Factors to Determine Inclusion Compositions in Molten Steel during the Secondary Refining Process of Case-Hardening Steel

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A study was carried out to observe inclusions during the secondary refining process of case-hardening steel to understand the factors to determine inclusion compositions. During the LF refining, inclusions changed from the primary deoxidation product of Al₂O₃ to MgO-Al₂O₃ and the CaO-Al₂O₃ system. At the end of LF refining, the compositions were placed on the tie-line connecting the areas of MgO-Al₂O₃ and CaO–Al₂O₃–MgO⁻⁶ in the CaO–Al₂O₃–MgO diagram. This change took place by the composition evolution targeting the thermodynamic equilibrium states. After the RH treatment, the inclusion compositions changed mainly to Al₂O₃ and the CaO–Al₂O₃ system because MgO-Al₂O₃ inclusions were removed, while the CaO–Al₂O₃ system inclusions, the most stable oxide, were remained. This behavior could be described by the interfacial properties between the oxides and the molten steel. Al₂O₃ inclusions were considered to be newly generated during the RH treatment. It was confirmed that three factors of (1) equilibrium state (2) removal and (3) generation of inclusions dominated to determine the inclusion compositions.

KEY WORDS: secondary refining; alumina; MgO-Al₂O₃ spinel; calcium aluminate; non-metallic inclusion; generation; removal; evolution; thermodynamics; interfacial energy; wettability; case-hardening steel.

1. Introduction

Non-metallic inclusions affect not only product quality but also manufacturing process of steels. This is why demands of steels with much higher cleanliness are very high. It is generally known that inclusions deteriorate mechanical properties of the steels. For example, inclusions significantly deteriorate fatigue properties of the bearing steels and the case-hardening steels. Therefore, for commercial mass production of steels containing high contents of C and Cr, such as bearing steel and case-hardening steel, it is of primary importance to decrease oxygen content to minimize the inclusion amount and size.¹,² Today, a novel technology to control oxygen content less than 5 ppm has been developed to improve steel cleanliness.²,³,⁵

In addition to the above studies, a number of researchers have conducted work on the inclusion evolutions in detail including the variations from Al₂O₃ to the CaO–Al₂O₃ system from Al₂O₃ to MgO-Al₂O₃ or partially to MgO, and from MgO-Al₂O₃ to the CaO–Al₂O₃ system or to the CaO–MgO–Al₂O₃ system.¹¹–¹⁸ It should be pointed out that most of researches stated above were done in laboratory scales. Thus, information about inclusion formation in practice is still lacking to understand inclusion evolution occurring in the practical refining stages. In fact, one has to consider various factors such as additives, gas blow, agitation, reoxidation and slag entrainment in practice. This is why it is still strongly required to collect the plant data focusing on actual steelmaking processes.

In the actual steelmaking, especially in the secondary
refining process, steels are deoxidized and desulfurized to ensure steel quality as high as possible. It is not too much to say that this process determines the quality of the final products. Deoxidizers such as aluminum have to be appropriately added in combination with the fluxes such as CaO to create slag. In fact, at this stage, attention should be paid to the evolution of the inclusion composition from the primary deoxidation products to adequately control inclusion amount and composition. It has been pointed out that it is not enough only to consider the evolution mentioned above, but both generation of newly formed inclusions\(^2\)\(^,\)\(^19\)\) and removal from the molten steel\(^20\)\(^–\)\(^24\)\) have to be also taken into account. However, few studies have been so far reported with considering all of the factors documented above.

From this viewpoint, a study was carried out aiming at clarifying the evolution mechanism of inclusions contained in case-hardening steel focusing on formation, variation and removal as well as generation on the way of the process. In practice, steel samples were taken from the ladle during the LF-RH process. As the inclusions consisted of CaO, MgO and Al\(_2\)O\(_3\) oxides described later in detail, the inclusion compositions were analyzed by projecting on the CaO–MgO–Al\(_2\)O\(_3\) diagram in order to understand the formations of various inclusions with multiple phases. Finally, the behavior of the inclusion evolution was elucidated with considering these factors.

2. Experimental

2.1. Practice

The experiment was carried out in practice of the case-hardening steel standardized as JIS SCM420. The procedure of our melt shop was as follows; the process began with melting at a 150 t EAF followed by the secondary refining process in a LF and a RH and finally the molten steel was cast by means of a CC. The ladle was lined by MgO–C bricks. The refining conditions are shown in Table 1.\(^19\)\) Table 2 shows the chemical composition of the present steel featuring 0.2%d C, 1% Cr and 0.15% Mo. The LF practice mainly aims at deoxidation and precise control of composition and temperature. Aluminum flake was used as a deoxidizer, which was added to the molten steel. To promote deoxidation and desulfurization, the slag with relatively high basicity was applied for refining, which had the composition doubly saturated with both CaO and MgO. In the RH practice, degassing was the main purpose to decrease N and H contents along with further deoxidation and separation of inclusions.

2.2. Samples and Evaluation Method

Steel samples were taken during the LF refining and RH treatment processes. Liquid steel samples were taken at 900, 1 800 and 2 700 seconds during the LF practice, which were indicated as “LF initial”, “LF middle” and “LF end”, respectively. In the RH process, a sample was taken at the end of RH indicated as “RH end”. The composition of inclusions on the cross section of each steel sample were analyzed by using automated SEM/EDS inclusion analyzer,\(^25\)\) which can automatically detect inclusions by searching for the particles by identifying the difference of the BSED signal intensity. The scanning area was determined as 100 mm\(^2\). All the inclusions larger than 1 μm in diameter were analyzed. The number of inclusions analyzed depended on the sample; approximately 1 500 data were taken in the three samples of the LF and approximately 800 data were taken in the RH end. Smaller amount of inclusions in the RH end was owing to the decrease in total O content.

As the inclusions consisted of CaO, MgO and Al\(_2\)O\(_3\) oxides described later, their compositions were projected on the CaO–MgO–Al\(_2\)O\(_3\) diagram.\(^26\) Composition was compensated when inclusion contained S; the corresponding content was allotted firstly to Mn and successively to Ca accounting for the formation of MnS and CaS. After this procedure, the rest of Ca was allotted to CaO.\(^19\)\) SEM equipped with EDS was used to observe the morphology and the element distribution of inclusions. Spark discharge atomic emission spectrometric analysis was applied for the measurement of Al content. The concentrations of Ca and

<table>
<thead>
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<th>Process</th>
<th>Time</th>
<th>Function</th>
<th>Remarks</th>
<th>Stirring gas</th>
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<td>EAF</td>
<td>(4.2 \times 10^3) seconds/heat</td>
<td>1) Scrap melting, 2) Steelmaking</td>
<td>1) Oxidation Refining, 2) Only carbon deoxidation</td>
<td>N(_2)</td>
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<td>LF</td>
<td>(3.0 \times 10^3) seconds/heat</td>
<td>1) Complete slag-off, 2) Reduction refining, 3) Raising temperature</td>
<td>1) Al deoxidation, 2) Slag-making, CaO,MgO sat, CaO–MgO–Al(_2)O(_3)–SiO(_2)–F system slag, 3) Composition adjustment, 4) Temperature adjustment</td>
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<td>RH</td>
<td>(1.2 \times 10^3) seconds/heat</td>
<td>Degassing</td>
<td>1) Degassing (H,N), 2) Deoxidation, 3) Flotation separation of inclusions</td>
<td>Ar</td>
</tr>
<tr>
<td>CC</td>
<td>(4.2 \times 10^3) seconds/heat</td>
<td>Shrouded atmosphere casting</td>
<td>Floatation separation</td>
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Table 2. Chemical composition of SCM420 (mass%).

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<th>C</th>
<th>Si</th>
<th>Mn</th>
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<td>0.26</td>
<td>0.83</td>
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Mg were measured by ICP mass spectrometry method. Total oxygen content was measured by the inert gas fusion-infrared absorptiometry.

3. Results
3.1. Variation of Minor Elements in the Steel

It is generally known that the behavior of the deoxidizing elements such as Al, Mg and Ca affects the inclusion compositions, morphology and size. Figure 1 shows the variations of Al, Mg and Ca contents during the secondary refining. The increase of Al content from LF end to RH end was due to the addition of Al because Al was consumed during the RH process. This consumption might be attributed to the reaction between metal and slag, oxygen supply from the atmosphere and desulfurization. According to the previous studies, Ca and Mg were supplied through reduction of CaO and MgO contained in the slag by the Al addition. The concentrations of Ca and Mg were 5.9 and 2.5 ppm, respectively, at the LF initial. After the middle of LF, Ca increased to 6.5–7.9 ppm while Mg slightly decreased to 0.9–1.6 ppm. Finally, Ca and Mg contents decreased to less than 2 ppm, and less than 1 ppm, respectively during the RH treatment. The reason of Ca and Mg decrease was considered to its vaporization. This behavior is quite important in understanding the evolution of inclusions. Total O content was measured as 25 ppm during the LF treatment and it decreased to less than 10 ppm after the RH treatment.

3.2. Variation of Inclusion Compositions

Figures 2(a) to 2(d) show the variation of inclusion compositions at each stage. At the step of LF initial (a), inclusion compositions were located at the vicinity of Al₂O₃, which was resulted from Al deoxidation. Subsequently, inclusion compositions spread simultaneously to MgO-Al₂O₃ and the CaO-Al₂O₃ system at the step of LF middle (b). At the end of LF (c), inclusion compositions were positioned on the tie-line connecting the two areas of MgO-Al₂O₃ and CaO-Al₂O₃-MgOₙₙ, but majority was at the MgO-Al₂O₃ side. Lastly, at the end of RH (d), the CaO–Al₂O₃ system inclusions were still remained in the molten steel while MgO-Al₂O₃ inclusions disappeared and Al₂O₃ inclusions were detected again.

The element mappings of the typical inclusions are shown in Figs. 3(a), 3(b), 3(c) and 3(d), which indicate LF initial, LF middle, LF end and RH end, respectively. Obviously, Al₂O₃ inclusion formed at LF initial (a). At the middle of LF (b), three species of inclusions were observed that were Al₂O₃, MgO-Al₂O₃ and the CaO–Al₂O₃ system with the elements homogeneously distributed. At the end of LF (c), the inclusions of the CaO-MgO-Al₂O₃ system with MgO-rich phase core were observed along with MgO-Al₂O₃ and the CaO–Al₂O₃ system inclusions with the elements homoge-
neously distributed. At the RH end (d), Al2O3 inclusions were detected together with the homogeneous CaO–Al2O3 system inclusions. Accordingly, Fig. 3 evidently shows the variations described in Fig. 2.

Further observation was made to more clearly identify what oxide phases consisted of the inclusions whose compositions were plotted on the tie-line connecting the two areas of MgO·Al2O3 and CaO–Al2O3–MgO liq. The result is shown in Fig. 4 with the liquidus area at 1 873 K calculated by FactSage. Some inclusions at the end of LF consisted of two separate phases of MgO·Al2O3 and the CaO–Al2O3 system while one was the single phase inclusion of the CaO–Al2O3 system. It is evident that the CaO–Al2O3 system inclusions were melt during refining because it is within the liquidus line. This observation has proved that solidus MgO·Al2O3 and the CaO–Al2O3 system are able to coexist. This is the result same as previously reported.11–18)

4. Discussion

As shown above, inclusion compositions varied from the LF refining to RH treatment as the sequence of Al2O3→MgO·Al2O3 + CaO–Al2O3→Al2O3 + CaO–Al2O3. In the following section, the mechanism is discussed from the view point of equilibrium as well as interfacial properties between the inclusions and the molten steel.

4.1. Equilibrium

Thermodynamic calculations were carried out under the present experimental conditions. The used parameters include the measured contents of Al, Ca and Mg as well as the values shown in Table 2 and the first and second order interaction coefficients listed in Table 3.30–35) It is noticed that the effect of Mo on the activity coefficient of the other components was not taken into account due to the lack of thermodynamic data.3) The temperature substituted to the calculations was 1 873 K considering the actual operation condition. Paying attention to the observed phases, thermodynamic calculations were carried out to output the stability diagrams considering the three systems of (1) MgO–Al2O3, (2) CaO–Al2O3 and (3) CaO–MgO–Al2O3.

4.1.1. MgO–Al2O3 System

Equations (1) and (2) were used to determine the most stable phase in the MgO–Al2O3 system.32) The MgO/ MgO·Al2O3 boundary was drawn by considering Eq. (1), with the activity data of MgO = 1 and MgO·Al2O3 = 0.80.33) The MgO·Al2O3/Al2O3 boundary was drawn by considering Eq. (2), with the activity data of MgO·Al2O3 = 0.47 and Al2O3 = 1.33) The activities of components in molten steel were relative to a dilute solution of one mass% standard state. The activities of the oxides are relative to pure solids.

\[
4\text{MgO(s)} + 2\text{Al} = \text{MgO·Al2O3(s)} + 3\text{Mg} \quad \log K_{\text{MgO·Al2O3/Al2O3}} = -23.856 + 32280/T \quad \ldots \ldots \ldots \ldots \ldots \ldots (1)_{32}^2
\]

\[
3\text{MgO·Al2O3(s)} + 2\text{Al} = 4\text{Al2O3(s)} + 3\text{Mg} \quad \log K_{\text{MgO·Al2O3/Al2O3}} = -26.274 + 27950/T \quad \ldots \ldots \ldots \ldots \ldots \ldots (2)_{32}^2
\]

where \(K\) is equilibrium constant and \(T\) is temperature (K). The result is shown in Fig. 5 with the plots of the measured Al and Mg contents at each stage. Under the condition of this practice, it is clear that the most stable phase considering the MgO–Al2O3 system is MgO·Al2O3. The result is quite consistent with the observations since MgO·Al2O3 was one of the detected phases at the LF middle and end, prov-
ing that MgO-Al2O3 formation is thermodynamically stable accounting for Al and Mg contents.

### 4.1.2. CaO–Al2O3 System

Referring to the method proposed by Taguchi et al., Eqs. (3) and (4) were used to determine the most stable phase in the CaO–Al2O3 system. Table 4 shows the activities of CaO and Al2O3 at each boundary calculated by FactSage, which were substituted to these equations.

\[
\text{CaO(s)} = \text{Ca} + \text{O} \quad \log K_{\text{CaO}} = -3.29 - 7 \text{ 220} / T \quad (3)
\]

\[
\text{Al2O3(s)} = 2\text{Al} + 3\text{O} \quad \log K_{\text{Al2O3}} = 11.62 - 45 \text{ 300} / T \quad (4)
\]

The result is shown in Fig. 6 with the plots of the measured Al and Ca contents at each step. Under the condition of this practice, the most stable phase of the CaO–Al2O3 system is clearly CaO-Al2O3 liquid, which agreed to the phases detected in the LF end and the RH end. Thus, the formation of the liquid CaO-Al2O3 inclusions is thermodynamically reasonable by considering Al and Ca contents.

### 4.1.3. CaO–MgO–Al2O3 System

As explained above, the coexistence of two different inclusion compositions may imply the temporary non-equilibrium state. To determine the most stable phase of the three species of (1) Al2O3, (2) MgO–Al2O3 system and (3) CaO–Al2O3 system, the stability diagram was calculated for the CaO–MgO–Al2O3 system referring to the method proposed by Deng.

CaO-Al2O3 was chosen as the phase of the CaO–Al2O3 system. The Al2O3/MgO-Al2O3 boundary was calculated by the Eq. (2), the Al2O3/CaO-Al2O3 boundary was by Eq. (6) which was derived by the combination of Eqs. (3), (4), and (5). The MgO-Al2O3/CaO-Al2O3 boundary was obtained by Eq. (9) which was derived by the combination of Eqs.
describe the formation of Al\textsubscript{2}O\textsubscript{3} inclusions observed at the end of RH. This may imply that those Al\textsubscript{2}O\textsubscript{3} inclusions were generated in the manner different from the endogenous composition evolution. This reason will be discussed later in detail.

### 4.2. Factors to Determine Inclusion Composition

It is generally recognized that the factors of the variation of the inclusion compositions during secondary refining process includes the phenomena of generation,\textsuperscript{2,19} removal,\textsuperscript{20–24} and composition evolution according to equilibrium state.\textsuperscript{6–18} Discussion in the following sections focuses on how each phenomenon is related to the variation at each process based on the thermodynamic calculation results.

#### 4.2.1. Contribution of Generation and Removal during LF Refining Process

Regarding the formation of inclusions during LF refining, a possible cause is the local oxygen supply from slag or atmosphere, which creates Al\textsubscript{2}O\textsubscript{3} via FeO, MnO, or SiO\textsubscript{2} according to Mukai \textit{et al.}\textsuperscript{19} Another cause could be the slag entrapment caused by the gas stirring. Despite these possibilities, the inclusions detected in the LF end did not locate at the vicinity of Al\textsubscript{2}O\textsubscript{3}. Furthermore, these did not locate at the CaO and MgO double-saturation position, corresponding to the present slag chemistry, at the LF initial. Thus, the inclusion compositions during LF refining were not the ones affected by the local oxygen supply or the slag entrapment. As mentioned before, the activity of Al\textsubscript{2}O\textsubscript{3} in the slag at the CaO and MgO double-saturation position was 0.005 calculated by FactSage, with which the dissolved oxygen content could be calculated\textsuperscript{9} as 2 ppm by Eq. (4). Throughout the LF treatment, the dissolved oxygen content was considered to be almost constant as 2 ppm. Moreover, the total O content was mostly kept constant as explained earlier showing that the amount of the oxide inclusion was almost constant in the molten steel during the LF refining. This means that removal of inclusions did not happen so extensively.

According to the above descriptions, it is concluded that the generation and removal of inclusions during the LF refining process is not considerable. The decrease in Al content during the period of the LF refining seen in Fig. 1 is the proof of the generation of Al\textsubscript{2}O\textsubscript{3} inclusions.\textsuperscript{2,27} It is considered that the generated Al\textsubscript{2}O\textsubscript{3} inclusions were mostly absorbed by the slag bulk at the slag/metal interface.

#### 4.2.2. Composition Evolution during LF Refining Process

The thermodynamic calculations showed that MgO-Al\textsubscript{2}O\textsubscript{3} and the CaO–Al\textsubscript{2}O\textsubscript{3} system inclusions are more stable than Al\textsubscript{2}O\textsubscript{3} resulting in the spontaneous changes of Al\textsubscript{2}O\textsubscript{3}→MgO-Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}→CaO–Al\textsubscript{2}O\textsubscript{3} occurring by the reactions between Ca, Mg dissolved in the molten steel and the inclusions. The composition evolution process of Al\textsubscript{2}O\textsubscript{3} in molten steel is reported in several manners. Especially, Todoroki \textit{et al.},\textsuperscript{7} Jiang \textit{et al.}\textsuperscript{12} and Deng \textit{et al.}\textsuperscript{15} reported that under the condition of the higher Mg activity rather than Ca, the evolution occurs in the sequence of Al\textsubscript{2}O\textsubscript{3}→MgO-Al\textsubscript{2}O\textsubscript{3} in advance of Al\textsubscript{2}O\textsubscript{3}→CaO–Al\textsubscript{2}O\textsubscript{3}. Following this theory, the effects of the Ca and Mg activities on the composition evolution of Al\textsubscript{2}O\textsubscript{3} was examined.
under the present conditions. The calculations to obtain the activity coefficients of the components were carried out by
using the values shown in Table 3.

The variation of the activities of Ca and Mg are shown in Fig. 8. This result shows that the values of Mg activity are 1/2–1/5 times of those of Ca activity. Supposing that the above theory would be applicable, this condition would address the composition change of $\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ rather than $\text{Al}_2\text{O}_3 \rightarrow \text{MgO}–\text{Al}_2\text{O}_3$. As explained above, however, the both reactions of $\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3 \rightarrow \text{MgO}–\text{Al}_2\text{O}_3$ took place at the same time in this practice. In other words, the evolution direction from $\text{Al}_2\text{O}_3$ cannot be explained by the difference of the activities of Mg and Ca. This tells us that each reaction independently takes place with the independent driving force.

As mentioned above, $\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ can progress under the condition of Ca content of 1 ppm or higher, however, it is thought as for the composition evolution that the driving force much greater than the calculated value is required to cause in the actual refining process. In the following, the condition for the inclusion change of $\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ is proposed by comparing the previous studies. The Ca contents were compared to estimate the condition because it was very difficult to compare the activities of Ca because their experimental situations were very different from each other. Some were for carbon steels and tool steels, while some were for stainless steels. The data at the step of 1800 seconds after LF or of the LF middle stage were applied for comparison as shown in Table 5. It should be noted that not all the values listed in Table 5 were shown in the literatures. When the values were expressed as a certain range, the mean ones were read from the plots of their figures. As for Ref. 17, it was presumed that Ca content might be similar to ours by considering the slag compositions despite no descriptions regarding Ca content in the middle stage of LF refining.

According to this comparison, Ca content of 4 ppm seems to be the approximate threshold whether or not $\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ reaction proceeds in the Al-killed steels; $\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ reaction can occur with Ca contents higher than 4 ppm. As shown in Fig. 1, the present steel contained Ca contents higher than the threshold value of 4 ppm throughout the LF refining. Thus, the driving force was considered to be high enough for the two reactions to simultaneously take place from $\text{Al}_2\text{O}_3$ toward $\text{MgO}–\text{Al}_2\text{O}_3$ and the $\text{CaO}–\text{Al}_2\text{O}_3$ system.

As proven in Fig. 7, $\text{MgO}–\text{Al}_2\text{O}_3$ is less stable than the $\text{CaO}–\text{Al}_2\text{O}_3$ system leading to the composition evolution of $\text{MgO}–\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$. This happens along the tie-line connecting the areas of $\text{MgO}–\text{Al}_2\text{O}_3$ and $\text{CaO}–\text{Al}_2\text{O}_3–\text{MgO}_\text{liq}$ as seen in Fig. 2(c). Many reports have indicated that it takes a long time for the composition evolution of $\text{MgO}–\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ system. Our result was quite similar to these reports in that the unreacted $\text{MgO}–\text{Al}_2\text{O}_3$ core surrounded by the $\text{CaO}–\text{Al}_2\text{O}_3$ system was observed as shown in Fig. 3(c2). Thus, the composition evolution mechanism of $\text{MgO}–\text{Al}_2\text{O}_3 \rightarrow \text{CaO}–\text{Al}_2\text{O}_3$ was the same as previously reported. According to the stability of the oxide species, Mg atoms diffuse toward outside while Ca atoms diffuse toward inside. Then, inclusion compositions would converge into the $\text{CaO}–\text{Al}_2\text{O}_3$ system in the LF refining step when the reaction time is longer enough.

As explained above, in the LF refining process, the dominant factors to determine the inclusion compositions are not generation and removal but equilibrium states addressed by the chemical potentials of the deoxidizing elements. The evolution degree and direction are affected by the content of each component in the molten steel.

4.2.3. RH Treatment

This stage is the most important for the steel cleanliness because this is the final refining stage before casting. As Fig. 2 indicates, the inclusion compositions changed from the plots, on the tie-line connecting the areas of $\text{MgO}–\text{Al}_2\text{O}_3$ and $\text{CaO}–\text{Al}_2\text{O}_3–\text{MgO}_\text{liq}$ mainly to the vicinity of $\text{Al}_2\text{O}_3$ and the $\text{CaO}–\text{Al}_2\text{O}_3$ system. The effects of generation and removal on the inclusion compositions are considered to understand this change.

The decrease of total O content clearly proves the occurrence of removal of inclusions from the molten steel. Miki et al. reported that the attachment of inclusions to Ar

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<td>1.3</td>
<td>0.052</td>
<td>7</td>
<td>observed</td>
</tr>
</tbody>
</table>

*CaO is abbreviated as C, SiO$_2$ as S, Al$_2$O$_3$ as A and CaO–Al$_2$O$_3$ as C–A.
bubbles plays a significant role of inclusion removal during the RH treatment. Arai et al.\textsuperscript{24} reported that the particles with the large contact angle against the solvent easily attach to the bubbles and are more likely to be removed. Yin et al.\textsuperscript{40} and Wikström et al.\textsuperscript{41} observed the inclusion behavior at the metal/gas interface reporting that attraction force was applied between the solid inclusions which are not wet with the molten steel. On the other hand, attraction force was not applied between the liquid inclusions which can intimately wet with the molten steel. This result indicates that solid inclusions tend to collide and aggregate with each other after attaching to a single bubble while liquid inclusions stay separated. Thus, the interfacial properties of inclusions strongly affect removal behavior during the RH treatment.

From this point of view, the contact angle and the interfacial energy of the oxides should be considered. Table 6\textsuperscript{42–45} clearly shows that MgO·Al\textsubscript{2}O\textsubscript{3}, solid in the refining temperatures, does not wet while the CaO–Al\textsubscript{2}O\textsubscript{3} system, liquid in the refining temperatures, does wet to the molten steel. As well, according to the calculation in 4.1.3, MgO·Al\textsubscript{2}O\textsubscript{3} was in the transient stage to the CaO–Al\textsubscript{2}O\textsubscript{3} system during the RH treatment. Therefore, it was considered that MgO·Al\textsubscript{2}O\textsubscript{3} inclusions not only varied its composition toward the CaO–Al\textsubscript{2}O\textsubscript{3} system but also they were separated during the RH treatment. Meanwhile, the CaO–Al\textsubscript{2}O\textsubscript{3} system inclusions were remained due to the behavior of wetting well to the molten steel. This was how the variation of MgO·Al\textsubscript{2}O\textsubscript{3} to CaO–Al\textsubscript{2}O\textsubscript{3} was considered to proceed. For deoxidation, it is primarily important to decrease total O content by decreasing the inclusion population. It could be said that removal of the singular type Mg\textsubscript{2}O·Al\textsubscript{2}O\textsubscript{3} inclusions from the molten steel was considered to contribute to the decrease of total O content.

Obviously in Fig. 4, some MgO·Al\textsubscript{2}O\textsubscript{3} phases are coexisted with the CaO–Al\textsubscript{2}O\textsubscript{3} system. This indicates that the interfacial properties of these multi-component inclusions are affected by the wetting CaO–Al\textsubscript{2}O\textsubscript{3} system, which lowers the removability from the molten steel. This can evidence that some inclusions containing MgO were still left as can be seen in Fig. 2(d).

Al\textsubscript{2}O\textsubscript{3} inclusions were also formed again until the end of the RH treatment. According to the thermodynamic consideration of section 4.1, Al\textsubscript{2}O\textsubscript{3} inclusions are not stable at this stage under the present Al, Mg and Ca contents. It is reported that there is a certain probability of oxygen supply from slag and/or refractory to the molten steel during the RH treatment.\textsuperscript{21} Furthermore, it is confirmed that this oxygen supply affects to lower the decreasing rate of total O content by generating Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{27} Hence, detected Al\textsubscript{2}O\textsubscript{3} inclusions are considered to be generated during the RH treatment. The removal of MgO·Al\textsubscript{2}O\textsubscript{3} inclusions could overcome the generation of Al\textsubscript{2}O\textsubscript{3} inclusions during RH treatment. This could contribute to the decrease in the total O content during this stage.

4.3. Evolution Mechanism of Inclusion Compositions

According to the experimental results and discussion, the variation mechanism of the inclusion compositions can be summarized as illustrated in Fig. 9. The variation can be classified as the following three steps:

1) At the initial stage of LF refining, the inclusion compositions start at the location of the vicinity of Al\textsubscript{2}O\textsubscript{3}, which are generated by Al deoxidation.
2) In the stage between the middle and the end of the LF refining, the inclusion composition of Al\textsubscript{2}O\textsubscript{3} evolves toward the MgO–Al\textsubscript{2}O\textsubscript{3} system and the CaO–Al\textsubscript{2}O\textsubscript{3} system simultaneously. This can occur due to the sufficient driving force accounting for Al, Mg and Ca contents. The liquid

\textbf{Table 6.} Interfacial energy and contact angle of various oxides.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Interfacial Energy/mJ·m\textsuperscript{-2}</th>
<th>Contact Angle/deg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3} (solid)</td>
<td>2 050 (at 1 873 K)\textsuperscript{42}</td>
<td>140 (at 1 873 K)\textsuperscript{42}</td>
</tr>
<tr>
<td>CaO–Al\textsubscript{2}O\textsubscript{3} (liquid)</td>
<td>1 600 (at 1 853 K)\textsuperscript{43}</td>
<td>54–65 (at 1 873 K)\textsuperscript{44}</td>
</tr>
<tr>
<td>MgO·Al\textsubscript{2}O\textsubscript{3} (solid)</td>
<td>3 700 (at 1 823 K)\textsuperscript{45}</td>
<td>134 (at 1 823 K)\textsuperscript{45}</td>
</tr>
</tbody>
</table>

\textbf{Fig. 9.} Schematic diagram of variation of inclusion compositions during secondary refining process. (Al\textsubscript{2}O\textsubscript{3} is abbreviated as A, MgO as M, MgO·Al\textsubscript{2}O\textsubscript{3} as MA and CaO–Al\textsubscript{2}O\textsubscript{3} system as C–A.)
CaO·Al₂O₃ system inclusions have been proved to be the most stable phase in the CaO–MgO–Al₂O₃ system. So, MgO·Al₂O₃ inclusions can evolve to the CaO–Al₂O₃ system inclusions. Owing to this composition evolution, the inclusion compositions are distributed on the tie-line connecting the areas of MgO·Al₂O₃ and CaO–Al₂O₃–MgO₃H₂O.  

3) During the RH treatment, MgO·Al₂O₃ inclusions are likely to be removed due to their high interfacial energy against the molten steel. As for the multiphase inclusion with MgO·Al₂O₃ core surrounded by the CaO–Al₂O₃ system, MgO·Al₂O₃ core becomes smaller due to the thermodynamic instability. On the other hand, the CaO–Al₂O₃ system inclusions possess low interfacial energy so that they tend to be remained in the molten steel. In addition, Al₂O₃ inclusions are generated during the RH treatment due to the local oxygen supply. Thus, three phenomena including removal of MgO·Al₂O₃ inclusions, remaining the CaO–Al₂O₃ system inclusions and generation of Al₂O₃ determine the inclusion compositions after the RH treatment.

5. Conclusion

Experiments were undertaken to observe inclusions during the actual secondary refining process. The present study aimed at clarifying the factors to determine the inclusion compositions in practice. The following conclusions summarize this study.

(1) During the LF refining, inclusions changed from the primary deoxidation product of Al₂O₃ to MgO·Al₂O₃ and the CaO–Al₂O₃ system. The compositions were positioned on the tie-line connecting the areas of MgO·Al₂O₃ and CaO–Al₂O₃–MgO₃H₂O. This change took place by the composition evolution targeting the thermodynamic equilibrium states.

(2) After the RH treatment, the inclusion compositions changed mainly to Al₂O₃ and the CaO–Al₂O₃ system. MgO·Al₂O₃ inclusions were removed while the CaO–Al₂O₃ system inclusions were remained, which was described by the interfacial properties between the oxides and the molten steel. Al₂O₃ inclusions were considered to be newly generated during the RH treatment.

(3) It was confirmed that three factors of the equilibrium states, removal and generation of inclusions dominated to determine the inclusion compositions in the molten steel during the LF-RH refining process.

REFERENCES

2) K. Kawakami: 182nd and 183rd Nishiyama Memorial seminar, ISIJ, Tokyo, (2004), 159.