Parameters influencing inclusion compositions in Al-killed steel melts during a secondary refining process

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Doctoral Thesis

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初心忘るべからず
Abstract

This study was carried out to clarify the factors influencing the evolution of inclusions in Al-killed steel melts during a secondary refining process. First, a case-hardening steel was the subject of study to understand the factors influencing the inclusion compositions in the steel melt. During the LF process, inclusions were transformed from the Al$_2$O$_3$ phase, which was the primary deoxidation product, to both MgO·Al$_2$O$_3$ and CaO·Al$_2$O$_3$-MgO$_{\text{liq}}$ phases simultaneously. This composition transition during the LF process occurred by composition evolutions toward thermodynamically stable phases. After the RH process, the inclusion compositions primarily consisted of the Al$_2$O$_3$ and CaO·Al$_2$O$_3$ phases. MgO·Al$_2$O$_3$ inclusions were removed, while the CaO·Al$_2$O$_3$ inclusions remained during the RH process. This behavior can be understood in terms of the interfacial properties of the oxide phases in a steel melt. The detected Al$_2$O$_3$ inclusions were considered to be generated by reoxidation during the RH treatment. Thus, it was confirmed that the equilibrium states, removal, and generation of inclusions determine the inclusion compositions in an Al-killed steel melt during an LF-RH refining process.

Subsequently, the effect of high Al contents in a steel melt on the change in inclusion compositions during the LF-RH process was studied. Due to the high Al content in the steel melt, the thermodynamic driving forces for Al$_2$O$_3$ modification became lower than those in ordinary Al-killed steels. Therefore, the degree of inclusion evolution was restricted. This contributed to the low CaO contents in the inclusions. Due to the low CaO contents, the removability of the inclusions remained high throughout the LF-RH process. According to thermodynamic calculations, the low T.O contents in this steel grade are due to the low insoluble O contents. This can be explained by the fast removal of inclusions. Because the inclusions were removed smoothly, the CaO content in the inclusions was lower than that in the thermodynamically stable phase.

In addition, a study was carried out to understand the formation and behavior of the CaS phase in an Al-killed high-S steel during the LF-RH process without Ca-treatment. In the initial stage of the LF process, a CaS phase was formed on the existing inclusions by a reaction between Ca and S. As the desulfurization of the steel melt progressed, the CaS phase started to be transformed into a CaO phase in the inclusions, which resulted in the formation of CaO-Al$_2$O$_3$-CaS inclusions. After desulfurization of the steel melt, the Al$_2$O$_3$ phase in the inclusions was transformed to the CaO-Al$_2$O$_{3\text{liq}}$ phase without being hindered by a CaS phase. During the following RH process, the addition of FeS increased the activity of S, which then reacted with both CaO in the inclusions.
and with Ca, forming a CaS phase. Consequently, the majority of the inclusions consisted of the Al₂O₃-CaS phase. Thus, a CaS formation during the LF-RH process without Ca-treatment progresses under the thermodynamic driving forces of the following two reactions: the reaction between CaO in the inclusions and S and the reaction between Ca and S. Due to the formation of a CaS phase during the RH process, inclusions in the high S steel melt were covered by a CaS phase, which is difficult to remove from steel melts. Therefore, the castability of the high S steels can be deteriorated by the CaS inclusions, even without using Ca-treatment.

In summary, it can be concluded that the removal of inclusions, generation, and composition evolution should be considered in order to control the inclusion compositions in Al-killed steel melts. In addition, steel components, such as Al and S, are important to monitor to control the inclusion evolution during secondary refining processes.

**Key words**: non-metallic inclusion; ladle furnace; RH; thermodynamics; contact angle; Al₂O₃; MgO·Al₂O₃ spinel; calcium aluminate; CaS.
Sammanfattning


Påverkan av höga aluminiumhalter i stålsmältan på förändringar i inneslutningars sammansättningar under LF-RH processen studerades också. På grund av den höga aluminiumhalten i stålsmältan så minskade den termodynamiska drivkraften för att omvandla Al₂O₃ inneslutningar i jämförelse med normala aluminiumdesoxiderade stål. Detta resulterade i låga CaO halter i inneslutningarna. På grund av de låga CaO halterna, så förblev avskiljningen av inneslutningarna hög genom hela LF-RH behandlingen. Enligt termodynamiska beräkningar, så är de låga totalsyrehalterna i denna stålsort beroende av den låga halten av inlöst syre. Detta kan förklaras av den snabba avskiljningen av inneslutningar. Eftersom inneslutningarna avskiljdes relativt enkelt, så blev CaO innehållet i inneslutningarna lägre än i den termodynamiskt stabila fasen. En studie genomfördes också för att klargöra bildningen och beteendet hos en CaS fas i ett aluminiumdesoxiderat stål med hög svavelhalt under LF-RH processen, där kalkiumbehandling inte användes. Under första behandlingen i LF processen så bildades en CaS fas på befintliga inneslutningar genom en reaktion mellan Ca och S. Allteftersom svavelreningen av stålet fortskred så började CaS att omvandlas till en CaO fas i inneslutningen, vilket resulterade i bildandet av CaO-Al₂O₃-CaS inneslutningar. Efter avsvavlingen av stålet så omvandlades Al₂O₃ fasen i inneslutningarna till en CaO-Al₂O₃ (flytande) fas, utan inblandning av en CaS fas. Under den efterföljande RH processen så resulterande FeS tillsatsen i en ökad S aktivitet, som ledde till ökade reaktioner med både CaO i inneslutningarna och Ca under bildandet av en CaS fas. Därför så utgjordes majoriteten av inneslutningarna av en Al₂O₃-CaS fas. Därför sker
bildningen av CaS under LF-RH processen utan Ca tillsats baserat på termodynamiska drivkrafter av följande två reaktioner: i) reaktionen mellan CaO i inneslutningen och S samt ii) reaktionen mellan Ca och S. Beroende på bildningen av en CaS fas under RH behandlingen så var inneslutningarna i ett stål med en hög svavelhalt täckta av en CaS fas, vilken är svår att avskilja från stålet. Därför så kan gjutbarheten av stål med höga S halter försämras på grund av närvaron av CaS inneslutningar, även om ingen Ca behandling har skett.

Sammanfattningsvis så är slutsatsen att avskiljning av inneslutningar, bildandet och förändringar i sammansättningar ska beaktas för att kontrollera inneslutningssammansättningen i aluminiumdesoxiderade stål. Dessutom så är element som Al och S, viktiga att följa upp för att följa upp för att kontrollera förändringen av inneslutningar under skänkbehandlingsprocesser.

**Nyckelord:** icke-metalliska inneslutningar; skänkugn; RH; termodynamik; kontaktvinkel; Al₂O₃; MgO·Al₂O₃ spineller; kalciumaluminater; CaS.
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Finally, I extend my warmest thanks to my wife Tomoko and my daughter Yuri for their love, encouragement, and understanding.

Takanori Yoshioka
Stockholm, June 2018
Supplements

Supplement I:
Factors to determine inclusion compositions in molten steel during the secondary refining process of case-hardening steel

Supplement II:
Study of formation behavior of CaO-Al$_2$O$_3$ inclusions in steel melts during an LF process

Supplement III:
The effect of a high Al content on the variation of the total oxygen content in the steel melt during a secondary refining process

Supplement IV:
Mechanism of a CaS formation in an Al-killed high-S containing steel during a secondary refining process without a Ca-treatment

Supplement V:
The effect of a sulfur addition on the formation and behavior of CaS inclusions during a secondary refining process without using a Ca-treatment

Contribution to the supplements:
1. Literature review, experimental work, thermodynamic calculations, major part of the writing.
2. Literature review, experimental work, thermodynamic calculations, major part of the writing.
3. Literature review, experimental work, thermodynamic calculations, major part of the writing.
4. Literature review, experimental work, thermodynamic calculations, major part of the writing.
5. Literature review, experimental work, thermodynamic calculations, major part of the writing.
**Part of the work presented at the conferences:**

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T. Yoshioka, K. Nakahata, T. Kawamura, Y. Ohba,
170th ISIJ meeting, Kyushu University, Fukuoka Japan, 16-18 September 2015.

“CaS Formation in Al-killed High-S Containing Steel during Ladle Treatment without Ca-treatment”
T. Yoshioka, Y. Shimamura, A. Karasev, Y. Ohba, P. Jönsson
173th ISIJ meeting, Tokyo Metropolitan University, Tokyo Japan, 15-17 March 2017.

“The Influence of Aluminum Concentration on the Formation of CaO-Al$_2$O$_3$ Inclusions in a Steel Melt during an LF Process”
T. Yoshioka, T. Ideguchi, A. Karasev, Y. Ohba, P. G. Jönsson
3rd International Conference on Science and Technology of Ironmaking and Steelmaking (STIS-2017), Kanpur India, 11-13 December 2017.

“The Effect of a Sulfur Addition on the Formation and Behavior of CaS Inclusions During a Secondary Refining Process Without Using a Ca-Treatment”
T. Yoshioka, Y. Shimamura, A. Karasev, Y. Ohba, P. G. Jönsson
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Chapter 1 Introduction

1.1 Research background

The demand for high cleanliness steels has increased not only to obtain improved material properties, but also for a higher productivity in the manufacturing processes.[1-4] There is no specific and prevalent definition for the term “High cleanliness steel”, because prerequisites to be recognized as a clean steel can vary with the application.[5-7] Furthermore, the prerequisites have been described as “moving targets” since they can also vary depending on the quality requirements for final products.[1] However, the steel cleanliness can be evaluated by the characteristics of non-metallic inclusions in the steel melts or the products in any case.[2,5,8]

The number of inclusions is an important factor of the cleanliness.[5,9-11] Regarding the measurement of inclusion number, the most common method applied in steel mills is the total oxygen (T.O) measurement.[2,4-11] The T.O value roughly indicates how many inclusions that exist in the steel, since the amount of soluble oxygen in Al-killed steels cannot change to a large degree.[5] In practice, the T.O value of a steel sample is measured using LECO total oxygen analysis or PDA total oxygen analysis methods.[2,8] Figure 1-1 shows an example of the relationship between the T.O content and the fatigue life of bearing steels.[4]

![Figure 1-1. Relationship between the fatigue life and T.O content for bearing steels.](image-url)
Today, a novel technology has been developed to control the T.O content to a level of 5 ppm in a final product. Generally, a high reliability of steel products can be ensured with the presence of fewer inclusions. During steel refining processes, the number of inclusions can be decreased by the removal of inclusions from the steel melt. It is clear that the inclusion composition strongly influences the removability of inclusions, because it affects the interfacial property between an inclusion and the steel melt. The number of inclusions can also be increased by reoxidation of a steel melt. The inclusion composition generated by reoxidation is the Al$_2$O$_3$ phase, which is the same as the primary deoxidation product when a secondary refining process starts in an Al-killed steel. The inclusion number can also increase by slag entrapment. In this case, the inclusion compositions correspond to the slag composition.

It has been reported that the maximum size of inclusions in the steel product can have a significant impact on the performance. It can be recognized in Figure 1 that there are large deviations in the fatigue life of the steel products, even when they have the same amount of T.O. These deviations can be understood by the differences in the maximum size of inclusions. Therefore, the maximum inclusion size should be controlled so that it is as small as possible to ensure a high reliability of a steel product. In an actual mass production scale, these large-size inclusions are inspected using cast steel with off-line inspection methods, such as extreme value distribution and ultra-sonic testing methods. Monnot et al. studied the relationship between the inclusion compositions and their harmful effect on the fatigue life of a bearing steel. As shown in their study, CaO-Al$_2$O$_3$ inclusions are known to exist in large sizes, so these inclusions can seriously deteriorate the fatigue life. From this viewpoint, the inclusion compositions is an important factor to control to obtain the designed inclusion size in a steel product.

Nozzle clogging can cause deterioration in not only the productivity of a casting but also the quality of steel products. The accretion can be detached in large sizes, generating large-size inclusions flowing into the mold. These inclusions can be entrapped by a solidifying shell. Also, the detachment of the accretion can cause a large fluctuation of the meniscus level in the mold. This instability in the steel casting also increases the probability of entrapment of the mold flux into the cast melt. Thus, a prevention technique of the nozzle clogging is also important in order to obtain a high cleanliness steel product. Generally, solid oxides, such as Al$_2$O$_3$ and MgO-Al$_2$O$_3$, have a tendency to accrete to the inside wall of nozzles because of their high sinterabilities. CaS inclusions also exist as solid state in steel melts, so they can accelerate the growth of the accretion. In other words, liquid inclusions, namely liquid CaO-Al$_2$O$_3$ inclusions, are preferable to realize a stable casting. Besides, the liquid CaO-Al$_2$O$_3$ phase is well-known to be the thermodynamically most stable phase in Al-killed steel melts, even when the dissolved Ca content is as low as 1 or 2 ppm in a steel melt. Therefore,
it is important to understand the process of the inclusion evolution in steel melts during steelmaking processes.

In some steelmaking processes, inclusions are actively modified or controlled to desired compositions, instead of being removed. To achieve a stable casting, Ca-treatment is widely applied during the later part of the secondary refining processes.[3,21-23,29] The use of a Ca-treatment, which turns the oxide inclusions into the liquid CaO-Al2O3 phase, is one of the countermeasures to decrease the clogging tendency.[3,21-23,29] It is also applied in order to produce a steel with a hydrogen-induced cracking resistance. For this steel grade, MnS inclusions should be modified into spherical CaS inclusions by adjusting the Ca/S ratio.[33] Other specific grades need some type of inclusions to control the microstructure of steel matrix. This concept is called as “Oxide Metallurgy”.[34,35] These above-mentioned techniques, where inclusions are actively modified, need the presence of inclusions in the steels. However, they are not primarily aiming to obtain high cleanliness steels. Since the main purpose of the present study is to achieve much higher cleanliness of steel melts and products, these techniques are not subject to be further mentioned here.

1.2 Objectives of this work

As mentioned above, the inclusion compositions during refining processes are considerably connected to the cleanliness of steel melts and products. During the actual steelmaking processes, especially during a secondary refining process of Al-killed steels, steel melts are deoxidized with aluminum, and desulfurized with a high basicity slag to ensure that both the quality and the specification of the product are met. At this stage, the attention should be paid to the evolution of the inclusion composition from the primary deoxidation products, namely Al2O3, in order to control inclusions’ numbers and compositions thoroughly. So far, many researchers have carried out work focusing on the inclusion formation in Al-killed steel melts where both MgO·Al2O3 and the CaO-Al2O3 system inclusions were detected.[20,24,28-32,36-42] These researchers have discussed the inclusion evolutions in detail including the transformation of Al2O3 to CaO-Al2O3 system,[36] to MgO·Al2O3,[24,31,37] and to MgO inclusions.[28] In addition, MgO·Al2O3 inclusions can be transformed into CaO-MgO-Al2O3 inclusions.[29,30,32,38-42] However, it should be pointed out that the inclusion compositions are not determined only by the inclusion evolution mentioned above in an actual secondary refining process. Both the generation of newly forming inclusions[1,16] and the removal from the steel melt[12-15] also need to be taken into account to clarify the factors to control the inclusion compositions and to understand their effect on the cleanliness of steel melts. In addition, the inclusion evolution can be affected by the chemical compositions of steel melts, such as Al and S. However, few studies have so far been reported which considered all of these aspects indicated above.
From this viewpoint, this study has been carried out aiming to clarify the evolution process of inclusions detected in Al-killed steel melts during a secondary refining process. Figure 1-2 illustrates how the supplements are connected to this aim of the study. The secondary refining process in this study consists of a Ladle Furnace (LF), a Ruhrstahl Heraeus (RH) degassing station, and a vertical Continuous Casting (CC), which has been acknowledged as a suitable line to produce high cleanliness steels.[4,43] Steel and slag samples were taken from the ladle during the LF-RH process. The analyzed inclusion compositions were projected on CaO-MgO-Al₂O₃ or CaO-Al₂O₃-CaS diagrams, in order to understand the inclusion evolutions during the process. The factors that determine the inclusion compositions in actual secondary refining processes were investigated with respect to the compositions change, the generation of newly formed inclusions, and the removal from steel melts in supplements 1 and 2. The effects of a high Al concentration on the inclusions’ compositions and their removability from a steel melt were investigated in supplements 2 and 3. Also, the effects of the S concentration on the inclusion evolution and nozzle clogging behavior were discussed in supplements 4 and 5. The overview of the objectives, the approaches and parameters being studied in the supplements is summarized in Table 1-1.

**Figure 1-2.** A schematic overview of the relationship between the aim of this study and the supplements in this study.
Table 1-1. Overview of the supplements in this study.

<table>
<thead>
<tr>
<th>Study</th>
<th>Objective</th>
<th>Approach</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>· Inclusion compositions in a case-hardening steel melt during a secondary refining process</td>
<td>· Clarifying the determining factors of inclusion compositions during an actual secondary refining process</td>
<td>· Generation, evolution, and removal behavior of inclusions · Steel, slag and inclusion compositions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Analysis of the variation of the inclusion compositions</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Calculation of stability diagrams of inclusion phases</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>· Formation behavior of CaO-Al$_2$O$_3$ inclusions in steel melts</td>
<td>· Effects of slag entrapment and inclusion evolution on determining inclusion compositions in steel melts during actual secondary refining processes</td>
<td>· Generation, evolution, and removal behavior of inclusions · Steel, slag and inclusion compositions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Comparing the inclusion compositions between low and high Al content steel melts</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Calculation of stability diagrams of inclusion phases</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>· Inclusion compositions in a high Al containing steel melt during a secondary refining process</td>
<td>· Effect of a high Al content of the variations of inclusion compositions and total O contents in a steel melt</td>
<td>· Evolution, and removal behavior of inclusions · Steel, slag and inclusion compositions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Analysis of the variation of the inclusion compositions</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Investigation of the morphology of inclusions</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>· Calculation of stability diagrams of inclusion phases</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Analysis of the variation of inclusions and driving forces of inclusion evolution</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>· Inclusion compositions in an Al-killed high-S containing steel melt during a secondary refining process</td>
<td>· Formation mechanism of CaS inclusions and its role in the variation of inclusion compositions in a steel melt</td>
<td>· Steel and inclusion compositions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Analysis of the variation of the inclusion compositions</td>
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<tr>
<td></td>
<td></td>
<td>· Calculation of stability diagrams of inclusion phases</td>
<td></td>
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<tr>
<td>5</td>
<td>· Formation and behavior of CaS inclusions in steel melts during a secondary refining process</td>
<td>· Elucidating the formation mechanism and the behavior of CaS inclusions in steel melts</td>
<td>· Steel and inclusion compositions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Comparing the inclusion compositions between low and high S content steel melts</td>
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<td></td>
<td></td>
<td>· Investigation of the morphology of inclusions and the accretion of a tundish nozzle</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Calculation of stability diagrams of inclusion phases</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 2 Methodology

2.1 Production procedure

The procedure of the melt shop for this study is as follows: The process begins with scrap melting in a 150 t electric arc furnace (EAF) followed by the secondary refining process using an LF and an RH vacuum degassing. Finally, the steel melt is cast by means of a vertical CC to produce blooms. The ladle is lined by MgO-C bricks and it is equipped with two porous plugs to enhance the homogenization of the composition and temperature of the steel melt. The LF practice mainly aims at deoxidation and a precise control of the composition and temperature of the steel melts. To promote the deoxidation and desulfurization, a slag with a relatively high basicity is applied for the refining process, which has the composition saturated both with CaO and MgO phases. In the RH practice, degassing is the main purpose to decrease the N and H contents in steel melts by lowering the partial pressures of the gases so that the following reactions take place, along with further deoxidation and separation of non-metallic inclusions.

\[
\begin{align*}
    N &= \frac{1}{2} N_2(g) \\
    H &= \frac{1}{2} H_2(g)
\end{align*}
\]  

(1) (2)

2.2 Sampling and analysis of steels

Steel samples were obtained during the LF refining and RH treatment processes. Several liquid steel samples were taken at designated timings for each experiment. Regarding the sample names, when a sample was taken at 15 min after starting the LF practice, it was indicated as a “LF 15” sample. The same way was applied to the samples taken during the RH process. The compositions of inclusions on the cross-section of each steel sample were determined using a scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) analyzer.

Sulfur in the inclusions was considered to be present as a MnS phase, while the rest of sulfur was present as a CaS phase. Then, the rest of the Ca content was considered to be present as a CaO phase. The morphology and the elemental distributions in some inclusions were also investigated using the SEM/EDS analyzer. The spark discharge atomic emission spectrometric analysis was applied for the measurement of the Al content. The concentrations of Ca and Mg in steel samples were measured by the inductively coupled plasma mass spectrometry method. Also, the T.O contents were measured using inert gas fusion-infrared absorptiometry.
Chapter 3 Result and Discussion

3.1 Factors to determine inclusion compositions in actual secondary refining processes

This experiment was carried out during the production of a case-hardening steel. The steel composition in the product is shown in Table 3-1. Liquid steel samples were taken at 15, 30, and 45 min from the start of the LF process, which were indicated as “LF 15”, “LF 30” and “LF 45”, respectively. In addition, a steel sample was taken after 20 min treatment using the RH process, and it was indicated as “RH 20”. The scanning area of the inclusion detection and analysis was 100 mm². In this experiment, all inclusions larger than 1μm in diameter were subjected to the analysis, and their compositions were projected on a CaO-MgO-Al₂O₃ diagram.

Table 3-1. Chemical composition of the steel [mass%].

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.20</td>
<td>0.26</td>
<td>0.83</td>
<td>1.02</td>
<td>0.15</td>
</tr>
</tbody>
</table>

3.1.1 Variations of the steel and inclusion compositions

The variations of the Al, Mg and Ca contents are shown in Figure 3-1. Regarding the Al concentration, the increase during the RH treatment was due to an Al addition aiming at the compensation of Al consumption due to reoxidation during this process. The concentrations of Ca and the Mg in the LF 15 sample were 5.9 and 2.5 ppm, respectively. Thereafter, the Ca concentration increased to 6.5-7.9 ppm, while the Mg concentration slightly decreased to 0.9-1.6 ppm during the LF process. The Ca and Mg might be supplied through the reduction of the CaO and MgO phases in the slag by the Al addition or they might derive from the residuals in the ferroalloys. Finally, the Ca and Mg contents decreased to values below 2 ppm and below 1 ppm, respectively, at the end of the RH treatment. These decreases in the Ca and Mg contents were due to both vaporization and due to the removal of Ca- and Mg-containing inclusions. The T.O content was measured as 25 ppm during the LF process and it decreased to below 10 ppm after the RH treatment.

The variation of the inclusion compositions during the LF-RH process is shown in Figure 3-2. In the LF 15 sample, the inclusions mainly consisted of Al₂O₃ oxide, which was the deoxidation product formed due to the Al addition into a steel melt (Figure 3-2(a)). Subsequently, the inclusion compositions spread simultaneously to MgO·Al₂O₃ and CaO·Al₂O₃.
system (Figure 3-2(b)). At the end of the LF process (LF 45 sample), the inclusion compositions were positioned on a tie-line connecting the MgO·Al$_2$O$_3$ and liquid CaO-Al$_2$O$_3$-MgO phases (Figure 3-2(c)). At the end of the RH process, the inclusion compositions were located in the area between Al$_2$O$_3$ and CaO-Al$_2$O$_3$ system, while the MgO·Al$_2$O$_3$ inclusions disappeared (Figure 3-2(d)).

**Figure 3-1.** Variations of the contents of Al, Ca, and Mg in the melts during the LF-RH process.

**Figure 3-2.** Composition of inclusions at each stage of the sampling during the LF-RH process: (a) LF 15, (b) LF 30, (c) LF 45, and (d) RH 20.
The element mappings of the typical inclusions found in this study are shown in Figure 3-3. The inclusions consisted of a single phase of Al₂O₃ oxide were detected in the LF 15 sample (Figure 3-3(a)). In the LF 30 sample, three types of inclusions were observed: Al₂O₃, MgO·Al₂O₃, and CaO-Al₂O₃ type inclusions (Figure 3-3(b)). At the end of the LF process, the inclusions of the CaO-MgO-Al₂O₃ system with a MgO·Al₂O₃ core were observed in addition to the inclusion types detected in the LF 30 sample (Figure 3-3(c)). At the end of the RH process (RH 20 sample), the Al₂O₃ inclusions and the CaO-Al₂O₃ inclusions were detected (Figure 3-3(d)). These observation results correspond well both to the result described in Figure 3-2, and to the previously reported research results.[29,30,32,38-42]

Figure 3-3. Element mapping of the main components in typical inclusions found at different stages of the LF-RH process: (a) LF 15, (b) LF 30, (c) LF 45, and (d) RH 20.

3.1.2 Thermodynamic discussion

Thermodynamic calculations were carried out to discuss the variation of the inclusion compositions during the secondary refining process. In this study, the measured contents of Al, Ca, and Mg were considered in the calculations. This is the same approach which has been applied in other studies performed so far.[29,30,41] Additionally, the steel compositions shown in Table 3-1 were taken into account. Note that the effect of Mo on the activity coefficients of the other components was not considered owing to the lack of thermodynamic data.[28] The first- and second-order interaction parameters listed in Table 3-2 were considered in the following calculations.[46-51] The temperature assumed in the calculations was 1873 K by considering the actual operation condition. Based on the observation results shown in Figures 3-2 and 3-3, the
stability diagrams of the inclusion phases were drawn for the following three systems: (1) MgO-Al₂O₃, (2) CaO-Al₂O₃, and (3) CaO-MgO-Al₂O₃.

Table 3-2. First- (εᵢ) and second-order (rᵢ, rᵢⱼ, rᵢⱼₖ) interaction parameters of the main elements in the melt used in the present study (at 1873 K)*.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Al</th>
<th>Ca</th>
<th>Mg</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>-0.34</td>
<td>-0.096</td>
<td>-0.0156</td>
<td>0.014</td>
<td>-0.072</td>
<td>-0.002</td>
<td>-</td>
<td>-780⁴⁴⁸</td>
</tr>
<tr>
<td>Mg</td>
<td>-0.31</td>
<td>-0.096</td>
<td>-</td>
<td>0.022</td>
<td>-0.27</td>
<td>-</td>
<td>-</td>
<td>-430⁵¹</td>
</tr>
<tr>
<td>Al</td>
<td>0.091</td>
<td>0.056</td>
<td>-0.004</td>
<td>0.0096</td>
<td>0.043</td>
<td>-0.047</td>
<td>-</td>
<td>-1.98⁵⁰</td>
</tr>
<tr>
<td>O</td>
<td>-0.45</td>
<td>-0.131</td>
<td>-0.021</td>
<td>-0.052</td>
<td>-1.17⁴⁸⁰</td>
<td>-310⁴⁸⁸</td>
<td>-280⁵¹</td>
<td>-0.17</td>
</tr>
<tr>
<td>N</td>
<td>0.13</td>
<td>0.047</td>
<td>-0.02</td>
<td>-0.007</td>
<td>0.017⁴⁹</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*All data without notation are from ref. [46]

\[ r_{O}^{Al} = -0.01, \quad r_{Al}^{O} = 40, \quad r_{Al}^{AlO} = -0.0284, \quad r_{O}^{AlO} = 47.4^{[50]} \]

\[ r_{O}^{MgAl} = -150, \quad r_{O}^{CaAl} = 0, \quad r_{O}^{MgMg} = -230, \quad r_{Al}^{OAl} = -260^{[47]} \]

\[ r_{O}^{Ca} = -18000, \quad r_{Ca}^{O} = 650000, \quad r_{Ca}^{CaO} = -90000, \quad r_{O}^{CaO} = 520000^{[48]} \]

\[ r_{O}^{Mg} = -20000, \quad r_{Mg}^{O} = 350000, \quad r_{Mg}^{MgO} = -61000, \quad r_{O}^{MgO} = 462000^{[51]} \]

3.1.2.1 MgO-Al₂O₃ system

Equations (3) and (4) were employed to calculate the most stable phase in the MgO-Al₂O₃ system.[47] The MgO/MgO-Al₂O₃ boundary was drawn based on equation (3) by considering the activity data of \( a_{MgO} = 1 \) and \( a_{MgO\cdotAlO_3} = 0.80^{[52]} \). Likewise, the MgO-Al₃O₇/Al₂O₃ boundary was drawn based on equation (4) by considering the activity data of \( a_{MgO\cdotAlO_3} = 0.47 \) and \( a_{AlO_3} = 1^{[52]} \)

The activities of the components in a steel melt were relative to a dilute solution of one mass % standard state, and the activities of the oxides were relative to pure solids. These standard states are also applied to the following calculations throughout this study.

\[ 4\text{MgO(s) + 2Al} = \text{MgO} \cdot \text{Al}_2\text{O}_3(s) + 3\text{Mg} \quad \log K_3 = -23.856 + 32 280/T \] (3)

\[ 3\text{MgO} \cdot \text{Al}_2\text{O}_3(s) + 2\text{Al} = 4\text{Al}_2\text{O}_3(s) + 3\text{Mg} \quad \log K_4 = -26.274 + 27 950/T \] (4)

where K represents the equilibrium constant and T represents the temperature of the steel melt (K). The result is shown in Figure 3-4 with the plots of the measured Al and Mg contents in each steel sample. It is clear that the most stable phase of the inclusion phases in the steel melt is the
MgO∙Al₂O₃ phase when considering the MgO-Al₂O₃ system. This result is quite consistent with the observation results illustrated in Figures 3-2 and 3-3, since the MgO∙Al₂O₃ phase was the one detected in the LF 30 and LF 45 samples. Thus, the formation of the MgO∙Al₂O₃ phase is thermodynamically reasonable based on consideration of the present steel compositions.

Figure 3-4. Phase stability diagram of the MgO/MgO·Al₂O₃/Al₂O₃ system at 1873 K.

3.1.2.2 CaO-Al₂O₃ system

The method proposed by Taguchi et al. was applied to determine the most stable phase in the CaO-Al₂O₃ system. Equations (5) and (6) were employed in this calculation. Table 3-3 shows the activities of the CaO and Al₂O₃ phases at each phase boundary in the CaO-Al₂O₃ system, which were calculated with FactSage™ 7.1. These activity values were substituted to the following equations.

\[
\begin{align*}
\text{CaO(s)} &= \text{Ca} + \text{O} \quad \log K_5 = -3.29 - 7220 / T \\
\text{Al}_2\text{O}_3(s) &= 2\text{Al} + 3\text{O} \quad \log K_6 = 11.62 - 45300 / T
\end{align*}
\]

(5)  
(6)

Table 3-3. Activities of CaO and Al₂O₃ in various boundaries of the CaO-Al₂O₃ system at 1873 K.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>(a_{\text{CaO}})</th>
<th>(a_{\text{Al}_2\text{O}_3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2\text{O}_3/\text{CaO-6Al}_2\text{O}_3)</td>
<td>0.0049</td>
<td>1.0</td>
</tr>
<tr>
<td>(\text{CaO-6Al}_2\text{O}_3/\text{CaO-2Al}_2\text{O}_3)</td>
<td>0.010</td>
<td>0.88</td>
</tr>
<tr>
<td>(\text{CaO-2Al}_2\text{O}_3/\text{CaO-Al}_2\text{O}_3)</td>
<td>0.10</td>
<td>0.29</td>
</tr>
<tr>
<td>(\text{CaO-Al}_2\text{O}_3/\text{CaO-Al}_2\text{O}_3\text{liq})</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>(\text{CaO-Al}_2\text{O}_3\text{liq}/\text{CaO})</td>
<td>0.99</td>
<td>0.0089</td>
</tr>
</tbody>
</table>
The result is shown in Figure 3-5, which shows plots of the measured Al and Ca contents in each steel sample. The most stable phase in the CaO-Al$_2$O$_3$ system was calculated as the CaO-Al$_2$O$_{3\text{liq}}$ phase, which agreed to the phases detected in the LF 45 and RH 20 samples. Thus, the formation of CaO-Al$_2$O$_{3\text{liq}}$ inclusions is also thermodynamically reasonable based on the steel compositions.

Figure 3-5. Phase stability diagram of various CaO-Al$_2$O$_3$ phases at 1873 K. (Al$_2$O$_3$ is abbreviated as A, and CaO as C.)

Note that the inclusion compositions should converge to a single phase, when considering the phase rule. However, multiple phases were observed in the obtained samples. This result may imply that a non-equilibrium state was established in the steel melt. For this point, some kinetic conditions or some differences in the evolution procedures among Al$_2$O$_3$ → MgO-Al$_2$O$_3$, Al$_2$O$_3$ → CaO-Al$_2$O$_3$ system, and MgO-Al$_2$O$_3$ → CaO-Al$_2$O$_3$ system can be thought to be the reasons for the non-equilibrium state.

3.1.2.3 CaO-MgO-Al$_2$O$_3$ system

As discussed above, the coexistence of different inclusion phases may imply that a temporary non-equilibrium state existed. To determine the thermodynamically most stable phase in the three phases of (1) Al$_2$O$_3$, (2) MgO-Al$_2$O$_3$ system, and (3) CaO-Al$_2$O$_3$ system, a stability diagram was calculated for the CaO-MgO-Al$_2$O$_3$ system, according to the method performed by Deng et al.\cite{30} In this calculation, the CaO-Al$_2$O$_3$ phase was chosen as the representative phase of the CaO-Al$_2$O$_3$ system. The Al$_2$O$_3$/MgO-Al$_2$O$_3$ boundary was calculated by using equation (4). The Al$_2$O$_3$/CaO-Al$_2$O$_3$ boundary was drawn using equation (8), which was derived by combining equations (5), (6), and (7).\cite{54} The MgO-Al$_2$O$_3$/CaO-Al$_2$O$_3$ boundary was obtained by using equation (11), which was derived by combining equations (5), (7), (9)\cite{51} and (10).\cite{52} In this calculation, the activities of all the oxide phases were assumed as unity. Furthermore, the Al content was taken as 0.035 mass% by considering the actual concentration in this experiment.
\[
\text{CaO} \cdot \text{Al}_2\text{O}_3(s) = \text{CaO}(s) + \text{Al}_2\text{O}_3(s) \quad \Delta G_7^0 = 17910 + 17.38T \quad [\text{J} \cdot \text{mol}^{-1}]
\] (7)

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3(s) + 2\text{Al} = 4\text{Al}_2\text{O}_3(s) + 3\text{Ca} \quad \Delta G_8^0 = -398934 + 463.64T \quad [\text{J} \cdot \text{mol}^{-1}]
\] (8)

\[
\text{MgO}(s) = \text{Mg} + \text{O} \quad \log K_9 = -4.28 - 4700/T
\] (9)

\[
\text{MgO} \cdot \text{Al}_2\text{O}_3(s) = \text{MgO}(s) + \text{Al}_2\text{O}_3(s) \quad \Delta G_{10}^0 = 20682 + 11.57T \quad [\text{J} \cdot \text{mol}^{-1}]
\] (10)

\[
\text{MgO} \cdot \text{Al}_2\text{O}_3(s) + \text{Ca} = \text{CaO} \cdot \text{Al}_2\text{O}_3(s) + \text{Mg} \quad \log K_{11} = -0.689 - 2360/T
\] (11)

**Figure 3-6** presents the calculated stability diagram of the \(\text{CaO-MgO-Al}_2\text{O}_3\) system with the plots of the measured Mg and Ca contents in each steel sample. This figure illustrates that the most thermodynamically stable phase is the \(\text{CaO} \cdot \text{Al}_2\text{O}_3\) phase throughout the LF-RH processes. A number of reports point that the most stable phase of inclusions in an Al-killed steel melt is the \(\text{CaO} \cdot \text{Al}_2\text{O}_3\) system when the steel melt contains more than 1 ppm of Ca.\(^{[31,32,37]}\) The steel samples in this research contained approximately 6 ppm of Ca during the LF process and 2 ppm of Ca at the end of the RH process. Thus, the calculation result in this study is in line with the results of previous studies.\(^{[31,32,37]}\)

![Figure 3-6](image)

**Figure 3-6.** Phase stability diagram of \(\text{Al}_2\text{O}_3/\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{CaO} \cdot \text{Al}_2\text{O}_3\) in the steel melt.

As discussed from the equilibrium viewpoint, the variation of the inclusion compositions in an Al-killed steel melt is expected to be as follows. The inclusion compositions mainly consist of the \(\text{Al}_2\text{O}_3\) phase at the initial stage of the LF process, because of the primary deoxidation by an Al addition. Thereafter, the \(\text{Al}_2\text{O}_3\) inclusions evolve toward both the MgO-\(\text{Al}_2\text{O}_3\) phase and the CaO-\(\text{Al}_2\text{O}_3\) phase under the non-equilibrium states that exist in the following period of the LF refining. The CaO-\(\text{Al}_2\text{O}_3\) inclusions detected at the end of the LF and RH processes were the thermodynamically most stable phases in the \(\text{CaO-MgO-Al}_2\text{O}_3\) system. As for the multiphase inclusion with a MgO-\(\text{Al}_2\text{O}_3\) core surrounded by the CaO-\(\text{Al}_2\text{O}_3\) system found in Figure 3-3(c2),
the MgO·Al₂O₃ core is thought to become smaller and smaller as the refining time progresses owing to the thermodynamic instability.

The thermodynamic discussion above cannot explain the existence of the Al₂O₃ inclusions detected in the RH 20 sample. This implies that those Al₂O₃ inclusions were generated in a manner which is different from the endogenous composition evolution. This reason will be discussed later.

3.1.3 Factors to determine the inclusion composition

It is generally recognized that the factors influencing the inclusion compositions in a steel melt during secondary refining processes can include various phenomena such as generation,[4,7] removal,[12-15] and composition evolution toward a thermodynamic stable phase.[24,29-32,36-42] The following discussion focuses on the relationship between each phenomenon and on the variation in the inclusion compositions during the secondary refining processes, by considering the thermodynamic calculation results.

3.1.3.1 During the LF refining process

Regarding the formation behavior of inclusions during the LF process, one possible cause is the local oxygen supply from the slag or the atmosphere. This, in turn, creates Al₂O₃ via some other phases such as FeO, MnO, and SiO₂.[17,55] However, the inclusion compositions detected in the LF 45 sample were not located at the Al₂O₃ corner in the CaO-MgO-Al₂O₃ ternary diagram. Therefore, the local oxygen supply is considered not to have a significant influence in this experiment. Another possibility of the inclusion formation can be slag entrapment caused by gas stirring. Despite this possibility, the inclusion compositions were not located in the CaO and MgO double-saturation region, which is the present slag composition, at the LF initial stage (in the LF 15 sample). Thus, it can be understood that the inclusion compositions during the LF refining were affected neither by the local oxygen supply nor by the slag entrapment.

As mentioned before, the activity of the Al₂O₃ phase in the slag in the CaO and MgO double-saturation compositions is 0.005, which was calculated using FactSage™ 7.1. With this activity value of the Al₂O₃ phase, the O content in the steel melt in this study can be calculated as 2 ppm by using equation (6). Therefore, the O content was considered to have an almost constant value of 2 ppm throughout the LF process. Moreover, the T.O contents in the steel samples were mostly kept constant, as explained earlier. This fact shows that the amount of the oxide inclusions in the steel melt was not changed largely during the LF refining. This information indicates that the removal of inclusions from the steel melt did not happen extensively during this experiment.
According to the descriptions above, it can be concluded here that the generation and removal of inclusions did not have considerable influence on the inclusion compositions in the steel melt during the LF process. It should be noted that the decrease in the Al content during the period of the LF refining seen in Figure 3-1 is an indication of the generation of Al$_2$O$_3$ inclusions.$^{[4,16]}$ It can be considered that the generated Al$_2$O$_3$ inclusions were mostly absorbed by the slag phase at the slag/metal interface.

3.1.3.2 During the RH treatment process

As Figure 3-2 indicates, the inclusion compositions changed from the tie-line connecting the areas of MgO·Al$_2$O$_3$ and CaO·Al$_2$O$_3$-MgO$_{liq}$ to the area between Al$_2$O$_3$ and the CaO·Al$_2$O$_3$ system during the RH process. The effects of the generation and removal on the inclusion compositions in the steel melt were considered to understand this composition change.

The decrease in the T.O content during this process (mentioned in section 3.1.1) clearly indicated the occurrence of the inclusion removal from the steel melt. On this point, many researchers$^{[15,56,57]}$ have reported that nonwet particles ($\theta > 90^\circ$) against a liquid phase easily attach to gas bubbles and are more likely to be removed. From this viewpoint, the contact angles as well as the interfacial energies of the inclusion phases are listed in Table 3-4. Based on this information, the MgO·Al$_2$O$_3$ phase does not wet to a steel melt, so the MgO·Al$_2$O$_3$ inclusions are easy to remove from a steel melt. However the CaO·Al$_2$O$_3$$_{liq}$ phase does wet to a steel melt. This means that the CaO·Al$_2$O$_3$$_{liq}$ inclusions tend to remain in a steel melt. According to the calculation result in section 3.1.2.3, the MgO·Al$_2$O$_3$ phase existed in a transient stage toward the CaO·Al$_2$O$_3$ system during the RH treatment. Therefore, it can be understood that MgO·Al$_2$O$_3$ inclusions not only varied its composition toward the CaO·Al$_2$O$_3$ system in the steel melt, but also that they were removed from the steel melt during the RH treatment. Meanwhile, the CaO·Al$_2$O$_3$ system inclusions remained in the steel melt owing to that they had a high wettability to a steel melt.

Table 3-4. Interfacial energies and contact angles of various oxides.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Interfacial energy / mJ·m$^{-2}$</th>
<th>Contact angle / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ (solid)</td>
<td>2 050 (at 1873 K)$^{[58]}$</td>
<td>140 (at 1873 K)$^{[58]}$</td>
</tr>
<tr>
<td>CaO·Al$_2$O$_3$ (liquid)</td>
<td>1 600 (at 1853 K)$^{[59]}$</td>
<td>54-65 (at 1873 K)$^{[27]}$</td>
</tr>
<tr>
<td>MgO·Al$_2$O$_3$ (solid)</td>
<td>3 700 (at 1823 K)$^{[60]}$</td>
<td>134 (at 1823 K)$^{[60]}$</td>
</tr>
</tbody>
</table>
Al₂O₃ inclusions were also detected in the RH 20 sample. According to the thermodynamic consideration in section 3.1.2, the Al₂O₃ phase is not thermodynamically stable at this stage of the process for the investigated steel compositions. It has been reported that there is a certain probability of oxygen supply from the slag and/or the refractory materials to a steel melt during the RH treatment. Furthermore, it has been confirmed that this oxygen supply deteriorates the decreasing rate of the T.O content by generating Al₂O₃ inclusions. Hence, the detected Al₂O₃ inclusions are thought to be generated during the RH treatment. The frequency of the removal of the MgO·Al₂O₃ inclusions was higher than the generation rate of the Al₂O₃ inclusions during the RH treatment. This likely contributed to the remarkable decrease in the T.O content during this stage of the process.

3.1.4 Evolution mechanism of the inclusion compositions

According to the experimental results and the discussions, the variation mechanism of the inclusion compositions in a steel melt can be summarized to take place in the following three steps:

1) At the initial stage of LF refining, the inclusion compositions start at the location of the Al₂O₃ phase. This is the deoxidation product by an Al addition into a steel melt.

2) During the stage between the middle and the end of the LF refining, the Al₂O₃ inclusions evolve simultaneously toward a MgO·Al₂O₃ phase and a CaO·Al₂O₃(liq) phase. This evolution progresses with respect to the thermodynamic driving forces. The CaO·Al₂O₃(liq) phases is confirmed to be the most stable phase in the CaO·Al₂O₃-MgO system. Therefore, MgO·Al₂O₃ inclusions can evolve to CaO·Al₂O₃(liq) inclusions. Owing to this composition evolution, the inclusion compositions are distributed on a tie-line connecting the areas of MgO·Al₂O₃ and CaO·Al₂O₃-MgO(liq).

3) During the RH treatment, the MgO·Al₂O₃ inclusions are likely to be removed owing to the high contact angle against a steel melt. As for the multiphase inclusion with a MgO·Al₂O₃ core surrounded by the CaO·Al₂O₃(liq) phase, the MgO·Al₂O₃ core becomes smaller because of the thermodynamic instability. The CaO·Al₂O₃(liq) inclusions have low contact angles, so they tend to remain in a steel melt. In addition, Al₂O₃ inclusions are generated during the RH treatment because of local oxygen supply. Thus, three phenomena including the removal of MgO·Al₂O₃ inclusions, remaining of CaO·Al₂O₃(liq) inclusions, and the generation of Al₂O₃ inclusions determine the inclusion evolution in a steel melt during the RH treatment.
3.2 Effect of a high Al concentration on the inclusion compositions and its effect on the cleanliness of steel melts

High-Al containing steels, such as nitriding steels and high-Al TRIP steels, are well-known as steel grades with quite low T.O contents (~ 3 ppm). However, the reason for the low T.O contents has not been thoroughly clarified. From this viewpoint, this study focused on both the variations of T.O contents and the inclusion evolution in a high-Al containing steel melt during the LF-RH process. The target steel for this study contained 0.46%C-0.18%Si-0.54%Mn-1.6%Cr-1.1%Al. In this experiment, three liquid steel samples were obtained after undergoing the LF process for 15, 30, and 45 min. These samples were named “LF 15”, “LF 30”, and “LF 45”, respectively. In addition, one liquid steel sample was obtained at the end of the RH process (35 min), named “RH 35”. More than 10 inclusions larger than 2 μm were detected and analyzed for each sample.

3.2.1 Variations of the steel and inclusion compositions

Figure 3-7 shows the composition variations of the steel melt during the LF and RH processes. The Al content was adjusted to approximately 1.1 mass% after the initial deoxidation of the steel melt during the LF process. The T.O content in the steel melt decreased throughout the processes. It eventually reached a value of 5.7 ppm at the end of LF process and 4.5 ppm at the end of the RH process. The T.O contents during the LF process were extraordinary low, which will be discussed in detail later. The total Ca (T.Ca) and total Mg (T.Mg) contents in the steel melt increased to 5.5 ppm and 11.0 ppm, respectively, after the LF process progressed for 30 min. These enhancements are due to both the chemical reduction of CaO and MgO phases in the slag, and the residuals contained in the ferroalloys. The decrease in the T.Ca and T.Mg contents in the later part of the LF process can be explained by the removal of Ca- and/or Mg-containing inclusions. The decrease in the T.Ca and T.Mg contents during the RH process can be explained both by inclusion removal and by vaporization of Ca and Mg into the RH vacuum chamber, as mentioned in section 3.1.1.

The variations of the number-averaged compositions of the inclusions during the processes are shown in Figure 3-8. Similar to the result described in section 3.1.1, the inclusion compositions consisted mostly of the Al₂O₃ phase after the LF process progressed for 15 min. Thereafter, the Al₂O₃ contents of the inclusions decreased, whereas the MgO contents increased as the LF process progressed. This composition variation likely represents a reduction of the Al₂O₃ phase in inclusions by Mg, which led to the formation of MgO-Al₂O₃ inclusions similar to what have been reported in previous studies. Meanwhile, the CaO contents in inclusions remained quite low throughout the LF-RH process. This feature is quite unique when one considers the results in other studies. The increased Al₂O₃ content in the inclusions in
the RH 35 sample was due to both the generation of Al\(_2\)O\(_3\) and the removal of inclusions which contained other phases. The CaS phase in the inclusions was thought to be formed by the reaction between Ca and S, since the activity of CaO in inclusions is seemingly quite low considering the CaO contents during the whole process.\(^{[36]}\) This formation behavior of the CaS phase will be further discussed in section 3.3.2.

![Figure 3-7](image)

**Figure 3-7.** Variations of the total contents of Al, O, Ca, and Mg in the melts during the LF-RH process.

![Figure 3-8](image)

**Figure 3-8.** Variations of the average compositions of inclusions at each stage of the LF-RH process.

The inclusion compositions detected in each sample are projected on CaO-MgO-Al\(_2\)O\(_3\) diagrams, as shown in **Figure 3-9**. The open circle in each figure corresponds to the number-averaged composition at each stage. In the LF 15 sample, the inclusion compositions are located at the Al\(_2\)O\(_3\) phase. Thereafter, they spread toward an MgO-Al\(_2\)O\(_3\) phase after the LF process.
progressed for 30 min. CaO-Al\textsubscript{2}O\textsubscript{3}\textsubscript{liq} inclusions (CaO content = 36\% - 58\% at 1873 K\textsuperscript{64}) were not detected throughout the refining process. As mentioned before, this result is not in line with previous results for other steel grades.\textsuperscript{29,30,32,38-42} The present experimental result also supports the consideration mentioned in section 3.1.3.1, where the detected inclusions in this study were not greatly influenced by slag entrapment.

![Diagram](image1)

**Figure 3-9.** Composition of inclusions at each stage of the sampling during the LF-RH process: (a) LF 15, (b) LF 30, (c) LF 45, and (d) RH 35.

Elemental mapping results for the typical inclusions observed in each sample are shown in **Figure 3-10.** The MnS phase in the inclusions are thought to be formed during and/or after the solidification of the steel samples.\textsuperscript{7} In the LF 15 sample, the oxide phases in the inclusions consisted mostly of the pure Al\textsubscript{2}O\textsubscript{3} phase (Figure 3-10(a)). In the LF 30, LF 45, and RH 35 samples, an MgO·Al\textsubscript{2}O\textsubscript{3} phase was identified in the inclusions. Furthermore, the CaO contents in the inclusions were consistently low (Figure 3-10(b) to (d)). These observed results agree with the inclusion composition variations shown in Figure 3-9. In addition, some of the inclusions were surrounded by an AlN phase (Figure 3-10(c) and (d)). Inclusions which consist only of the AlN phase were also observed in the high-Al steel samples.
Figure 3-10. Element mapping of the main components in typical inclusions found at different stages of the LF-RH process: (a) LF 15, (b) LF 30, (c) LF 45, and (d) RH 35.

3.2.2 Thermodynamic discussion

MgO·Al₂O₃ and CaO·Al₂O₃ phases are known to be thermodynamically more stable than the Al₂O₃ phase in Al-killed steel melts in reduction refining processes. In the present study, the MgO·Al₂O₃ phase was detected in inclusions similar to previously published results. However, the CaO contents in the inclusions in the steel melts were extraordinarily low throughout the processes. Moreover, an AlN phase was also observed. Considering the phases observed in the inclusions shown in Figures 3-8 to 3-10, the following thermodynamic calculations were carried out. First, the stage of the AlN formation in the steel melt during the refining process was specified by illustrating a stability diagram of the AlN phase. Thereafter, the stability diagrams of the (1) MgO·Al₂O₃ and (2) CaO·Al₂O₃ systems were drawn in order to discuss the inclusion evolution in this steel grade. Lastly, a modification of the Al₂O₃ phase into a CaO·Al₂O₃ system was discussed from a thermodynamic viewpoint.

3.2.2.1 Calculation of the Ca and Mg contents in the steel melt

Yang et al. studied the behavior of the CaS formation in Ca-treated steel melts. Specifically, they discussed the formation mechanism using the calculated Ca content, since the measured Ca value includes both the Ca and insoluble Ca (Ca₉insol) contents. Following their practice, the Ca and Mg contents in this study were calculated in the manner described below.

First, equation (6) was used to calculate the O content in a steel melt. The activity of the Al₂O₃ phase in the slag was set as 0.005, as mentioned in section 3.1.3.1. Thereafter, the insoluble O
content \((O_{\text{insol}})\) at each sampling step was calculated by subtracting the \(O\) content from the measured T.O content in the melt, as expressed in equation (12):

\[
O_{\text{insol}} = \text{T.O} - O
\]

(12)

By assuming that the inclusion compositions in the steel melts are composed of the quaternary system of \(\text{CaO-}\text{MgO-}\text{Al}_2\text{O}_3\text{-CaS}\) shown in Figure 3-8, the \(\text{Ca}_{\text{insol}}\) and insoluble \(\text{Mg} (\text{Mg}_{\text{insol}})\) contents were calculated by considering both the average inclusion compositions and the \(O_{\text{insol}}\) contents in a steel melt. This is expressed in equation (13):

\[
M_{\text{insol}} = \frac{\%M_{\text{inclusions}}}{\%O_{\text{inclusions}}} \cdot O_{\text{insol}} \quad (M = \text{Ca, Mg})
\]

(13)

Then, the \(\text{Ca}\) and \(\text{Mg}\) contents at each sampling step were calculated based on both the \(\text{Ca}_{\text{insol}}, \text{Mg}_{\text{insol}}\) contents and the T.Ca and T.Mg contents in a steel melt \((M = \text{T.M} - M_{\text{insol}})\). The calculation results are shown in **Table 3-5**. These calculation results were used in the following discussions. The effect of the steel compositions on the activity coefficients was considered by using the interaction parameters listed in Table 3-2. Note that although these calculated values could be affected by uncertainties with respect to both the T.O and the inclusion compositions (including the formation of \(\text{CaS}\) phase during solidification of the steel samples\([68,69]\)), they are believed to be more suitable than the measured total values when discussing variations in the inclusion compositions in the following sections.

**Table 3-5.** Contents of \(\text{Ca, and Mg}\) in the steel samples [ppm].

<table>
<thead>
<tr>
<th>Sample</th>
<th>T.Ca</th>
<th>T.Mg</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF 15</td>
<td>2.4</td>
<td>1.4</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>LF 30</td>
<td>5.5</td>
<td>11.0</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>LF 45</td>
<td>3.1</td>
<td>8.8</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>RH 35</td>
<td>1.5</td>
<td>1.1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

3.2.2.2 AlN formation

A thermodynamic consideration was carried out to identify the stage of the AlN formation. The formation of an AlN phase in a steel melt is expressed by equation (14):\([49]\)

\[
\text{Al} + \text{N} = \text{AlN(s)} \quad \Delta G^0_{14} = 303 \, 500 - 134.6T \quad [\text{J} \cdot \text{mol}^{-1}]
\]

(14)

In this calculation, the interaction parameters listed in Table 3-2 were taken into account. The activity of the AlN phase was set to unity. **Figure 3-11** shows the calculation result with a plot
of the measured Al and N contents in the LF 45 sample. According to this calculated result, the AlN phases detected in inclusions cannot be formed in this high-Al steel melts at the steelmaking temperatures. Therefore, they are thought to be formed during the cooling of the steel melts after sampling, where the temperature dropped below 1773 K. Thus, the calculation result indicates that the AlN phases were not involved in the inclusion evolution process during the refining processes. Therefore, the inclusion evolution in this high-Al steel grade can be further discussed based on information regarding the oxide phases observed in the inclusions (Figures 3-8 to 3-10). It is noteworthy here that an AlN phase can be formed during an LF process if the Al and/or N concentrations are higher than those in the present steel grade. In these cases, AlN phases are supposed to be formed on existing inclusions to reduce the interfacial energy between inclusions and the steel melt. This can delay inclusion evolution, since the AlN phase exists as a solid phase in steel melts.[29,30,39]

![Stability diagram of AlN phase at various temperatures ranging from 1773 K to 1873 K.](image)

**Figure 3-11.** Stability diagram of AlN phase at various temperatures ranging from 1773 K to 1873 K.

### 3.2.2.3 MgO-\(\text{Al}_2\text{O}_3\) system

The MgO/MgO-\(\text{Al}_2\text{O}_3\) boundary for this steel grade was drawn in the same manner as described in section 3.1.2.1. The calculated result is shown in **Figure 3-12** along with plots of the Al and Mg contents in each sample. Regarding the Al contents in the melts, note that the measured Al values were treated as the Al contents, since the T.O amounts in the steel melts were not large and the AlN phases seemed to be absent from the steel melts during the LF process, as discussed above. After the LF process progressed for 15 min, the stable phase was determined to be \(\text{Al}_2\text{O}_3\). Thereafter, it moved to the MgO-\(\text{Al}_2\text{O}_3\) phase during the latter part of the LF process due to the increased Mg content. At the end of the RH process (RH 35 min), the stable phase was calculated to be \(\text{Al}_2\text{O}_3\) owing to the decreased Mg content. This variation of the stable phase is quite consistent with the observed results shown in Figures 3-8 and 3-9.
3.2.2.4 CaO-Al₂O₃ system

The most stable phase in the CaO-Al₂O₃ system was determined following the same manner as described in section 3.1.2.2. **Figure 3-13** shows the calculated result along with plots of the Al and Ca contents at each sampling step. According to this figure, the thermodynamically stable phase in the CaO-Al₂O₃ system was determined to be the CaO·2Al₂O₃ phase throughout the whole LF-RH process in this steel grade. This result is quite different from those in other previously reported studies.[28-32,38-42] Many researchers have concluded that the CaO-Al₂O₃liq phase is the most stable phase in an Al-killed steel melt even when the steel melt contains only 1 or 2 ppm of Ca.[28-32,37] However, the present results point out that this does not apply to high Al containing steel grades.

![Phase stability diagram of the MgO/MgO·Al₂O₃/Al₂O₃ system at 1873 K.](image)

**Figure 3-12.** Phase stability diagram of the MgO/MgO·Al₂O₃/Al₂O₃ system at 1873 K.

![Phase stability diagram of various CaO-Al₂O₃ phases at 1873 K.](image)

**Figure 3-13.** Phase stability diagram of various CaO-Al₂O₃ phases at 1873 K. (Al₂O₃ is abbreviated as A, and CaO as C.)
3.2.2.5 Modification of the Al₂O₃ phase into a CaO-Al₂O₃ system

As indicated above, the stable phase of the inclusions in a high-Al steel melt can be different from that in other Al-killed steels. Here, the driving forces (ΔG) of the modification of an Al₂O₃ phase into a CaO-Al₂O₃ system in steel melts are compared between high-Al containing steels and in other ordinary Al-killed steels, whose Al contents are around 0.03%.[61] This reaction is expressed by equation (15), which was derived by combining equations (5) and (6). In this calculation, the Ca value was set to 3 ppm by considering the value at the end of the LF process (LF 45 min) in this plant experiment.

\[
\frac{1}{3} \text{Al}_2\text{O}_3(s) + \text{Ca} = \text{CaO(s)} + \frac{2}{3} \text{Al} \quad \Delta G_{15}^{\text{init}} = 150900 - 137.2T \quad [\text{J} \cdot \text{mol}^{-1}]
\]  

The calculated result is shown in Figure 3-14. As can be seen in this figure, the driving forces decrease as the Al concentration in the steel melt becomes high. In the present high-Al steel grade, the stable phase was determined to be the CaO·2Al₂O₃ phase.

![Figure 3-14. Comparison of the thermodynamic driving forces (ΔG) for an Al₂O₃ modification by Ca at 1873 K. (Al₂O₃ is abbreviated as A and CaO as C.)](image)

The CaO contents in inclusions detected in this experiment were generally lower than that of the CaO·2Al₂O₃ phase. Many researchers have proposed a process where the transformation of an Al₂O₃ phase to a CaO-Al₂O₃ system progresses from the outer layer of the inclusions.[30,36,38-41] In ordinary Al-killed steels, the outer layer can be transformed into a CaO-Al₂O₃(liq) phase, which may facilitate mass diffusion inside the inclusions, because it exists as a liquid phase in a steel melt. This may promote an inclusion evolution. On the other hand, in high Al steel melts, the CaO-Al₂O₃(liq) phase cannot be formed on inclusions as illustrated in Figure 3-13. Therefore, the inclusion evolution can probably be delayed in high-Al steel melts. This can be considered as one reason for the discordance of the CaO contents between the detected inclusion and in the calculated stable phase, namely CaO·2Al₂O₃. This discordance will be further discussed in the following section.
3.2.3 Effect of high Al contents on the T.O contents and the inclusion compositions

Thus far, two features have been confirmed in this experiment: low T.O contents during the LF process and low CaO contents in the inclusions. Table 3-6 lists the T.O contents at the end of the LF refining process in various steel grades. It is obvious that the T.O content in this high-Al steel grade was extraordinary low. Since the measured T.O value consists of both the O and $O_{\text{insol}}$ contents, the following discussion will elucidate which of these two dominates the low T.O contents in this high-Al steel.

**Table 3-6.** Comparison of total O contents at the end of the LF process with results from previous studies.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Process</th>
<th>time [min]</th>
<th>S [mass%]</th>
<th>Al [mass%]</th>
<th>T.O [mass%]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-Al steel</td>
<td>EAF-LF</td>
<td>45</td>
<td>0.005</td>
<td>1.1</td>
<td>5.7</td>
<td>Present work</td>
</tr>
<tr>
<td>Al-killed steel</td>
<td>BOF*-1-LF</td>
<td>-</td>
<td>0.001</td>
<td>0.036</td>
<td>11</td>
<td>[70]</td>
</tr>
<tr>
<td>Al-killed steel</td>
<td>BOF-LF</td>
<td>-</td>
<td>0.001</td>
<td>0.052</td>
<td>20</td>
<td>[42]</td>
</tr>
<tr>
<td>Al-killed steel (0.04%C)</td>
<td>BOF-LF</td>
<td>29</td>
<td>0.007</td>
<td>0.045</td>
<td>30</td>
<td>[29]</td>
</tr>
<tr>
<td>Al-killed steel (0.17%C)</td>
<td>BOF-CAS*-2-LF</td>
<td>45</td>
<td>0.004</td>
<td>0.053</td>
<td>18</td>
<td>[71]</td>
</tr>
<tr>
<td>Al-killed steel (0.56%C)</td>
<td>BOF-LF</td>
<td>-</td>
<td>0.012</td>
<td>0.022</td>
<td>18</td>
<td>[72]</td>
</tr>
<tr>
<td>High-C chromium steel</td>
<td>EAF-LF</td>
<td>-</td>
<td>-</td>
<td>0.030</td>
<td>10</td>
<td>[73]</td>
</tr>
<tr>
<td>High-C chromium steel</td>
<td>BOF-LF</td>
<td>-</td>
<td>0.003</td>
<td>0.024</td>
<td>12</td>
<td>[74]</td>
</tr>
</tbody>
</table>

*-1 Basic Oxygen Steelmaking, *-2 Composition Adjustment by Sealed argon bubbling

Figure 3-15 shows the calculated O contents as well as the calculated O activities ($a_O$) for various Al concentrations as obtained with equation (6). In this calculation, the activity of Al₂O₃ was set to 0.005 and the temperature was set to 1873 K based on the condition of the actual LF process. It is well-known that the O content in a steel melt reaches a minimum value at an Al concentration of approximately 0.1 %, while the O activity steadily decreases with increased Al concentrations. The O contents of the steel melt were calculated to be approximately 1 ppm after the LF process progressed for 15 min, and approximately 4 ppm after the LF process progressed for 30 min and at the end of the RH process based on the steel compositions. By comparing the T.O contents shown in Figure 3-7 and the calculated O contents, one can see that the low T.O contents in this high-Al steel grade are not due to low O contents, but rather due to the quite low O_{insol} contents in the steel melts during the refining process. This fact indicates that the removal of oxide inclusions during the LF process is efficient in the steel melts with such high Al contents.
Figure 3-15. Variation of the $O$ content and $O$ activity, $a_O$, in the liquid steel with various Al contents at 1873 K.

As described in section 3.1.3.2, the interfacial properties between the inclusions and a steel melt influence the inclusion removal tendency. A contact angle of 90° is the critical value that determines whether or not an inclusion can be removed smoothly.\cite{15,56,57} Figure 3-16 illustrates the contact angles for various CaO-Al$_2$O$_3$ phases as a function of the CaO content.\cite{27,75} Whereas the contact angles of inclusions in an ordinary Al-killed steel are below 90°, those in high-Al steels are greater than 90°. These high contact angles promote the removal of inclusions from a steel melt, which contributes to lowering the T.O content in the steel melt. In addition, this fast removal of inclusions can prevent inclusions from being transformed into the CaO-Al$_2$O$_3$ phase after a sufficient time, which is the thermodynamically stable phase. Thus, these two factors, namely the low thermodynamic driving force shown in section 3.2.2.5 and the fast removal of inclusions, can explain why the detected inclusions have much lower CaO contents than that in the thermodynamically stable phase.

Figure 3-16. Contact angles of various CaO-Al$_2$O$_3$ phases in a steel melt.\cite{27,75}
3.3 Effect of $S$ concentration on the inclusion compositions and its effect on the cleanliness of steel melts

In Al-killed steel melts, the inclusions are mainly oxides and sulfides such as CaS. These CaS inclusions are known to cause nozzle clogging.\cite{3,21-23,65,76-78} Nozzle clogging can deteriorate not only the castability of the steel melt, but also the steel cleanliness of the produced steel.\cite{3,21-24,65,76-78} From this standpoint, an experiment has been carried out to clarify the formation and behavior of CaS inclusions in Al-killed steel melts without using a Ca-treatment. The present steel grade used in this experiment contained 0.36%C-0.76%Si-1.33%Mn-0.18%Cr-0.055%S. Three steel samples were obtained after the LF process progressed for 15, 30, and 45 min, and these samples were named “LF 15”, “LF 30”, and “LF 45”, respectively. In addition, five steel samples were obtained at five-minute intervals during the RH treatment, which were named “RH 5”, “RH 10”, “RH 15”, “RH 20”, and “RH 25”, respectively. To study the variation of the inclusion compositions, inclusions larger than 3 μm detected in an area of 100 mm$^2$ on a polished surface were analyzed for each sample.

3.3.1 Variations of the steel and inclusion compositions

The variations of the measured Al, S, and Ca contents in the steel samples are shown in Figure 3-17. The Al content decreased continuously during the LF and RH processes, except during the initial stage of the RH process. This decrease in the Al content was found to be the same as described in section 3.1.1. The increased Al content after the RH process progressed for 10 min was due to the Al addition, which aimed at compensating for the Al consumption, as described in section 3.1.1. During the LF process, the S content steadily decreased because of the slag/metal reactions. During the RH process, the S content was accurately adjusted by an FeS addition, since the slag/metal reaction is not considerable in this stage. The T.Ca content in Figure 3-17 consists of both Ca and Ca$_{\text{insol}}$, as described in section 3.2.2.1. As can be seen in Figure 3-17, the T.Ca content in the steel melt increased from 9.4 ppm to 14 ppm during the LF process. Then, it decreased to 12 ppm and 5.1 ppm in the RH 10 and RH 25 samples, respectively. This decrease in the T.Ca content could be due to the vaporization of Ca into the vacuum phase and the removal of Ca-containing inclusions. The T.O contents were measured to be 32 ppm and 23 ppm in the LF 15 and LF 45 samples, respectively. In the following RH process, the T.O content decreased to 18 ppm and to 8.2 ppm after the RH process progressed for 10 min and 25 min, respectively.

Variations in the number-averaged inclusion compositions during the LF-RH process are shown in Figure 3-18. During the LF process, the Al$_2$O$_3$ content in the inclusions decreased, whereas the CaO content increased. This likely indicates the chemical reduction of the Al$_2$O$_3$ phase by Ca, forming CaO-Al$_2$O$_3$ inclusions.\cite{29-31,36,38-42} The CaS content was found to be higher than the CaO content in the inclusions in the LF 15 sample. Thereafter, the CaS content decreased
During the following LF process. After adding FeS (in the RH 10 sample), the CaS content increased and the CaO content decreased simultaneously. Thereafter, the CaS content slightly increased, while the Al₂O₃ content decreased. The MgO contents in the inclusions were relatively low and did not show large fluctuations throughout the LF-RH process.

![Figure 3-17](image1.png)

**Figure 3-17.** Variations of the contents of Al, S, and Ca in the melts during the LF-RH process.

![Figure 3-18](image2.png)

**Figure 3-18.** Variations of the average compositions of inclusions at each stage of the LF-RH process.

Focusing on the formation behavior of CaS inclusions, the inclusion composition variations observed in this experiment are projected in a CaO-Al₂O₃-CaS diagram, as shown in **Figure 3-19**. The circle mark in the figure represents the number-averaged inclusion composition at each sampling step. As described above, the MgO contents in the inclusions were consistently low. In addition, the effect of MgO on the CaS formation behavior is thought to be small. Therefore, the MgO content in the inclusions was not considered in the following discussions. It is
noteworthy that most of the inclusions already contained some amount of CaS in the LF 15 sample. In the LF 45 sample, CaO-Al$_2$O$_3$liq inclusions were observed, which is consistent with the previous result described in section 3.1.1. At the end of the LF process (LF 45 sample), inclusions were primarily located on a tie-line connecting an Al$_2$O$_3$-CaS phase and a CaO-Al$_2$O$_3$liq phase. After the FeS addition during the RH process (in the RH 10 sample), the CaO content in the inclusions decreased significantly. Furthermore, the CaS content in the inclusions was generally higher than that in the inclusions before the addition of FeS. Finally, the majority of the inclusions consisted primarily of Al$_2$O$_3$-CaS phases in the RH 25 sample.

Figure 3-19. Composition of inclusions at each stage of the sampling during the LF-RH process: (a) LF 15, (b) LF 30, (c) LF 45, (d) RH 10, and (e) RH 25. (f): Liquid region in CaO-Al$_2$O$_3$ system at 1873 K.$^{[64]}$

Elemental mapping results of the typical inclusions which contain a CaS phase are shown in Figure 3-20. In the LF 15 sample, inclusions with a CaS phase surrounding a CaO-MgO-Al$_2$O$_3$ phase were observed (Figure 3-20(a)). Similar inclusions were also observed in the LF 45 sample, but they contained much higher CaO contents than those in the LF 15 sample (Figure 3-20(b)). After the addition of FeS during the RH process, the CaO content in the CaO-Al$_2$O$_3$ phase decreased while the CaS content increased (Figure 3-20(c)). Thereafter, inclusions consisted of both Al$_2$O$_3$-MgO and CaS phases in the RH 25 sample (Figure 3-20(d)). These observed results were consistent with the inclusion composition variations shown in Figure 3-19.
3.3.2 Thermodynamic discussion

As shown above, CaS phases were observed throughout the LF-RH process. In the following sections, the CaS formation in a steel melt will be discussed from a thermodynamic viewpoint. The Ca content in the samples was calculated according to the procedure described in section 3.2.2.1. The calculated results are shown in Table 3-7. In the following discussion, the interaction parameters listed in Table 3-8 have been used.\[46,80,81\]

**Table 3-7.** Contents of Ca and O in steel samples [ppm].

<table>
<thead>
<tr>
<th>Sample</th>
<th>T.O</th>
<th>T.Ca</th>
<th>Ca_{insol}</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF 15</td>
<td>32</td>
<td>9.4</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>LF 45</td>
<td>23</td>
<td>14</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>RH 10</td>
<td>18</td>
<td>12</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>RH 25</td>
<td>8.2</td>
<td>5.1</td>
<td>5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Table 3-8.** First-order interaction parameters ($e_{ij}$) of the main elements in the melt used in the present study (at 1873 K)*.

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Al</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
<td>-0.34</td>
<td>-0.096</td>
<td>-0.0156</td>
<td>0.014</td>
<td>-0.072</td>
<td>-0.002</td>
<td>-9 000[81]</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>0.091</td>
<td>0.056</td>
<td>-0.004</td>
<td>0.0096</td>
<td>0.043</td>
<td>-0.047</td>
<td>-6.6[80]</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.45</td>
<td>-0.131</td>
<td>-0.021</td>
<td>-0.052</td>
<td>-3.9[80]</td>
<td>-3 600[81]</td>
<td>-0.17</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>0.11</td>
<td>-</td>
<td>-0.026</td>
<td>-</td>
<td>0.041</td>
<td>-260[80]</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

*All data without notation are from ref. [46]
3.3.2.1 CaS formation due to a reaction between Ca and S in the melt

One possible process responsible for forming a CaS phase in a steel melt is the direct reaction between Ca and S, which is expressed by equation (16):[80]

\[
Ca + S = CaS(s) \quad \Delta G_{16}^0 = -530000 + 115.6T \quad [J\cdot mol^{-1}]
\] (16)

The CaS stability diagram for this reaction was calculated at 1873 K and 1823 K, which represent the temperatures of the LF and RH processes, respectively. The activity of the CaS phase was taken to be unity, based on its low solubility in CaO-Al2O3 phases.[82] Figure 3-21 shows the calculated results. The plots in this figure correspond to the calculated activity values of Ca (\(a_{Ca}\)) and S (\(a_S\)) in each steel sample. As described in section 3.2.2.1, although this calculation may contain possible inaccuracies, it indicates that the \(a_{Ca}\) and \(a_S\) values during the LF-RH process are high enough to enable the formation of a CaS phase in the steel melt, except after that the LF process had progressed for 45 min. Thus, inclusions in the LF 15 sample contained some amount of CaS phase due to the reaction between Ca and S, as expressed in equation (16).

Figure 3-21. Stability diagram of the CaS phase due to the reaction between Ca and S in the melt.

3.3.2.2 CaS formation due to a reaction between the CaO phase in inclusions and S in the melt

Another possible CaS formation process is the reaction between the CaO phase in inclusions and S.[3,29,65] The reaction can be derived by combining equations (16) to (18),[80] and the result is expressed below in equation (19). The values of \(a_{CaO}\) and \(a_{Al2O3}\) at each boundary of the CaO-Al2O3 system were already displayed in Table 3-3 and were used in equation (19). In addition, the activity of CaS was set to unity when performing the calculations.

\[
Ca + O = CaO(s) \quad \Delta G_{17}^0 = -644000 + 148.1T \quad [J\cdot mol^{-1}]
\] (17)

\[
2Al + 3O = Al_2O_3(s) \quad \Delta G_{18}^0 = -1225600 + 393.8T \quad [J\cdot mol^{-1}]
\] (18)

\[
CaO(s) + S + \frac{2}{3}Al = CaS(s) + \frac{1}{3}Al_2O_3(s) \quad \Delta G_{19}^0 = -294500 + 98.8T \quad [J\cdot mol^{-1}]
\] (19)
Figure 3-22 shows the stability diagram of the CaS phase for this reaction regarding the various CaO-Al2O3 phases. The plots in the figure correspond to the $a_{Al}$ and $a_{S}$ values in each steel melt. This calculation result indicates that the particular CaO-Al2O3 phase which can react with S to form the CaS phase can vary depending on the values of the following three parameters: $a_{Al}$, $a_{S}$, and temperature. After the LF process progressed for 15 min, it is possible for the CaO-Al2O3_{liq} phase to react with S. However, as the LF process had progressed for 45 min, the CaO-Al2O3_{liq} phase cannot react with S. This implies that the CaO-Al2O3_{liq} phase can coexist with a CaS phase under the low $a_S$ condition. After the addition of FeS during the RH process (Figure 3-22(b)), modified CaO-Al2O3 phases, such as the CaO-Al2O3 and CaO-Al2O3_{liq} phases, can react with S. This is because of the high $a_S$ value, i.e., these modified CaO-Al2O3 phases are thermodynamically unstable at the high $a_S$ values after that the addition of FeS has been made.

![Stability diagram of CaS](image)

Figure 3-22. Stability diagram of CaS due to the reaction between CaO in various CaO-Al2O3 phases and S in the melt at (a) 1873 K and (b) 1823 K. (Al2O3 is abbreviated as A, and CaO as C.)

It is generally known that a modification of the Al2O3 phase to form CaO-Al2O3 system phases progresses in Al-killed steel melts during secondary refining processes.[30,31,36] Therefore, it is important to know the most stable phase in the CaO-Al2O3 system at each step of the present refining processes for this steel grade. Equation (20) was derived by combining equations (17) and (18) and was employed for this calculation. Likewise, the values of $a_{CaO}$ and $a_{Al2O3}$ displayed in Table 3-3 were substituted into equation (20):

$$\frac{1}{3}Al_2O_3(s) + Ca = CaO(s) + \frac{2}{3}Al \quad \Delta G_{298}^0 = -235500 + 16.8T \quad [\text{J} \cdot \text{mol}^{-1}] \quad (20)$$

Figure 3-23 shows the thermodynamically stable phase in the CaO-Al2O3 system at each sampling step with plots of the $a_{Al}$ and $a_{Ca}$ values. Similar to previous studies,[28-30] the CaO-Al2O3_{liq} phase was determined to be the most stable phase throughout these processes, except after that the RH process had progressed for 25 min. At this stage, the CaO-Al2O3 phase is the stable phase due to the relatively low $a_{Ca}$ value in the steel melt. Thus, according to the outlined
thermodynamic considerations, inclusions were being transformed into the CaO-Al₂O₃liq phase during the LF refining process. This result is consistent with the fact that CaO-Al₂O₃liq inclusions were observed in the LF 45 sample. After the addition of FeS during the RH process, these transformed inclusions reacted with S, forming CaO-Al₂O₃-CaS inclusions. The presence of these inclusions were confirmed based on the composition variations shown in Figure 3-19(c) to (d).

![Figure 3-23. Phase stability diagram of various CaO-Al₂O₃ phases at (a) 1873 K and (b) 1823 K. (Al₂O₃ is abbreviated as A, and CaO as C.)](image)

3.3.3 CaS formation mechanism in a steel melt and its role in inclusion evolution

3.3.3.1 During the LF process

From the calculated results shown above, the CaS formation mechanism during the LF process can be understood by the following discussion. As shown in Figure 3-20(a), a CaS phase surrounding a CaO-MgO-Al₂O₃ phase was observed in the LF 15 sample. The CaO content in the CaO-MgO-Al₂O₃ phase was relatively low (Figure 3-19(a)). According to the result shown in Figure 3-22, these low-modified CaO-Al₂O₃ phases, such as CaO·6Al₂O₃ and CaO·2Al₂O₃, cannot react thermodynamically with S to form a CaS phase during the LF process. Therefore, the detected CaS phase on the inclusions in the LF 15 sample was thought to be formed by the reaction between Ca and S, as expressed in equation (16). In addition, the sizes of the CaO-Al₂O₃ inclusions were generally larger than those of the Al₂O₃-CaS inclusions, as shown in Figure 3-19(c). This fact also supports the proposed theory that the Al₂O₃-CaS inclusions formed during the LF process were formed by nucleation of the CaS phase on the existing inclusions, and not by the reaction between the CaO phases in the inclusions and S, which is expressed in equation (19).

As described before, there may be two elements available to react with Ca: one is S to form a CaS phase, as expressed in equation (16); and the other is an Al₂O₃ phase in different CaO-Al₂O₃ systems to form a CaO-Al₂O₃ phase, as expressed in equation (20). Figure 3-24 compares
calculated thermodynamic driving forces in these two reactions. The temperature was set to 1873 K in these calculations. According to these calculated results, the reaction in equation (16) can progress when the Ca content becomes larger than 1 ppm, after that the LF process has progressed for 15 min. This is because the S content is relatively high at this process stage. Especially, for the period just after starting the LF process (before 15 min), the S content in the melt is supposed to be higher than that in the LF 15 sample. This high S content could promote a CaS formation early in the LF process. Once a CaS phase was formed on the outer layer of the existing inclusions, the supply of Ca into the core of the inclusion should be hindered, since mass diffusion in the solid phase is comparatively slow. \[29,30,39\] This can be one reason why the inner CaO-Al\(_2\)O\(_3\) phase in the inclusions detected in the LF 15 sample had a lower CaO content compared to that of the thermodynamically stable phase shown in Figure 3-22. One can expect that if a CaS layer was not formed on the inclusions, they could smoothly be modified to a thermodynamically stable phase, namely the CaO-Al\(_2\)O\(_3\)\(_{3\text{liq}}\) phase during the LF process.

![Figure 3-24](image)

**Figure 3-24.** Comparison of the thermodynamic driving forces between a CaS formation by the reaction between Ca and S, and a modification of Al\(_2\)O\(_3\) in different CaO-Al\(_2\)O\(_3\) phases by Ca at (a) LF 15 and (b) LF 45 at 1873 K. (Al\(_2\)O\(_3\) is abbreviated as A, and CaO as C.)

During the period between 15 min and 45 min into the LF process, both the driving forces of the CaS formation expressed by equation (16) and the thermodynamic stability of the CaS phase decreased. This was due to the progress of desulfurization of the steel melt. As shown in Figure 3-24(b), Ca in the steel melt apparently prefers to modify Al\(_2\)O\(_3\) in inclusions, rather than to react with S. This is due to the low S activity after that the LF process has progressed for 45 min. Therefore, the modification of the Al\(_2\)O\(_3\) phases to form CaO-Al\(_2\)O\(_3\) systems can progress without being hindered by a CaS layer enclosing the inclusions. This direct modification of Al\(_2\)O\(_3\) phases by Ca could contribute to the composition evolution of Al\(_2\)O\(_3\) to the CaO-Al\(_2\)O\(_3\)\(_{3\text{liq}}\) phase, which
can be seen in Figures 3-19(b) and (c). Moreover, as also recognized in Figure 3-24(b), the driving force of the composition change $\text{CaS} \rightarrow \text{CaO}$, which is the leftward reaction in equation (19), increases as the $S$ activity decreases. This increase in the driving force could contribute to a transformation of the $\text{Al}_2\text{O}_3$-$\text{CaS}$ inclusions into $\text{CaO}$-$\text{Al}_2\text{O}_3$-$\text{CaS}$ inclusions, which was confirmed as the tie-line shown in Figure 3-19(c). Some researchers have reported that a transient CaS phase can be formed on $\text{Al}_2\text{O}_3$ inclusions after a Ca-treatment, which acts as an intermediate product before the modification of $\text{Al}_2\text{O}_3$ inclusions progresses.\textsuperscript{[83-85]} Therefore, it is proposed here that a similar phenomenon can occur during an LF process, even without using a Ca-treatment. Note, that some amount of CaS content was confirmed to exist in the inclusions in the LF 45 sample (Figure 3-19(c)). This is most likely due to the difficulty of mass diffusion in the solid phase, which prevented an equilibrium state to be reached.

3.3.3.2 During the RH process

FeS addition during the RH process contributes to an increase in the $S$ activity. This enhances not only the reaction between the CaO phase in inclusions and $S$, but also the reaction between Ca and $S$. According to Figure 3-22(b), the modified CaO-$\text{Al}_2\text{O}_3$ phases, which include the CaO-$\text{Al}_2\text{O}_3$ and CaO-$\text{Al}_2\text{O}_{3\text{liq}}$ phases, could react with $S$ to form CaO-$\text{Al}_2\text{O}_3$-CaS inclusions following the reaction expressed in equation (19). In addition, a heterogeneous CaS formation, expressed by equation (16), could occur particularly on the surface of the existing inclusions to reduce the total interfacial energy between inclusions and the steel melt. These two reactions can generate inclusions with high CaS contents, as shown in Figures 3-19(d) and (e). It is well known that $\text{Al}_2\text{O}_3$ inclusions can be formed during an RH process due to the consumption of $\text{Al}$, as already explained in section 3.1.3.2. Therefore, a CaS precipitation occurs on these $\text{Al}_2\text{O}_3$ inclusions, which results inclusion formations with the compositions located on the line connecting the two corners of CaS and $\text{Al}_2\text{O}_3$ phases, shown in Figures 3-19(d) and (e). Thus, these two CaS formation reactions (equations (16) and (19)) can take place simultaneously in the steel melt after the FeS addition during the RH process.

3.3.3.3 Formation and transition of the CaS phase in Al-killed steel melts without applying Ca-treatment

According to the experimental results and discussions above, the CaS formation mechanism in this steel grade will take place in the following steps:

1) During the initial stage of the LF process, a CaS phase can form on both $\text{Al}_2\text{O}_3$ and low-modified CaO-$\text{Al}_2\text{O}_3$ inclusions by the reaction between Ca and $S$.

2) As the desulfurization of the steel melt progresses during the LF refining process, CaS continues to change its composition into a CaO phase. This results the formation of a CaO-$\text{Al}_2\text{O}_3$-
CaS phase. In addition, Ca prefers to modify the Al$_2$O$_3$ phases in inclusions rather than to react with S. This reaction generates inclusions in the CaO-Al$_2$O$_3$ system, which do not contain a CaS phase.

3) After the addition of FeS during the RH process, the CaS phase can form due to two possible reactions: one is the reaction between a CaO phase in the inclusions and S, and the other is the reaction between Ca and S.

### 3.3.4 Behavior of the CaS inclusions in a steel melt

As described in sections 3.1.3.2 and 3.2.3, the removability of inclusions from a steel melt is greatly affected by their contact angles. As shown in Table 3-4 and Figure 3-16, solid oxides generally have large contact angles against a steel melt (> 90°). On the other hand, liquid oxides have small contact angles (< 90°). This indicates that liquid oxide inclusions are difficult to remove from a steel melt. However, they cannot cause nozzle clogging, because they exist as a liquid phase at steelmaking temperatures. Here, the contact angle of a CaS phase with a steel melt has been reported to be 87°.[64] Therefore, it can be understood that the CaS-covered inclusions, which were identified in this study shown in Figure 3-20, are difficult to remove. Therefore, they tend to remain in a steel melt even after the completion of the RH process. In addition, the CaS phase exists as a solid phase (melting point ≈ 2800 K[64]). Based on these information, it can be pointed out that the CaS-covered inclusions are likely to deteriorate the castability of the steel melt.[3,21-23,65,76-78] Thus, CaS-covered inclusions have quite undesirable characteristics, which causes them to remain in a steel melt and to accumulate on a nozzle wall. This, in turn, can cause nozzle clogging. Table 3-9 summarizes the present discussion.

<table>
<thead>
<tr>
<th>Table 3-9. Dominant inclusion types and their behavior in Al-killed steel melts.</th>
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</thead>
<tbody>
<tr>
<td><strong>Inclusion type</strong></td>
</tr>
<tr>
<td>--------------------</td>
</tr>
<tr>
<td>Solid oxide*</td>
</tr>
<tr>
<td>Liquid oxide*</td>
</tr>
<tr>
<td>CaS inclusion</td>
</tr>
</tbody>
</table>

*At steelmaking temperatures
Chapter 4 Concluding discussion

This study was carried out with the aim to clarify the influencing factors to the evolution process of inclusions in Al-killed steel melts during a secondary refining process. The following concluding remarks are drawn from this study:

1. Factors to determine the inclusion compositions in actual secondary refining processes (Supplement 1 and 2)

   After the discussion above, the removal, generation, and composition evolution of inclusions are the factors determining inclusion compositions in a steel melt during a secondary refining process. The removal behavior of inclusions from a steel melt is strongly related to their interfacial properties. In addition, the reoxidation of a steel melt influences the inclusion compositions in the steel melt. Moreover, it is recognized that thermodynamic calculation is a useful method to predict the transition of the inclusion compositions in a steel melt during ladle treatments.

2. Effect of a high Al concentration on the inclusion compositions and its effect on the cleanliness of steel melts (Supplement 2 and 3)

   A high Al concentration of a steel melt restricts the degree of the inclusion evolution by decreasing the driving force. This also contributes to a high removability of inclusions. Therefore, there are fewer inclusions in a high-Al steel melt compared to a steel melt with a lower Al content.

3. Effect of S concentration on the inclusion compositions and its effect on the cleanliness of steel melts (Supplement 4 and 5)

   Before the desulfurization of a steel melt, a CaS phase can be formed on inclusions even when Ca-treatment has not been applied. Thereafter, the CaS phase is transformed into a CaO phase in inclusions as the desulfurization of the steel melt progresses. Thus, the S concentration in the steel melt influences the process of the Al\textsubscript{2}O\textsubscript{3} modification in the steel melt. In the case of production of high-S containing steels, the CaS phase can be formed again when adding FeS during the RH process. Therefore, inclusions mostly consist of Al\textsubscript{2}O\textsubscript{3}-CaS phases.

   Thus, the removal of inclusions, generation, and composition evolution should be considered to control the inclusion compositions in steel melts. As discussed in this study, steel components, such as Al and S, are considerably involved in the process of the inclusion evolution during secondary refining processes.
Chapter 5 Conclusion

Plant experiments were carried out to observe the evolution of inclusions during the actual secondary refining process. The present study aimed at clarifying the factors to control the inclusion compositions in Al-killed steel melts during a secondary refining process. Steel samples were collected during the LF and RH processes. The inclusion characteristics were determined using an SEM in combination with an EDS. Also, thermodynamic modeling was used to predict the evolution of the inclusion composition during the process. The following conclusions and Figure 5-1 summarize the main findings in this study:

1. Factors to determine inclusion compositions in actual secondary refining processes (Supplement 1 and 2)

(1) During an LF refining of an Al-killed steel, inclusion compositions were transformed from an Al₂O₃ phase, which is the primary deoxidation product, to complex MgO-Al₂O₃ (line 1) and CaO-Al₂O₃ (line 2) inclusions. Thereafter, the inclusion compositions were positioned on a tie-line connecting the two areas of MgO·Al₂O₃ and CaO-Al₂O₃-MgO_liq (line 3). This change took place by composition evolution targeting the thermodynamic equilibrium states.

(2) After an RH treatment, the inclusion compositions consisted of Al₂O₃ and complex CaO-Al₂O₃ phases. MgO·Al₂O₃ inclusions were removed while the CaO-Al₂O₃ inclusions remained, which was understood based on the interfacial properties of the oxide phases to a steel melt. Al₂O₃ inclusions were considered to be generated due to reoxidation during the RH treatment (Figure 5-1(b)).

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

2. Effect of a high Al concentration on the inclusion compositions and its effect on the cleanliness of steel melts (Supplement 2 and 3)

(4) The contact angles of inclusions in high-Al-containing steel melts retain higher than 90°, since the degree of the Al₂O₃ modification is decreased due to the high Al content (line 4). Therefore, the removal tendency of inclusions in high Al steel melts is kept high throughout an LF-RH process.
(5) According to thermodynamic considerations, the low T.O contents of high Al steel grades are due to the low O_{\text{insol}} contents.

(6) In a high-Al steel melt, the CaO content in inclusions are much lower than that of the thermodynamically most stable phase. This can be explained by two reasons: one is the low thermodynamic driving force of Al_{2}O_{3} modifications and the other is the high removability of inclusions from steel melts.

3. Effect of S concentration on the inclusion compositions and its effect on the cleanliness of steel melts (Supplement 4 and 5)

(7) At the initial stage of an LF refining, CaS was formed due to the reaction between Ca and S in the melt due to a high S activity before the desulfurization of steel melt (line 5). As the desulfurization progresses during the LF refining, Ca can directly modify an Al_{2}O_{3} phase to form CaO-Al_{2}O_{3} inclusions (line 6). Furthermore, the driving force of the transformation of CaS into CaO in the CaO-Al_{2}O_{3}-CaS phase increases (line 7). However, this composition change takes a long time due to the difficulty of mass diffusion in the solid CaS phase. Therefore, it cannot be completed at the end of an LF refining process.

(8) During an RH treatment, an FeS addition increases the S activity in a steel melt. This high S activity transforms the CaO phase in inclusions into a CaS phase (line 8). In addition, Ca and S in the melt also react to form a CaS phase at the same time (line 9). Due to these CaS phase formations, inclusions in high-S containing steel melts are covered by a CaS layer, which is difficult to remove from steel melts. Therefore, the castability of high-S containing steels can be deteriorated by a deposition of CaS inclusions even in the case where a steel is made without a Ca-treatment.

(9) It was confirmed that a CaS phase can be formed even when a Ca-treatment has not been used. Specifically, this can take place in two manners: a reaction between Ca and S, and a reaction between CaO in inclusions and S.
Figure 5-1. Schematic description of the conclusions of this study: (a) LF refining process, (b) RH treatment process.
Chapter 6 Future Work

This work illustrates the parameters influencing the inclusion compositions in Al-killed steel melts during a secondary refining process. The removal, generation, and composition change should be considered in order to control the composition of inclusions during and after a refining process. Also, the steel compositions during a refining process should be adjusted to control the evolution of inclusions in the steel melt. The following subjects should be addressed in future in order to further understand the influencing parameters and for appropriate application of these findings to achieve desired steel qualities:

(1) There are huge fluctuations in the first- and second-order interaction parameters suggested so far, and they are still being re-examined. A better description of the interactions between steel compositions should be provided by accumulating more experimental and industrial data. This point also applies to the equilibrium constants, such as the logK value for Al₂O₃ formation in a steel melt. To decrease these fluctuations, a more accurate method should be obtained for measuring the dissolved concentrations of minor elements, such as O, S, Ca, and Mg.

(2) During refining processes, researchers have detected inclusion evolution from Al₂O₃ to MgO-Al₂O₃, Al₂O₃ to CaO-Al₂O₃, and MgO-Al₂O₃ to CaO-Al₂O₃ in an Al-killed steel melt. The kinetic understanding of these inclusion evolutions should be further investigated to control the composition of various inclusions during a secondary refining process.

(3) Many researchers have pointed out how large inclusions deteriorate the properties of steel. However, there are no decisive proposals regarding how these inclusions become large in a steel melt during a secondary refining process including a casting process. A detailed study connecting the refining conditions and the size distribution of inclusions should be carried out.
References


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