Change in Composition of Inclusions through the Reaction between Al-killed Steel and the Slag of CaO and MgO Saturation

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The inclusion of CaO–Al₂O₃ is occasionally observed during the secondary refining of Al-killed steel. In this study, MgO and CaO saturated slag was reacted with Al-killed steel in a MgO crucible, and the dissolution behaviors of Mg and Ca from the slag and the change in composition of inclusions were considered. Both the MgO and CaO in the slag were reduced from the presence of Al in the steel, and the concentration of dissolved Mg and Ca increased with the reaction time and Al concentration. When the Al concentration in the steel was 0.25 mass%, the concentration of dissolved Mg was 30 ppm or higher, whereas that of Ca was only 0.3 ppm. The initial Al₂O₃ inclusions transformed into a MgO·Al₂O₃ spinel, and finally changed into MgO inclusions rather than CaO–Al₂O₃ type inclusions. When the Al concentration was 0.75 mass%, the dissolved Ca concentration increased to 0.9 ppm, and the CaO–Al₂O₃ type inclusion with MgO was observed at 120 min. When the Al concentration further increased to 2.5 mass%, the concentrations of dissolved Mg and Ca increased to 110 and 3 ppm, respectively. The initial Al₂O₃ inclusions transformed into MgO inclusions within 5 min, and a CaO–Al₂O₃-type inclusion with MgO was observed after a 10 min reaction period. Finally, all inclusions transformed into a CaO–Al₂O₃-type inclusion with MgO at 120 min.

KEY WORDS: inclusion; composition change; slag and metal reaction; Al-killed steel; spinel; CaO–Al₂O₃–MgO inclusion.

1. Introduction

The CaO–Al₂O₃ inclusion is occasionally observed during the secondary refining of Al-killed steel.^{1–8)} Todoroki *et al.*¹⁾ studied the change in composition of the inclusions in Al-killed 18%Cr–8%Ni stainless steel through a reaction with the top slag of a CaO–Al₂O₃–MgO–F system. They found that alumina or MgO·Al₂O₃ spinel inclusions were formed immediately after the addition of Al. The amounts of MgO and CaO in the slag were then reduced owing to the presence of Al, and the concentrations of Mg and Ca in the steel increased. CaO–Al₂O₃-type inclusions, which are considered the most stable based on a thermodynamic calculation, formed during the final stage of refining when the Ca concentration reached 1 mass ppm or higher. A similar phenomenon in which an Al₂O₃ inclusion was changed into a CaO–Al₂O₃-type inclusion through a reaction between Al in the steel and the CaO-containing slag has also been observed.^{2–7)} However, because the equilibrium relation with Ca and oxygen differs widely in individual studies,^{9–14)} the most stable oxide in steel containing a small concentration of Ca (few ppm) remains unclear. Harada *et al.*⁸⁾

conducted a kinetic analysis of the compositional changes in inclusions through a reaction with slag using a laboratory-scale furnace under Ar bubbling conditions. They found that after the reaction between the slag and steel, a Al₂O₃ inclusion, which was observed just after the addition of Al, changed into a MgO·Al₂O₃ spinel inclusion. However, a CaO–Al₂O₃ inclusion containing MgO was observed during the entire experiment and its composition agreed well with the calculated composition of the inclusion originating from the slag. The authors concluded that the origin of the CaO–Al₂O₃-type inclusion was not Al₂O₃ but rather entrapped slag droplets in which unstable oxides (*i.e.*, SiO₂, FeO and MnO) were reduced from the presence of Al in the steel. Based on the above studies, the main formation mechanism of CaO–Al₂O₃-type inclusions in steel during secondary refining remains unclear. To control the composition of an inclusion, the mechanism forming CaO–Al₂O₃-type inclusions needs to be ascertained.

In this study, laboratorial experiments were conducted to determine the dissolution behavior of Mg and Ca from MgO- and CaO-saturated CaO–MgO–Al₂O₃ slag into Al-killed molten steel with various concentrations of Al, and the compositional change of the inclusion during the refining process was investigated.

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2. Experimental Method

2.1. Raw Materials

The slag employed in this study was composed of 55 mass% CaO-15 mass% MgO-30 mass% Al_2O_3 (all compositions in this paper are given in mass percentage, unless specifically stated). As shown in **Fig. 1**, the liquid phase of this slag was saturated with both MgO and CaO. To prepare the slag, CaO was prepared by heating CaCO_3 at 1 273 K for 12 h, which was subsequently mixed with reagent grade MgO and Al_2O_3 . The mixture was pressed into tablets and sintered at 1 473 K for 12 h, and then solidified and formed into a lump slag. After the solidification, the slag composition was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Similar to many studies conducted on the compositional change of inclusions with ferritic stainless steel, Fe-11%Cr alloy was used.^{15,16} To prepare this metal, electrolytic Fe and high-purity Cr (99.9%) metal were melted in an argon arc furnace to produce the master alloy. The compositions of the mother alloy were analyzed using ICP-AES, and the total oxygen (T.O.) of the alloy was measured using an infrared X-ray absorption method. A deoxidizer of Fe-Cr-Al alloy with various concentrations of Al was prepared through the melting of electrolytic Fe, high-purity Cr (99.9%), and Al (99.999%). The concentration of Al in the deoxidizer was changed to 4.9%, 16.5%, and 53.2%. The compositions of the deoxidizer were analyzed using ICP-AES and an infrared X-ray absorption method.

2.2. Experiment Procedure

The experiment setup is shown in **Fig. 2**. The experiment was conducted using an induction furnace. Prior to heating, 140 g of the prepared master steel along with 13 g of lump slag were loaded into a dense MgO crucible. Subsequently, the chamber of the furnace was subjected to vacuum conditions, and thereafter purged with purified argon. This process was repeated three times. To remove the oxygen, argon (99.9999%) was passed through heated Mg chips (573 K) and allowed to flow into the chamber of the furnace. Subsequently, the metal was heated to 1 873 K and the deoxidizer was added. This moment was set as the starting point of the experiment. The concentration of deoxidizer

was determined based on the target Al concentration. After a pre-determined concentration of time, the crucible was unloaded from the furnace and quenched with water. The temperature of the molten steel was measured by immersing a thermocouple into the steel melt, and the thermocouple was covered using a dense MgO protection tube.

The experiment conditions are summarized in **Table 1**. Three target Al concentrations, namely, 0.25% (low Al steel), 0.75% (medium Al steel), and 2.5% (high Al steel), were selected for this study. In the aforementioned experiment method, the homogeneous melting of the deoxidizer took several minutes, particularly in the case of high Al steel. Therefore, the experiments on high Al steel were conducted for longer than 10 min, and a different experimental method was adopted to clarify the phenomenon during the initial period after de-oxidation. For this method, the deoxidizer was loaded with master steel in a MgO crucible. After their melting, the slag was added to the molten steel, and this moment was set as the starting point of the experiment. The additional experiment conditions are written as high Al (short) in Table 1, and the conditions for the original experiment method are written as high Al (long).

After quenching, the center portion of the metal (5 mm above the base) was cut for both a chemical analysis and an observation of the inclusions. For the chemical analysis, the Al and Mg concentrations in steel were analyzed using ICP-AES. The TO of the alloy was measured using

Fig. 1. Composition of the slag employed.

Fig. 2. Schematic of the experimental setup.

Table 1. Experiment conditions.

Condition	Al content/%	Reaction time/min
Low Al	0.25	0, 5, 10, 30, 60, 90, 120
Medium Al	0.75	30, 60, 120
High Al (long)	2.5	10, 30, 60, 120
High Al (short)	2.5	0, 2, 5, 10

the infrared X-ray absorption method. The Ca in steel was analyzed using glow discharge mass spectrometry (GDMS) and inductively coupled plasma mass spectroscopy (ICP-MS). The slag composition was analyzed using ICP-AES. The inclusion was analyzed manually using an electron probe micro analyzer with a field emission electron gun (FE-EPMA), and the concentrations of Mg, Al, Fe, Ca, O, and Cr were analyzed. The inclusions were assumed to consist of MgO, Al_2O_3 , and CaO, and the analyzed values of Mg, Al, and Ca were converted into oxide values using a stoichiometric relationship. The values of Fe and Cr were ignored because it was assumed that they were due to the analysis of the metal phase. The value of S was also ignored owing to its low concentration. Ten to 15 inclusions were analyzed for each sample, and their average composition was used. The interface of the crucible and molten steel after the reaction was analyzed using EPMA.

3. Experimental Results

The changes in the concentrations of Al and Mg in the steel are shown in Figs. 3 and 4, respectively. In the case of a high Al, the results of the short experiment were combined with those of the long experiment. The Al concentration remained almost constant throughout the reaction time. The difference in Al concentration at 10 min between the long and short experiments was caused by the undissolved deoxidizer present during the long experiment. The Mg concentration increased until about 30 min and then gradually decreased. The concentration of Mg increased with an increase in Al concentration, and in the case of high Al steel, reached about 100 ppm.

The change in the concentration of Ca in the steel is shown in Fig. 5. Because the Ca concentration in the steel was extremely low, it was analyzed using inductively coupled plasma mass spectroscopy (ICP-MS) and GDMS methods. The results obtained through these two methods were in good agreement, and the Ca concentration measured using GDMS was applied for the purposes of this discussion. The concentration of dissolved Ca was about 0.3 ppm in the case of the low Al steel, but increased to about 3 ppm

in the case of high Al steel.

The change in the concentration of total oxygen in steel is shown in Fig. 6. In each case, a stable value around 10 ppm of total oxygen was reached.

The change in slag composition is shown in Fig. 7 for high Al steel. During the reaction, the slag composition did not show a significant change. After the reaction, the slag remained as both saturated MgO and CaO.

The composition of the inclusions for low Al steel is shown in Fig. 8. During the reaction, the initial Al_2O_3 inclusion changed gradually through the $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel (which is denoted as a spinel in this paper for simplicity) into MgO inclusions. The CaO concentration in the inclusion was negligible.

For the medium Al steel, the composition of the inclusion is summarized in Fig. 9. MgO inclusions were only observed in steel after 30 min, and at 120 min, CaO–MgO– Al_2O_3 inclusions were also observed.

The compositions of the inclusions for high Al steel under both the short and long experiments are shown in Figs. 10 and 11, respectively. The initial inclusions were a mixture

Fig. 4. Change in Mg concentration in steel with the reaction time.

Fig. 3. Change in Al concentration in steel with the reaction time.

Fig. 5. Change in Ca concentration in steel with the reaction time.

Fig. 6. Change in the concentration of total oxygen in steel with the reaction time.

Fig. 7. Change in slag composition with the reaction time for the experiment using high Al steel.

Fig. 8. Inclusion composition for each reaction time during the experiment using low Al steel (black marks indicate the average composition at each reaction time).

Fig. 9. Inclusion composition for each reaction time during the experiment using medium Al steel (black marks indicate the average composition at each reaction time).

of spinel and Al_2O_3 , which was caused by the supplement of Mg through the reaction between the MgO crucible and Al in the steel. With an increase in the reaction time, the concentration of MgO in the inclusions gradually increased, and at 10 min, the concentration reached about 90% and inclusions containing CaO were also observed. At 120 min, all inclusions changed into CaO–MgO– Al_2O_3 and the MgO concentration in the inclusions was less than that formed in middle Al steel at 120 min. Compared with the Ca concentration shown in Fig. 5 and the average composition of the inclusions at 30 and 120 min, the concentration of Ca did not change regardless of the inclusion composition. This indicates that the analyzed Ca concentration shown in Fig. 5 is the concentration of dissolved Ca present in the steel.

Typical morphologies of the inclusions for each case are summarized in Fig. 12. No clear differences during the change in composition of the inclusions were observed in any of the cases.

The elemental mapping of the crucible before the reaction and at 120 min is shown in Fig. 13. Before the experiment, CaO and Al_2O_3 were detected in the grain boundary of the MgO. After the reaction, for each case, an enrichment of CaO and Al_2O_3 in the grain boundary was clearly observed.

4. Discussion

To summarize the transformation behavior of the inclusions, in the case of low Al steel (0.25 mass% Al), the inclusion was changed from Al_2O_3 into MgO rich oxide through the spinel after 90 min but did not change into oxide in the CaO– Al_2O_3 system. However, when the Al concentration increased to 0.75 mass% (middle Al steel), the inclusion changed into a CaO– Al_2O_3 system with MgO from MgO rich oxide. In the case of high Al steel (2.5 mass% Al), when slag was added after de-oxidation, during a 10 min period, the inclusion changed from Al_2O_3 into MgO rich

oxide through the spinel, and finally, the MgO rich oxide changed into a CaO–Al₂O₃ system with MgO. With the inclusion of the CaO–Al₂O₃ system, the MgO concentration decreased, and the time to change from MgO rich oxide shortened by the increase in Al content.

Based on the observed concentration of Ca, Mg, and Al during each experiment, the stable oxide was evaluated using a thermodynamic calculation.

The observed inclusions were simplified as pure Al₂O₃, Al₂O₃–MgO spinel, MgO rich oxide, and a CaO–Al₂O₃ system with MgO. First, the relation between the Al₂O₃, spinel and MgO was calculated through the following reaction. In this and the following calculations, a dilute solution was used as a standard to describe the activity of each dissolved

component in steel and mass% was used as unit. For oxide phase, pure substance of each oxide was used as standard.

The equilibrium constant of this reaction can be calculated through the reactions (2) and (3). However, many results have been published for reaction (3), as shown in **Table 2**.

The result of the calculation with the experimental data is shown in **Fig. 14**. In this calculation, the interaction

Fig. 10. Inclusion composition for each reaction time during the short experiment using high Al steel (black marks indicate the average composition at each reaction time).

Fig. 11. Inclusion composition for each reaction time during the long experiment using high Al steel (black marks indicate the average composition at each reaction time).

	0 min	30 min	60 min	120 min
(a) Low Al steel				
(b) Medium Al steel				
(c) High Al steel				

Fig. 12. Typical morphology of inclusion at each reaction time for the experiments using (a) low Al steel (b) medium Al steel, and (c) high Al steel.

Fig. 13. Elemental mappings of the bottom of the crucible (a) before the experiment, and after the experiment for 120 min using (b) low Al steel, (c) medium Al steel, (d) and high Al steel.

Table 2. Equilibrium constant of reaction (2) as measured by various researchers.

Resource	H. Ohta <i>et al.</i> ¹⁸⁾	H. Itoh <i>et al.</i> ¹⁹⁾	Q. Han <i>et al.</i> ²⁰⁾	J. D. Seo <i>et al.</i> ²¹⁾	W. G. Seo <i>et al.</i> ²²⁾	S. Du <i>et al.</i> ²³⁾
$\log K_{\text{Mg}}$ (1 873 K)	-7.86	-6.8	-6.03	-7.21	-7.24	-8.07

parameters used to calculate the activities of Al, Mg, Ca, and O in steel are summarized in **Table 3**. In Table 3, all data without a notation are from M. Hino and K. Ito.⁹⁾ The oxygen content was calculated using reaction (2), because the Al contents in steel were higher than that of Mg and Ca under current experimental conditions. This oxygen content was used in the calculation of the activity coefficients of Al and Mg. Moreover, the oxygen contents used in the following calculations were determined using the same method. The activities of Al_2O_3 and MgO in the spinel were 0.032 and unity for the MgO saturated spinel, and unity and 0.004

for the Al_2O_3 saturated spinel.²⁶⁾ Although it is difficult to evaluate the accuracy of the equilibrium relation, the experiment results of low and medium Al steel were mostly close to the equilibrium with MgO saturated spinel and pure MgO. Therefore, the Al_2O_3 , which was formed initially prior to the supplement of Mg from slag and refractory, can change into MgO rich oxide through the spinel. On the other hand, in the case of high Al steel, the composition of steel is located within the region where the spinel is stable. Thus, in this case, Al_2O_3 can change the spinel, although the formation of MgO rich oxide does not occur thermodynamically.

Second, the relationship between MgO and CaO is discussed. Based on the experiment, when the Al concentration was high, the inclusion changed from MgO rich oxide or a MgO saturated spinel into a $\text{CaO-Al}_2\text{O}_3$ system with MgO. In addition, when the Al concentration increased, the MgO concentration in the inclusion of the $\text{CaO-Al}_2\text{O}_3$ system decreased. It is difficult to imagine that pure MgO changed into the inclusion of a $\text{CaO-Al}_2\text{O}_3$ system containing MgO.

Fig. 14. Measured concentrations of Mg and Al for each experiment and a stability diagram of MgO–Al₂O₃ system.

Table 3. Interaction parameters used for the calculation.

e_i^j	Mg (j)	Al (j)	O (j)	Cr (j)	Ca (j)
Mg (i)	0	-0.27	-425.8	0.022 ⁽²⁴⁾	0
Al (i)	-0.3 ⁽²⁶⁾	0.043	-1.98	0.0122 ⁽²⁵⁾	-0.047
O (i)	-304.3	-1.17	-0.174	-0.052	-515
Ca (i)	0	-0.072	-580	0	-0.002
r_{Mg}^O	350 000	$r_{Mg}^{Mg,O}$	-61 000	$r_{Mg}^{Al,O}$	-230
r_{Al}^O	39.8	$r_{Al}^{Mg,O}$	-260	$r_{Al}^{Al,O}$	-0.028
r_{O}^{Mg}	-20 000	$r_{O}^{Mg,O}$	462 000	r_{O}^{Al}	-0.01
$r_{O}^{Al,O}$	47.45	r_{O}^{Cr}	-0.0006	r_{O}^{Ca}	2 240
r_{O}^{Ca}	357	$r_{O}^{Ca,O}$	1 801	$r_{O}^{Ca,O}$	1 788

e : primary interaction parameter; and r : secondary interaction parameter

Thus, the reaction of MgO in the spinel with Ca in the steel, resulting in the formation of CaO, should be discussed, as shown in Eq. (4).

Although the equilibrium constant of this reaction can be calculated through reactions (3) and (5), many results have been published on the equilibrium constant for reaction (5) only, as shown in Table 4.

The result of the calculation using the experimental data is shown in Fig. 15. The activity of MgO was unity, and that of CaO was assumed to be 0.2 when considering a CaO–Al₂O₃ binary system with a 0.55 molar fraction of CaO.⁽²⁷⁾ As a significant variation of the equilibrium constant of reactions (3) and (5), the calculated lines are widely different depending on the combination. Again, it is difficult to evaluate the accuracy of the equilibrium relation, although the experimental results were mostly located under the stable conditions of CaO–Al₂O₃. Based on the increase in Ca concentration, this indicates the possibility that MgO or a MgO saturated spinel becomes unstable and is transferred to

Table 4. Equilibrium constant of reaction (5) as measured by various researchers.

Resource	JSPS ⁽⁹⁾	Q. Han <i>et al.</i> ⁽¹⁰⁾	K. Wakasugi <i>et al.</i> ⁽¹¹⁾	K. Ogawa <i>et al.</i> ⁽¹²⁾	S. W. Cho <i>et al.</i> ⁽¹³⁾	H. Itoh <i>et al.</i> ⁽¹⁴⁾
$\log K_{Ca}$ (1 873 K)	-9.08	-8.26	-9.04	-7.60	-10.22	-7.15

the CaO–Al₂O₃ system. The result of the calculation when the activity of MgO decreased to 0.1 is shown in Fig. 16. In this case, CaO–Al₂O₃ is no longer stable for most of the calculated lines. This indicates that, for the transformation from a spinel to CaO–Al₂O₃, the MgO concentration of the spinel has to increase to saturation. This calculation agrees well with the result of the inclusion of the CaO–Al₂O₃ system observed after the formation of the MgO saturated spinel and MgO rich oxide.

Finally, the relation between Al₂O₃ and CaO is discussed.

The result of the calculation using the experimental data is shown in Fig. 17. In this calculation, the activity of Al₂O₃ was unity, and that of CaO was 0.2. The experimental data for low and middle Al steel are mostly located within the region where the CaO–Al₂O₃ is stable. This indicates that the Al₂O₃ or Al₂O₃ saturated spinel easily reacts with Ca present in the steel, thereby forming CaO. However, based on the experiment, no compositional change into the inclusion of the CaO–Al₂O₃ system from Al₂O₃ or the Al₂O₃ saturated spinel was observed. In contrast, for high Al steel, the spinel is stable, and no formation of CaO from the Ca occurs thermodynamically.

To summarize the thermodynamic calculation, the route of compositional change from Al₂O₃ into CaO–Al₂O₃ through the spinel and MgO, and the route directly from Al₂O₃ into CaO–Al₂O₃, were both predicted for low Al steel. On the contrary, for high Al steel, only the route of compositional change from Al₂O₃ into CaO–Al₂O₃ through the spinel without the formation of MgO was calculated. However, as the experiment results indicate, the route for low Al steel was Al₂O₃ into MgO rich oxide through the spinel, whereas

Fig. 15. Measured concentrations of Mg and Ca for each experiment and a stability diagram of MgO–CaO system ($a_{\text{MgO}} = 1$, $a_{\text{CaO}} = 0.2$).

Fig. 16. Measured concentrations of Mg and Ca for each experiment and a stability diagram of MgO–CaO system ($a_{\text{MgO}} = 0.1$, $a_{\text{CaO}} = 0.2$).

Fig. 17. Measured concentrations of Al and Ca for each experiment and a stability diagram of CaO–Al₂O₃ system ($a_{\text{Al}_2\text{O}_3} = 1$, $a_{\text{CaO}} = 0.2$).

no oxide in CaO–Al₂O₃ system was observed. In addition, for high Al steel, the formation of MgO rich oxide from the spinel was observed in the transformation route from Al₂O₃ into oxide of the CaO–Al₂O₃ system with MgO. As Figs. 14, 15, 16 and 17 show, the thermodynamic lines are widely different based on the combination of the equilibrium values found in the literature. Therefore, a precise prediction through a thermodynamic calculation is difficult to achieve. In general, because the slag is saturated with CaO and MgO, the reduction rate of MgO from Al is faster than that of CaO owing to the fact that CaO is more stable than MgO thermodynamically, although no clear difference in the rate of increase of Mg and Ca was observed during the experiment. Therefore, it is reasonable to conclude that the Al₂O₃ changes in direction toward MgO during the early stage of the reaction. The condition required to form oxide in the CaO–Al₂O₃ system depends on the concentration of Ca. If the mass transfer of Ca in the steel is the rate-controlling step of reactions (4) and (6), the transformation rate will depend on the Al concentration present in the steel, which determines the concentration of Ca, and is the reason why no oxide in the CaO–Al₂O₃ system was observed in low Al steel.

In this experiment, when the dissolved Ca and Mg were consumed by the reaction with the crucible, the concentrations of these elements were determined based on the balance between the supply rate from the slag and the consumption rate by the crucible. Thus, it is difficult to understand the critical conditions required for oxide formation in the CaO–Al₂O₃ system through this experiment, and future studies at an industrial scale will be necessary.

5. Conclusions

In this study, MgO and CaO saturated slag reacted with Al-killed steel, and the dissolution behaviors of Ca and Mg and the change in composition of these inclusions, were clarified. The following conclusions were drawn.

(1) Both MgO and CaO in slag were reduced through the presence of Al, and Mg and Ca were dissolved into the steel, the concentrations of which increased with the concentration of Al.

(2) When the Al concentration in steel was 0.25 mass%, the concentration of dissolved Mg was 30 ppm or higher, whereas that of Ca was only 0.3 ppm. The initial Al₂O₃

inclusions transformed into a MgO·Al₂O₃ spinel, and finally changed into MgO inclusions; however, a CaO–Al₂O₃-type inclusion was not observed.

(3) When the Al concentration was 0.75 mass%, the concentration of dissolved Ca increased to 0.9 ppm, and a CaO–Al₂O₃-type inclusion with MgO was observed at 120 min.

(4) When the Al concentration further increased to 2.5 mass%, the concentration of dissolved Mg and Ca increased to 110 and 3 ppm, respectively. The initial Al₂O₃ inclusions transformed into MgO inclusions within 5 min, and a CaO–Al₂O₃-type inclusion with MgO was observed after a 10 min reaction. Finally, all inclusions transformed into a CaO–Al₂O₃-type inclusion with MgO at 120 min.

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