followed by that with aluminum.¹¹ In the latter study, the experiments were carried out with the top slag of CaO–Al₂O₃–MgO–F system featuring silica-free. Alumina inclusions, which formed immediately after...
the addition of Al, changed to MgO·Al₂O₃ which further changed to MgO. Besides, MgO changed to liquid CaO–Al₂O₃–MgO system inclusions when Al was added onto the slag surface. This result is different from the other results mentioned above⁹,¹⁰ in that the change in the inclusion compositions was until spinel. This difference has to be made clear to fully understand the formation mechanism of spinel inclusions in Al deoxidation.

In practice, top slag usually contains appreciable amount of silica that could be originated from oxidation of Si contained in molten steels. The effect of silica in slag is considered to be significant because silica is not as stable as alumina when steel contains Al. In the present study, therefore, the effect of silica in slag on inclusion compositions is primarily focused on. In addition, the direction to avoid spinel inclusions will be indicated.

2. Experimental Details

The procedure is previously documented elsewhere.¹,²,⁵ 500 grams of premelted Fe–18mass%Cr–8mass%Ni stainless steel was contained in an MgO crucible and placed in a vertical KERAMAX resistance furnace. After the molten steel reached 1823 K under an Ar gas atmosphere, it was sampled followed by an addition of 0.5 mass% Si, 1.0 mass% Mn and Al into the melt. Amounts of Al added were varied at 0.05, 0.1, and 0.3 mass%. 40 grams of premelted slag, whose composition is shown in Table 1 comparing with the silica-free slag used in the previous study,⁵ was then added into the molten steel. The time when the slag addition was completed was defined as the starting time (time zero). Thereafter, the molten steel samples were taken at the times of 1, 5, 30, 60, 90 and 120 min. The concentrations of Si, Mn, Al, Mg, Ca and total O in the steel samples were measured by a wet chemical analysis except for total O by a vacuum fusion method (EMGA-520, HORIBA). The contents of Si, Mn, Al, Mg and Ca before deoxidation were not analyzed because they were already confirmed to be under analytical limitation in the previous studies.¹,²,⁵

Inclusions were analyzed by a EDS method (EMAX-7000, HORIBA). The inclusion compositions and O contents of all the samples were analyzed. 10 inclusions in each sample were randomly chosen for measurement.

3. Results

3.1. Variation of Metal Compositions

Representative results for the variation of metal compositions are shown in Figs. 1 to 5 in comparison with the previous results⁵ at the same Al addition of 0.3 mass%. Si slightly increased from 0.4 to 0.5 mass% within the first 30 min as shown in Fig. 1. After that, it became constant at 0.5 mass% which is the same as the previous results⁵ at 30 and 60 min. As shown in Fig. 2, Al showed a continuous decrease after the addition. When comparing at the same times, Al contents were higher with the present slag containing 10 mass% silica contrary to expectation. This reason is not understood but may be caused by some experimental error. In Fig. 3, Ca showed a significant increase up to 100 ppm immediately after Al was added even though Ca

<table>
<thead>
<tr>
<th>No.</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>CaF₂</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td>52.9</td>
<td>10.6</td>
<td>8.5</td>
<td>8.7</td>
<td>20.4</td>
<td>this study</td>
</tr>
<tr>
<td>S4</td>
<td>59.8</td>
<td>9.3</td>
<td>9.5</td>
<td>21.4</td>
<td></td>
<td>previous study⁵</td>
</tr>
</tbody>
</table>

Fig. 1. Representative results for the variation of Si content.

Fig. 2. Representative results for the variation of Al content.

Fig. 3. Representative results for the variation of Ca content.
was not intentionally added. Then it rapidly decreased to the constant values of 1 ppm which are the same as the previous result. Mg also showed a significant increase to 12 ppm even though Mg also was not intentionally added as seen in Fig. 4. Thereafter it decreased to 1 ppm. Mg contents of the previous study using the silica-free slag are higher comparing at the same times. (Note the contents of time 0 were not plotted in Figs. 3 and 4.) In Fig. 5, Oxygen contents were initially around 250 ppm prior to the Al addition followed by a rapid decrease in both cases. After 60 min, it attained the constant values of 5 ppm.

### 3.2. Variation of Inclusion Compositions

The variations of inclusion compositions are shown in Figs. 6, 7 and 8 at the Al additions of 0.05, 0.1 and 0.3 mass%, respectively. Every table above each figure, where the average values of 10 measurements are provided, shows the number of inclusion species observed. The blank at 120 min of Fig. 8 means that no inclusions were seen in the sample. In every case, the inclusions of Cr oxide were observed before deoxidation. The identification of this oxide was not made because it was out of focus of this study. Therefore, it was indicated as CrO$_x$ here. Immediately after the addition of Al, alumina inclusions formed with the morphology of a cluster similarly to the previous result. The size of the cluster was measured ranging from 10 µm composed of a couple of particles to 300 µm composed of several hundreds of particles. Each particle showed angular shape. At 5 min, a part of alumina inclusions changed to the
inclusions containing 20 to 30 mass% MgO and 70 to 80 mass% Al₂O₃ with a small amount of MnO and CrO.
These were assured to be homogeneously dissolved according to the observations by SEM and EDS. Therefore, this inclusion was confirmed as MgO·Al₂O₃ spinel referring to the phase diagram of MgO–Al₂O₃ system. After 30 min, they all changed to spinel inclusions. This variation in the compositions is schematically shown in the phase diagram of CaO–Al₂O₃–MgO system (Fig. 9). Spinel tended to have angular shape which is similar to alumina and the size ranged from 1 to 10 μm. In this study, the further change to MgO or CaO–Al₂O₃–MgO inclusions has never taken place. This phenomenon significantly differs from the previous results.

4. Discussion

In the following section, thermodynamic analysis was made to better understand how stably spinel inclusions are able to form under the given conditions. The standard free energy changes and the corresponding equilibrium constants of the reactions relevant to the present study are summarized in Table 2. The first and second order interaction coefficients employed are provided in Table 3. Since Fe–18 mass% Cr–8 mass% Ni alloy is studied, the coefficients related with Cr and Ni may provide significant influences on the thermodynamic calculation. Therefore, these values are very carefully chosen from the view points of available ranges. In fact, some of the values are different from those in the previous work due to the current progress in research in high alloys particularly for stainless steels. However, the coefficients are still not enough to calculate the activities of solutes in stainless steels because, strictly speaking, cross terms are needed. More exactly saying, the activities have to be defined based on Fe–18 mass% Cr–8 mass% Ni as a solvent. The corresponding data are not reported at this time. In this study, therefore, the activities were calculated using the coefficients based on molten iron as given in Table 3.

4.1. Equilibrium

In the present experiments, oxygen potential is determined by Al with respect to the following equation.

\[
\Delta G^\circ \text{(molke)} = \log K = \frac{0.57}{T} \times \frac{20.57 - 64000}{T} 
\]

Table 2. Equilibrium constants of reactions employed in the present study.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^\circ \text{(molke)} )</th>
<th>( \log K )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3(s) = 2\text{Al} + 3\text{O} )</td>
<td>1222000 - 393 BT</td>
<td>20.57 - 64000/T</td>
<td>13</td>
</tr>
<tr>
<td>( \text{MgO} + \text{Mg} = \text{Mg}_2\text{O} )</td>
<td>0.961 + 0.0T</td>
<td>-4.28 - 4700/T</td>
<td>14</td>
</tr>
<tr>
<td>( \text{MgO} - \text{Mg}_2\text{O} = \text{Al}_2\text{O}_3(s) - \text{Mg}_2\text{O} )</td>
<td>1828 - 6.7T</td>
<td>-0.32 - 9800/T</td>
<td>15</td>
</tr>
</tbody>
</table>

where, \( a_i \) is the activity of element \( i \) in molten steel relative to a dilute solution of one mass percent standard state and \( a_{\text{Al}_2\text{O}_3} \) is the activity of alumina relative to a pure solid standard state. \( T \) is temperature in Kelvin. \( f_i \), the activity coefficient of element \( i \) in molten steel, is expressed as the following equations.

\[
\log f_A = \sum e_i^A [\text{mass%}] 
\]

\[
\log f_O = \sum e_i^O [\text{mass%}] 
\]
where, $e_i$ is the first-order interaction coefficient.

Substituting Eqs. (3), (4) and (5) with the interaction coefficients and the chemical compositions into Eq. (2), one can obtain the oxygen contents in equilibrium with alumina in the slag. It was very difficult to estimate the activity values of alumina in the present slag accurately because it was complex CaO-SiO$_2$-Al$_2$O$_3$-MgO-F system simulating the practical slag in an AOD converter. Ohta and Suito$^{22)}$ proposed an equation obtained by a multiple regression analysis to estimate the $a_{Al_{2}O_{3}}$ in CaO-SiO$_2$-Al$_2$O$_3$-MgO system. With this equation, the value of 0.001 can be obtained assuming that the function of F is only to widen the liquid region and that CaF$_2$ is counted as CaO. This value was substituted into Eq. (3) as $a_{Al_{2}O_{3}}$, leading to the oxygen contents of 0.2 to 3 ppm at the Al contents ranging from 0.3 to 0.002 mass%. These values are lower than the measured total oxygen contents of about 5 ppm even at the later stages of deoxidation. Although it is difficult to argue the accuracy of oxygen analysis at the moment, the inclusions observed in the samples appeared as primary ones that are focused on.

### 4.2. Stability Diagram for Oxides

As explained above, alumina inclusions formed as soon as the molten steels were deoxidized. According to Figs. 3 and 4, the following reactions simultaneously occurred toward the right hand side of the slag and the steel.

$$3(MgO)_{in 	ext{ Slag}} + 2\Delta\rightarrow (Al_{2}O_{3})_{in 	ext{ Slag}} + 3Mg_{s}$$ (6)
$$3(CaO)_{in 	ext{ Slag}} + 2\Delta\rightarrow (Al_{2}O_{3})_{in 	ext{ Slag}} + 3Ca_{s}$$ (7)

The significant pickup in Mg and Ca may also be attributed to the entrainment of the slag. However, it was confirmed by SEM observation that the slag entrainment did not occur because the slag was not detected in the samples. After that, Mg reacted with alumina inclusions formed at the earliest stage to form MgO·Al$_2$O$_3$ spinel. The reason why Ca did not react will be mentioned in detail later.

To fully clarify the formation of spinel, a stability diagram for oxides of MgO, MgO·Al$_2$O$_3$ and Al$_2$O$_3$ has to be accounted for corresponding to the steel compositions. One can obtain the diagram assuming that local equilibrium between the inclusions and the molten steel is maintained. Actually this assumption should be correct because Okuyama$^{10)}$ proved that the reaction between inclusions and steel was fast enough. The following reaction was considered to calculate the MgO/MgO·Al$_2$O$_3$ boundary.

$$4MgO(s) + 2\Delta\rightarrow MgO·Al_{2}O_{3}(s) + 3Mg$$ (8)

The following equation can be derived from Table 2.$^{13–15)}$

$$\log K = -33.09 + 50.880/T$$ (9)

$$K = \frac{a_{MgO} \cdot a_{Al_{2}O_{3}} \cdot f_{Mg}}{a_{MgO} \cdot a_{Al_{2}O_{3}} \cdot f_{Mg}^{3} \cdot f_{Al_{2}O_{3}}^{3}}$$ (10)

To calculate the MgO·Al$_2$O$_3$/Al$_2$O$_3$ boundary, the following reaction was considered.

$$3MgO·Al_{2}O_{3}(s) + 2\Delta \rightarrow 4Al_{2}O_{3}(s) + 3Mg_{s}$$ (11)

The following equation can be derived from Table 2.$^{13–15)}$

$$\log K = -34.37 + 46.950/T$$ (12)

$$K = \frac{a_{MgO}^{3} \cdot a_{Al_{2}O_{3}}^{2} \cdot f_{Mg}^{3} \cdot f_{Al_{2}O_{3}}^{3} \cdot f_{Mg}^{3}}{a_{MgO}^{3} \cdot a_{Al_{2}O_{3}}^{2} \cdot f_{Mg}^{3} \cdot f_{Al_{2}O_{3}}^{3} \cdot f_{Mg}^{3}}$$ (13)

$$\log f_{Mg} = \sum e_{i}^{Mg} \cdot [\text{mass} \% O] + r_{Mg}^{O} \cdot [\text{mass} \% O]$$ (14)

where, $e_{i}^{Mg}$ is the first-order interaction coefficient and $r_{Mg}^{O}$, $r_{Mg}^{O}$ and $r_{Mg}^{O}$ are the second-order interaction coefficients of Mg.

The standard oxides of the oxides are taken as pure solids in Eqs. (10) and (13). By combining Eqs. (4), (9), (10) and (12) to (14) with the interaction coefficients, the chemical compositions and the activities of each oxide in equilibrium, the boundaries can be obtained. The oxygen contents in equilibrium with the slag are substituted. With regard to the activities of each oxide, the same manner as in the previous work$^{9)}$ was applied. Accordingly, in Eq. (10), the activity of MgO was taken as 0.99 because of very small solubility of Al$_2$O$_3$ into MgO,$^{12)}$ while that of MgO·Al$_2$O$_3$ as 0.80.$^{23)}$ In Eq. (13), the activity of MgO·Al$_2$O$_3$ was taken as 0.47,$^{23)}$ while that of Al$_2$O$_3$ as unity because of negligibly small solubility of MgO into Al$_2$O$_3$.$^{12)}$ The phase stability diagram calculated in this manner is shown in Fig. 10 along with the experimental results. The region below 0.001 mass% Al was not considered because MnO-SiO$_2$ oxides, which were not observed in this study, would be stable here owing to the higher oxygen potential.$^{13)}$ As can be seen in this figure, the measured inclusion compositions of spinel are well positioned at the MgO·Al$_2$O$_3$ region. It is realized

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**Table 3.** First and second order interaction coefficients $e_i$ and $r_j$ used in the present study

<table>
<thead>
<tr>
<th>$e_i$</th>
<th>$r_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-0.068$^{110)}$</td>
</tr>
<tr>
<td>Mn</td>
<td>0.047$^{110)}$</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.012$^{110)}$</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.12$^{110)}$</td>
</tr>
<tr>
<td>Mg</td>
<td>-0.066</td>
</tr>
<tr>
<td>Ca</td>
<td>-0.021</td>
</tr>
<tr>
<td>Al</td>
<td>-0.003$^{110)}$</td>
</tr>
<tr>
<td>O</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>-300$^{110)}$</td>
</tr>
<tr>
<td></td>
<td>-990$^{110)}$</td>
</tr>
</tbody>
</table>

All data without notation are from Ref. No.13

*) $\frac{\Delta_{lg} G}{R T} = 37000$, $\frac{\Delta_{lg} H}{R T} = 48000$, $\frac{\Delta_{lg} S}{R T} = 0$, $\frac{\Delta_{lg} H}{R T} = 1.34$
that no alumina inclusions are plotted. They were formed immediately after deoxidation with the oxygen contents of over 100 ppm, Ca contents of 100 ppm and Mg contents of 12 ppm for the experiment of 0.3 mass% Al addition. It was therefore considered that equilibrium was not yet attained at the earliest stages.

4.3. Effect of Silica on Inclusion Compositions

Along with the previous results using the silica-free slag, the relationship between the slag and the inclusion compositions at various amounts of Al addition was established by plotting in Figs. 11(a) and 11(b). At 30 min, MgO·Al2O3 inclusions were observed at Al additions lower than 0.3 mass% under the both slags. At 90 min, however, MgO·Al2O3 inclusions exist only at the slag containing 10 mass% silica while MgO and Ca-aluminate inclusions formed under the silica-free slag. This difference in phenomena seems to be so significant. To understand the difference, the present work was compared with the other results of Al deoxidation summarizing in Table 4. It can be realized that silica was contained in the top slag in the present, Nishi’s and Okuyama’s studies. It should be noticed in these studies that the inclusions finally observed were only MgO·Al2O3. In the previous work by the authors, on the other hand, the change in the inclusion compositions did not cease at MgO·Al2O3 but continuously proceeded to MgO or CaO·Al2O3·MgO system with the silica-free slag. It should be pointed out that Mg contents of 1 to 30 ppm associated with the silica-free slag are significantly higher than those with the slag containing silica including the other studies. Mg contents of the latter case are at most 10 ppm seen in this study. In every study, Mg was not intentionally added to the molten steel but supplied through the reducing reaction of MgO by Al. Therefore, silica appeared to act an important role on the determination of inclusion composition as a component to prevent an increase in Mg content. In order to more clearly see this relation, MgO content in the inclusions were plotted against silica content in the slag as shown in Figs. 12(a) and 12(b), where the data of 5 and 30 min after Al addition were

![Fig. 10. Phase stability diagram of inclusion compositions in the experiments with the slag containing 10 mass% silica. A: Alumina and S: Spinel.](image)

![Fig. 11. Effect of silica content in the slag and the amount of Al addition on inclusion compositions. 30 min after deoxidation (a) and 90 min after deoxidation (b).](image)

Table 4. Comparison with the previous studies of molten stainless steels deoxidized with Al.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Weight of steel (kg)</th>
<th>Slag</th>
<th>Al content (mass%)</th>
<th>Mg content (mass ppm)</th>
<th>Ca content (mass ppm)</th>
<th>Inclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Previous work</td>
<td>SUS304 (18Cr-8Ni)</td>
<td>0.5</td>
<td>CaO·Al2O3·MgO·CaF2</td>
<td>0.01~1</td>
<td>1~30</td>
<td>1~10</td>
</tr>
<tr>
<td>Present work</td>
<td>SUS304 (18Cr-8Ni)</td>
<td>0.5</td>
<td>CaO·Al2O3·MgO·SiO2·CaF2</td>
<td>0.002~0.2</td>
<td>1~10</td>
<td>1</td>
</tr>
<tr>
<td>Nishi and Shimizu</td>
<td>SUS304 (18Cr-8Ni)</td>
<td>15</td>
<td>CaO·Al2O3·MgO·SiO2·CaF2</td>
<td>0.02~0.05</td>
<td>&lt;1 (0.01~0.1)*</td>
<td>—</td>
</tr>
<tr>
<td>Okuyama et al</td>
<td>SUS430 (18Cr)</td>
<td>20</td>
<td>CaO·Al2O3·MgO·SiO2</td>
<td>0.05</td>
<td>0.8</td>
<td>—</td>
</tr>
</tbody>
</table>

*Estimated by thermodynamical calculation
given, respectively. Some data were not found on 5 and 30 min in the figures of Nishi and Okuyama. In such cases, the corresponding data were read from the straight line connected the neighbor points. Clearly, MgO content in the inclusions decreases with an increase in silica content in the slag as is seen in Fig. 12(a). However, MgO content of this work is lower comparing at similar silica content. This may be attributed to the difference in the apparatuses. Induction furnaces were used in the other studies while a resistant furnace in this study. It is postulated that attaining equilibrium between the molten steel and the inclusions is faster in induction furnaces because of induced metal flow resulting in the higher MgO contents. The same tendency can be seen at 30 min in Fig. 12(b). However, all the plots can be connected with a curved line. This implies that 30 min was long enough to reach equilibrium.

In addition to Mg, Ca contents were analyzed in the studies by the authors while no measurement was made in the other studies. It can be seen that Ca contents of this study with the slag containing silica are lower than with the silica-free slag. At the earliest stages, Mg and Ca contents significantly increased according to the reactions of Eqs. (6) and (7). However, it rapidly decreased with time as shown in Figs. 3 and 4. This decrease, especially of Ca, is more significant than with the silica-free slag. It is considered that the following reactions immediately took place at the next moment.

\[
\begin{align*}
(SiO_2)_{in \text{ slag}} + 2Mg &\rightarrow 2(MgO)_{in \text{ slag}} + Si \quad \text{(15)} \\
(SiO_2)_{in \text{ slag}} + 2Ca &\rightarrow 2(CaO)_{in \text{ slag}} + Si \quad \text{(16)}
\end{align*}
\]

The following mechanism is also probable other than mentioned above. Al was consumed by SiO in the slag according to the following reaction.

\[
3(SiO_2)_{in \text{ slag}} + 4Al \rightarrow 2(Al_2O_3)_{in \text{ slag}} + 3Si \quad \text{(17)}
\]

Then the ability of Al to reduce MgO and CaO in the slag can be weakened leading to the suppression of Mg and Ca pickup. However, the difference in the decrease of Al content comparing to the results with silica-free slag at the initial stage seen in Fig. 2 is recognized to be negligibly small. That is why the former mechanism explained with Eqs. (15) and (16) is considered to be more probable.

Consequently, Mg contents reached the range from 1 to 10 ppm at the Al contents from 0.02 to 0.006 mass%, respectively, where spinel inclusions are the most stable, as shown in Fig. 10. On the other hand, Ca contents of the specimens except for the earliest times were analyzed to be 1 mass ppm in this study. According to the previous thermodynamic calculation considering Ca, liquid inclusions of CaO–Al2O3–MgO system are the most stable under this condition. As mentioned above, however, this inclusion specie was not observed in this study. This may imply that Ca contents in this study were expected as below 1 mass ppm. At this moment, it is difficult to argue the analytical accuracy in Ca around 1 mass ppm that is critical in limitation. This should be one of the most important issues to be solved in the future to more precisely predict inclusion species corresponding to steel compositions.

Summarizing the experiments of Al deoxidation in conjunction with the previous study, the following attentions have to be paid to avoid spinel inclusions which are harmful not only for operation but also for steel quality. With regard to slag compositions, silica content in slag should be controlled as low as possible. Al content should be carefully controlled to a moderate range to modify inclusions to be MgO or CaO–Al2O3–MgO system which is liquid in molten steel.

5 Conclusions

Experiments were undertaken to understand the effect of silica in the slag on the formation of spinel inclusions in 304 stainless steel deoxidized with Al. The following conclusions summarize this study.

1. Alumina inclusions formed with the morphology of cluster soon after the addition of Al.
2. Alumina inclusions were reacted with Mg supplied from the slag phase by reduction of MgO by Al resulting in the change to spinel.
3. Thermodynamic calculation was well consistent with the experimental results.
4. Further change in inclusion compositions did not occur. This result was different from those of the previous experiments using the silica-free slag, with which spinel changed to MgO or CaO–Al2O3–MgO system.

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(5) It was found that silica in the slag enhanced the formation of spinel inclusions suppressing extensive reduction of MgO and CaO in the slag.

(6) To avoid spinel inclusions which are harmful, one should control silica content in slag as low as possible.

REFERENCES