Effect of CaO/Al₂O₃ Ratio of Ladle Slag on Formation Behavior of Inclusions in Mn and V Alloyed Steel

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The effect of CaO/Al₂O₃ (=C/A) ratio of the ladle slag on the formation behavior of non-metallic inclusions in the Mn-V-alloyed steel was investigated using both the experimental method and refractory-slag-metal-inclusion (ReSMI) multiphase reactions simulation. The formation behavior of inclusion was strongly affected by the activity of MgO in the initial slag at the early stage of the reaction. However, since the MgO activity converged to unity due to MgO dissolution from refractory to slag during the reaction, the formation behavior of inclusion was affected by the activity of CaO and Al₂O₃ in the slag rather than that of MgO at the final stage of the reaction. From the experimental results and ReSMI multiphase reaction model, the formation behavior of inclusions could be divided into three cases according to the C/A ratio of the slag as follows; 1) C/A < 1.5; Alumina → Spinel → Spinel + Liquid oxide, 2) 1.5 < C/A < 2.5; Alumina → Spinel → Liquid oxide, 3) C/A > 3.0; Alumina → Spinel → Liquid oxide → Magnesite. Therefore, it was concluded that the C/A ratio of the ladle slag should be controlled from about 1.5 to 2.5 in order to suppress the harmful solid inclusions such as spinel during secondary refining processes.

KEY WORDS: Mn-V-alloyed steel; non-metallic inclusions; secondary refining; ladle slag; refractory-slag-metal-inclusion (ReSMI) multiphase reactions simulation; MgAl₂O₄ spinel.

1. Introduction

The Mn and V alloyed steel, which has a ferrite-pearlite composite microstructure, have been widely used as automotive parts such as crankshafts, push rods, rotating bearings, *etc.* due to its excellent machinability and high-strength. However, the product performance can be significantly affected by the steel cleanliness. Gojić *et al.*⁽¹⁾ reported the resistance to hydrogen embrittlement could be improved by lowering the non-metallic inclusions. In addition, the MgAl₂O₄ spinel inclusion, which generally formed during the ladle refining process, potentially causes nozzle clogging as well as surface defects in products.^(2–14) Hence, it is crucial to predict and control the inclusion composition during the ladle refining process.

Thermodynamics of the formation behavior and modification of spinel inclusion in molten steel have been extensively investigated since the 1980's.^(2–15) Specifically, Park *et al.*^(8–13) reported the formation mechanism of spinel inclusion and suggested versatile countermeasures during stainless steel refining and casting processes. Todoroki and Mizno reported that silica in the slag enhanced the formation of spinel inclusions and suppressed extensive reduction of CaO in the slag.⁽⁷⁾ In fact, most of studies were carried out with respect to molten stainless steels. However, studies on the inclusion formation behavior of specialty steels such as Mn and V alloyed steels are insufficient.

Many researchers have investigated the effect of calcium treatment on the modification of alumina and spinel inclusions to improve the castability during continuous casting.^(16–30) Holappa *et al.*⁽²¹⁾ reported a thermodynamic evaluation of inclusion formation and modification in calcium treated steel transferring from ladle to tundish and mold until the steel solidified. Recently, Verma *et al.*^(24–26) reported a mechanism of using calcium to modify alumina and spinel inclusions.

More recently, the modification of spinel to liquid oxide inclusions by slag-metal reactions has been reported without the direct addition of calcium. Kumar and Pistorious studied the calcium transfer from slag to steel and determined its effect on the modification of alumina and spinel inclusions.⁽³¹⁾ They found that there could be a significant amount of calcium transfer from the slag in the presence of silicon in molten steel. Alternatively, we recently investigated the formation behavior of inclusions as a function of silica content in the slag using a refractory-slag-metal-inclusion (ReSMI) multiphase reaction model.^(32,33) It was confirmed that the evolution of inclusions from alumina to spinel and finally to liquid oxide inclusion was promoted by Mg and Ca transfer from slag to molten steel. Also, the starting and finishing points of the modification of spinel into the liquid oxides were delayed as the content of SiO₂ in the ladle slag increased from 7 to 19 wt%.

There are many investigations regarding the effect of slag composition on the spinel formation. Nishi and Shinme observed that the content of MgO in the Al₂O₃-based inclusions increased with increasing CaO/SiO₂ ratio of

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the CaO–SiO₂–MgO–Al₂O₃ slag.⁶⁾ They proposed that the small amounts of Mg (less than 1 ppm) are supplied into the molten steel due to reduction of MgO in the slag by Al in molten steel, resulting in an increase of MgO content in the Al₂O₃-based inclusions. From the analysis of plant data, Kim *et al.*⁵⁾ proposed that the aluminum content in steel melt and MgO content in an argon oxygen decarburization (AOD) converter slag should be lowered to suppress the formation of spinel. However, SiO₂ and CaO could also be reduced by such a large content of Al, which was not considered in these previous studies.

If the slag-metal reaction reaches the universal (or global) equilibrium, the inclusion composition should be identical to slag composition. However, in actual plants, the composition of inclusions is different from that of top slag. Therefore, in order to predict the formation behavior of inclusions during the ladle refining process, the process analysis not only based on the equilibrium study but also based on the kinetic study is necessary. In addition, because the inclusions are formed by the complicated refractory-slag-metal multiphase reactions, it is important to understand the complex multiphase reactions to control the inclusion formation behavior.

In the present study, therefore, the multiphase reactions among the Mn and V alloyed steel melt, the CaO–Al₂O₃–SiO₂–MgO–CaF₂ slag and the MgO refractory were investigated to understand the evolution mechanism of the inclusions using both high temperature experiments and ReSMI multiphase reactions simulation. The CaO/Al₂O₃ (=C/A) ratio of the ladle slag was varied to understand the effect of slag basicity on the formation behavior of inclusions. Moreover, the optimum range of slag basicity to suppress the harmful spinel inclusion will be proposed.

2. Experimental

Experiments were carried out using a high-frequency induction furnace as shown in Fig. 1. The quartz reaction chamber was initially evacuated prior to the experiments using a mechanical rotary pump. The chamber was subsequently filled with a highly purified Ar-3%H₂ gas mixture using a mass flow controller. An Fe-0.4%C-0.7%Si-1.4%Mn-0.2%V alloy (600 g) was placed in a fused MgO crucible (52 mm ID, 60 mm OD, 120 mm H) with a graphite heater for induction heating, which was surrounded by insulation. The steel with above composition was prepared using a vacuum induction melting furnace. Impurities in the Ar-3%H₂ gas mixture were removed by passing the gas through Drierite (W.A Hammond Drierite Co. Ltd., Xenia, OH), silica gel and Mg turnings at 723 K.

The experimental temperature was 1 873 K and tempera-

ture was controlled within ± 2 K using a B-type (Pt-30%Rh/Pt-6%Rh) thermocouple and a proportional integral differential controller. After the temperature reached 1 873 K, an Fe-16%Al alloy prepared using an induction furnace was added into the Fe–C–Si–Mn–V steel melt under an inert atmosphere to control the initial Al content (0.05%). The steel was maintained for 30 min to ensure a homogeneous composition.

The slag was prepared with a mixture of reagent grade CaO, calcined from CaCO₃ at 1 273 K, SiO₂, Al₂O₃, MgO, and CaF₂, and powder mixture was melted using a vertical resistance furnace at 1 873 K. The pre-melted slag (50 g) was injected through the quartz tube. Compositions of the pre-melted slags are listed in Table 1 and shown in Fig. 2. The C/A ratio of the slag was varied from 0.9 to 3.3. The moment of contact between the slag and liquid steel was taken as the starting time of the refractory-slag-metal reaction. After a certain reaction period, the liquid steel and slag samples were quickly taken using quartz suction tube and steel rods, respectively. The metal and slag samples were rapidly quenched by dipping them into the brine.

After the experiments, the steel samples were prepared for chemical analysis. The oxygen content was determined using a combustion analyzer (NO, TC-300, LECO), and the steel composition was obtained using inductively coupled plasma – atomic emission spectrometry (ICP-AES, ACROS, SPECTRO). An automatic feature analysis (AFA) system with a scanning electron microscopy – energy dispersive spectrometry (SEM-EDS, JSM-7800, JEOL) system was employed to characterize the inclusions. Chemistry, morphology and population statistics were obtained using this system. The accelerating voltage was 15 kV and the inclu-

Fig. 1. Schematic diagram for the experimental apparatus.

Table 1. Initial and final compositions of slags and metals in the present experiments.

C/A	Initial slag compositions (wt%)					Final slag compositions (wt%)				
	CaO	SiO ₂	Al ₂ O ₃	MgO	CaF ₂	CaO	SiO ₂	Al ₂ O ₃	MgO	CaF ₂
0.9	30	15	35	10	10	30.0 (± 2.0)	14.0 (± 2.3)	27.5 (± 1.0)	19.6 (± 1.0)	9.6 (± 1.0)
1.2	35	15	30	10	10	34.4 (± 0.4)	13.3 (± 1.0)	27.9 (± 1.0)	18.1 (± 1.0)	9.1 (± 1.3)
1.8	40	15	25	10	10	39.2 (± 0.5)	11.2 (± 1.0)	27.9 (± 1.0)	14.9 (± 1.0)	9.2 (± 1.2)
2.3	45	15	20	10	10	47.7 (± 2.1)	14.7 (± 2.1)	20.3 (± 1.0)	12.5 (± 2.0)	9.9 (± 1.1)
3.3	50	15	15	10	10	50.3 (± 1.2)	14.7 (± 2.1)	15.3 (± 1.0)	10.3 (± 0.2)	9.9 (± 2.0)

sion diameter detection limit was 1 μm .

ReSMI multiphase reaction model was also conducted to predict the evolution of inclusions during the slag-metal-refractory reactions. Calculation conditions were set to be the same as that of the experimental conditions, and the compositional changes in molten steel and inclusions were predicted as a function of reaction time. Details related to the calculation procedure and process variables are

described in our previous article.³²⁾

3. Results and Discussion

3.1. Changes in Metal and Slag Compositions by Refractory-Slag-Metal Reactions

The changes in the content of each element of molten steel by refractory-slag-metal multiphase reactions are shown in Fig. 3. The ReSMI multiphase reaction model results are also shown in Fig. 3 as solid lines. The process simulation results will be discussed in detail later (in Section 3.4). Immediately after the addition of slag, the oxygen content in the melt drastically decreased to approx. 10 ppm. The aluminium content in the steel melt gradually decreases as the slag-metal reaction proceeds, while the silicon content slightly increases. This tendency originated from the reduction of SiO_2 in the slag by aluminium in molten steel as given in the following equation.

The magnesium and calcium were also transferred from slag to metal phase by Eqs. (2) and (3).

Since the analytical error of Mg and Ca significantly depends on the analysis environment such as the amount

Fig. 2. Experimental composition of the present study represented in the CaO-Al₂O₃-SiO₂-10MgO-10CaF₂ (wt%) phase diagram at 1 873 K. Calculated by FactSage7.1.

Fig. 3. Calculated and measured results of the composition of molten steel; (a) aluminum, (b) silicon, (c) magnesium (d) calcium and (e) oxygen at 1 873 K.

of solvent or purity of distilled water, *etc.*, there are some scatters in chemical analysis data for Mg and Ca. However, it was confirmed that the content of Mg and Ca increased at the early stage of the slag-metal reaction as shown in Figs. 3(c) and 3(d). These changes of metal composition caused the modification of inclusions during the slag-metal reaction.

The change of MgO content in the slag during the reaction is shown in Fig. 4. The ReSMI process simulation results, which will be discussed in detail later in Section 3.4, are also shown in Fig. 4 as solid lines. The MgO content in the slag increased with reaction time, which originated from a chemical dissolution of MgO from refractory to slag. When the C/A ratio of the slag was lower than 1.2, the MgO dissolution severely occurred, whereas a dissolution of MgO was relatively mild when the C/A of the slag was higher than 1.8.

It is certain that the amount of MgO dissolution increases with decreasing C/A ratio of the slag. Although MgO was not saturated in the initial slag, MgO was finally saturated by the dissolution of MgO from refractory to slag during the reaction. This was confirmed by XRD analysis as shown in Fig. 5. The slag samples taken at experimental temperature

(1 873 K) were rapidly quenched by dipping them into the brine within 5 seconds in order to avoid the crystallization during cooling. When the C/A ratio of the slag was 0.9, only the MgAl_2O_4 spinel peak was detected before the refractory-slag-metal reaction, which was expected from the

Fig. 4. Calculated and measured results of the MgO content in the slag at 1 873 K.

Fig. 5. Results XRD analysis of initial slag and final slag; (a) C/A=0.9, (b) C/A=1.2, (c) C/A=1.8, (d) C/A=2.3 and (e) C/A=3.3.

CaO–Al₂O₃–SiO₂–10%MgO–10%CaF₂ phase diagram shown in Fig. 2. However, MgO and spinel coexisted after 90 min since the slag-refractory reaction started. When the C/A ratio of the slag was 1.2 and 1.8, although the initial slag was fully liquid (viz. amorphous as quenched state), MgO was finally saturated during the slag-refractory reaction. The MgO peak was detected both in initial and final slags when the C/A ratio of the slag was higher than 2.0, which was also expected from the phase diagram shown in Fig. 2.

3.2. Inclusion Evolution in Molten Steel during Refractory-Slag-Metal Reactions

The SEM images of typical inclusions observed in molten steel at each C/A ratio of the slag are shown in Fig. 6. When the C/A ratio of the slag was 1.2 or less, the alumina and spinel inclusions were mainly observed at the early stage of the reaction, *i.e.*, 5 min. However, both the spinel and the liquid oxide inclusion which consists of the CaO–Al₂O₃–SiO₂–MgO system mainly observed at the final stage of the reaction. When the C/A ratio of the slag was 1.8 or higher, the spinel inclusion was mainly observed at the early stage of the reaction. However, it was modified to the liquid oxide inclusion at the final stage of the reaction when the C/A ratio of the slag was from 1.8 to 2.3. The pure MgO inclusion was mainly observed at the final stage of the reaction when the C/A ratio of the slag was 3.3.

Approximately 50 inclusions per sample were observed by AFA-SEM analysis. The observed inclusions were classified into four types, viz. Al₂O₃, MgAl₂O₄ spinel, liquid oxide and MgO, based on the stable phase at the experimental temperature (1 873 K) which was confirmed using “Equilib” and “Phase Diagram” modules in FactSage™7.1 software.³⁴⁾ The variation of the relative fraction of each type of inclusion is represented as a function of reaction time in Fig. 7. The initial inclusion was mainly Al₂O₃, which originated from an Al deoxidation. When the C/A ratio of the slag was 1.2 or less, *i.e.*, Figs. 7(a) and 7(b), some of alumina inclusions, which initially formed before slag addition, transformed to spinel inclusion and liquid oxide inclusion 5 min after the refractory-slag-metal reaction occurred. The fraction of spinel inclusion increased to 60–70% until the reaction time goes up to 15 min. After 15 min since the reaction started, however, the fraction of spinel decreased, whereas that of liquid oxide inclusion increased.

When the C/A ratio of the slag was 1.8 and 2.3, *i.e.*, Figs. 7(c) and 7(d), the inclusion evolution procedure was very similar to each other. The Al₂O₃ inclusion transformed to spinel and the liquid oxide inclusions 5 min after the refractory-slag-metal reaction. At that time, the fraction of spinel inclusion was 50–60%, followed by an increase up to 70–75% 15 min after the reaction. After 30 min since the reaction started, however, most of the spinel inclusions were modified to liquid oxide inclusion.

When the C/A ratio of the slag was 3.3, *i.e.*, Fig. 7(e), the Al₂O₃ inclusion transformed to spinel, of which fraction is about 70% 5 min after the refractory-slag-metal reaction. Then the fraction of spinel continually decreased, whereas that of liquid oxide inclusion increased with the reaction time to 15 min. After 30 min since the reaction started, spinel inclusion transformed to MgO particle in molten steel. The relative fraction of MgO inclusion increased to about

Fig. 6. SEM images of the typical observed inclusions at early (5-min) and final (90-min) stage of the reaction.

50% until the final stage of the reaction.

From the changes in the composition of molten steel in conjunction with the relative fractions of each type of inclusion with the reaction time, the steps of the inclusion evolution in molten steel by the refractory-slag-metal multiphase reactions are considered as follows:

Step 1) Alumina inclusion is initially formed by an Al deoxidation, before addition of the slag.

Step 2) After slag addition, the composition of molten steel changes by the refractory-slag-metal reactions. MgO is dissolved to the slag, resulting in the saturation condition of slag by MgO, *i.e.*, the activity of MgO in molten slag converges to unity. Consequently, Mg and Ca are transferred from slag to molten steel according to Eqs. (2) and (3).

Step 3) Magnesium, transferred to molten steel, reacts with Al₂O₃ inclusion based on Eq. (5). Consequently, the spinel inclusion is formed in the steel.

Step 4) Spinel inclusion formed at step 3 is modified to liquid oxide inclusion by the reaction with Ca based on Eq. (6). At the same time, the MgO–Al₂O₃–CaO inclusions partly reacted with dissolved silicon. Consequently, the spinel inclusions are modified to the CaO–Al₂O₃–MgO–SiO₂ system liquid inclusions.

3.3. Effect of Activity of Slag Component on Formation Behavior of Inclusions

The inclusions formed during the ladle refining process are determined according to the composition of molten steel changing with reaction time. Especially, the contents of Mg

Fig. 7. Change in the relative fraction (population) of the inclusions in molten steel; (a) $C/A=0.9$, (b) $C/A=1.2$, (c) $C/A=1.8$, (d) $C/A=2.3$ and (e) $C/A=3.3$.

and Ca in molten steel, which influenced to the modification of spinel inclusion, are significantly affected by the activity of slag components such as MgO, CaO and Al_2O_3 . From Eqs. (2) and (3), it can be predicted that the content of Mg and Ca in the steel increases with increasing activity of MgO and CaO, respectively, and decreasing the activity of Al_2O_3 in the slag. Thus, the driving force of the spinel formation is higher as the activity of MgO in the slag increases, while that of liquid oxide formation becomes higher with increasing activity of CaO in the slag.

The activities of slag components at initial and final compositions (Table 1) are plotted against the C/A ratio of the slag in Fig. 8. The activity was calculated with an aid of computational thermochemical software package, FactSageTM7.1.³⁴⁾ The activity of MgO and CaO in the initial slag increases with increasing C/A ratio of the slag. Especially, the activity of MgO in the initial slag is unity when the C/A ratio of the slag is greater than 2.3. On the other hand, the activity of Al_2O_3 and SiO_2 in the initial slag decreases by increasing the C/A ratio of the slag. A difference in the activity of CaO, Al_2O_3 and SiO_2 between initial and final slags is very small. However, there is a significant difference in MgO activity between initial and final slags when the C/A ratio of the slag is lower than 2.3.

The relative fraction of each inclusion type at the early

Fig. 8. The activity of component of initial slag and final slag calculated with an aid of computational thermochemical software package, FactSageTM7.1.

stage of the reaction (5 min) as a function of C/A ratio of the slag is shown in Fig. 9. Although the activity of CaO increases with increasing C/A ratio of the slag, the fraction of spinel inclusion increases by increasing the C/A ratio of the slag. This means that the influence of MgO activity on the formation tendency of inclusion is higher than that of CaO, viz. Equation (5) is more dominant than Eq. (6) at the early stage of the reaction.

The fraction of each inclusion type at the final stage of the reaction (90 min) as function of C/A ratio of the slag is shown in **Fig. 10**. The fraction of spinel inclusion at the final stage of the reaction decreases by increasing the C/A ratio of the slag from 0.9 to 1.8, followed by a disappearance at C/A=2.3. Alternatively, MgO inclusion was formed in molten steel at C/A=3.3. Although the activity of MgO is unity regardless the C/A ratio of the slag at the final stage of the reaction, the spinel fraction decreased by increasing the C/A ratio of the slag. This means that the influence of CaO activity on the formation of inclusion is greater than that of MgO, viz. Equation (6) is more dominant than Eq. (5) at the final stage of the reaction.

The activity of Mg and Ca in equilibrium with the final slag can be calculated based on the equilibrium constant of Eqs. (2) and (3) (K_2 and K_3), respectively, as follows.

$$K_{2 \text{ or } 3} = \frac{a_M^3 \cdot a_{Al_2O_3}}{a_{MO}^3 \cdot a_{Al}^2} \quad (7a)$$

$$a_M = \left(\frac{K_{2 \text{ or } 3} \cdot a_{MO}^3 \cdot a_{Al}^2}{a_{Al_2O_3}} \right)^{\frac{1}{3}} = \left(\frac{K_{2 \text{ or } 3} \cdot f_{Al}^2 \cdot [\text{wt}\%Al]^2}{a_{Al_2O_3}} \right)^{\frac{1}{3}} \quad (7b)$$

where a represents the activity of M and MO (M=Mg, Ca). The f_{Al} represents the activity coefficient of Al with refer-

Fig. 9. Change in the relative fraction (population) of the inclusions in molten steel at early stage of the reaction (5-min) as function of C/A ratio of the slag.

Fig. 10. Change in the relative fraction (population) of the inclusions in molten steel at final stage of the reaction (90-min) as function of C/A ratio of the slag.

ence to 1 wt% standard state, which can be calculated using Wagner formalism as follows:

$$\log f_i = \sum e_i^j \cdot [\text{wt}\%j] \quad (8)$$

where i and j represent the dissolved elements in molten steel, e_i^j is the interaction parameter of j for i . The interaction parameters and the equilibrium constant of Eqs. (2) and (3) used in this study are listed in **Tables 2** and **3**.³⁵⁻³⁷⁾

The calculated activity of Mg and Ca in equilibrium with final slag is plotted against the C/A ratio of the slag in **Fig. 11**, wherein both of the activities of Mg and Ca increase with increasing C/A ratio. Since the Al_2O_3 activity of the slag decreases by increasing the C/A of the slag, the activity of Mg increases with increasing C/A ratio of the slag based on Eq. (7b) even though the activity of MgO is unity regardless of the C/A ratio. When the C/A ratio of the slag is 3.3, MgO inclusion was formed although the Ca activity is the highest. This phenomenon can be explained by the following discussions.

The MgO formation reaction is represented by Eq. (9) and the critical activity of Mg to form MgO inclusion (a_{Mg}^*) can be calculated based on the equilibrium constant of Eq. (9).

Table 2. First and second order interaction coefficients; e_i^j , (r_i^j).

i	j								
	Mn	Si	Cr	V	C	Al	O	Mg	Ca
Al	-0.004	0.056	0.0096	-	0.091	0.044	-1.98	-0.13	-0.047
O	-0.021	-0.066	-0.052	-0.14	-0.45	-1.17	-0.2	-300 ³⁶⁾ (16 000)	-990 ³⁶⁾ (42 000)

All data at 1 873 K and the ones without notation are from Ref. 35).

Table 3. Equilibrium constant used in this study.^{35,37)}

No.	Reactions	$\log K$	Ref.
R1	$(Al_2O_3) = 2[Al] + 3[O]$	$20.57 - 64\,000/T$	35
R2	$(MgO) = [Mg] + [O]$	$-4.28 - 4\,700/T$	37
R3	$(CaO) = [Ca] + [O]$	$-3.29 - 7\,220/T$	37
R4	$3(MgO) + 2[Al] = 3[Mg] + (Al_2O_3)$	$-33.41 + 49\,900/T$ ($3 \times R2 - R1$)	35, 37
R5	$3(CaO) + 2[Al] = 3[Ca] + (Al_2O_3)$	$-30.44 + 42\,340/T$ ($3 \times R3 - R1$)	35, 37

Fig. 11. The calculated activity of Mg and Ca equilibrated with final slag as function of the C/A ratio of the slag (filled square and filled circle, respectively). And critical activity of Mg of forming MgO inclusion (open square).

$$[\text{Mg}] + [\text{O}] = (\text{MgO})_{\text{inclusion}} \quad \text{..... (9)}$$

$$K_9 = \frac{a_{\text{MgO}}}{a_{\text{Mg}} \cdot a_{\text{O}}} \quad \text{..... (10a)}$$

$$a_{\text{Mg}}^* = \left(\frac{a_{\text{MgO}}}{a_{\text{O}} \cdot K_9} \right) = \left(\frac{a_{\text{MgO}}}{f_{\text{O}} \cdot [\text{wt}\% \text{O}] \cdot K_9} \right) \quad \text{..... (10b)}$$

where the activity coefficient of oxygen (f_{O}) was calculated using Eq. (8). The activity of MgO inclusion (a_{MgO}) was assumed unity since pure MgO was formed in molten steel in the present study. The interaction parameters and the equilibrium constant of Eq. (9) used in this study are listed in Tables 2 and 3.^{35–37)}

The a_{Mg}^* value to form MgO inclusion is also shown in Fig. 11 with the activity of Mg and Ca in molten steel equilibrated with final slag. When the C/A ratio of the slag is lower than 3.0, it is expected that pure MgO inclusion does not form because the Mg activity in molten steel is lower than a_{Mg}^* value. On the other hand, the Mg activity in molten steel is higher than a_{Mg}^* value at C/A=3.3, resulting in the formation of pure MgO inclusion. This thermodynamic estimation corresponds to the experimental findings that MgO inclusion was observed at the final stage of the reaction when the C/A ratio of the slag was 3.3 as shown in Figs. 6 and 10.

3.4. Simulation of Inclusion Evolution using ReSMI Multiphase Reaction Model

The ReSMI multiphase reaction model results are already shown in Figs. 3 and 4 as solid lines with the experimental data and it is confirmed that the calculated results are in good agreement with the experimental results in the viewpoint of slag-metal (*i.e.*, steel chemistry) and refractory-slag (*i.e.*, MgO dissolution from refractory) reactions. It is interesting that Mg and Ca pick-up from slag to metal phase is predicted to increase from about 7 to 11 ppm and from about 1 to 5 ppm as the C/A ratio of the slag increases from 0.9 to 3.3. The calculated Mg pick-up exhibits a good correspondence to the measured result, while there are some scatters in the prediction of Ca pick-up, which is probably due to the analytical errors.

Because the effect of Mg and Ca on the stability of inclusions in the steel melts are significantly meaningful, a phase stability diagram of the inclusions in the Fe-0.4%C-0.7%Si-1.4%Mn-0.2%V-0.015%Al melt containing Mg and Ca at 1873 K is newly calculated with an aid of computational thermochemical software package, FactSageTM7.1.³⁴⁾ As shown in Fig. 12, six solid phases, viz. MgO, MgAl_2O_4 spinel, Al_2O_3 , $\text{CaAl}_{12}\text{O}_{19}$, CaAl_4O_7 and Ca_2SiO_4 , and liquid oxide phase are in equilibrium with molten steel in the content range of Mg from 0.1 to 100 ppm, and Ca from 0.01 to 10 ppm. Spinel is the stable phase when the Mg content ranges from about 1 to 10 ppm. However, when the Ca content in molten steel is higher than about 1 ppm, the liquid oxide phase becomes stable. When the Mg content in the steel is higher than 10 ppm, pure MgO is stable regardless of Ca content in molten steel.

The symbols in Fig. 12 represent the Mg and Ca traces in

Fig. 12. Phase stability diagram of inclusions with iso-oxygen contours in the Fe-0.4C-0.7Si-1.4Mn-0.2V-0.015Al melt containing Mg and Ca at 1873 K. Calculated by FactSage7.1.

molten steel according to the reaction time calculated using the ReSMI multiphase reaction model. Alumina inclusion is stable at the initial stage of the reaction. When the C/A ratio of the slag is lower than 1.2, the stable phase changes from alumina to spinel within 3 min. The evolution traces of inclusions follow the dashed lines with an increase of Ca content (less than 1 ppm) but still remain in the spinel predominance area through the entire holding time, *i.e.*, 90 min (Ca < 1 ppm).

However, when the C/A ratio of the slag is 1.8 and 2.3, the stable phase rapidly changes from alumina to spinel within 1 min. The evolution traces of inclusions follow the dashed lines with an increase of Ca content for about 10 min, after which the traces get into the liquid inclusion predominance area (Ca ≥ 1 ppm) and remain until 90 min (Ca ≈ 2 ppm). Finally, when the C/A ratio of the slag is 3.3, the Ca content is predicted to exceed the threshold of the spinel-liquid transition within 3 min, but Mg content also exceeds 10 ppm at about 15 min and thus the evolution trace crosses the phase boundary from liquid oxide to MgO predominance area.

The change in the relative fraction of each inclusion type during the refractory-slag-metal reaction, which was calculated using the ReSMI multiphase reaction model is shown in Fig. 13. It is interesting that the calculation results exhibit a tendency which is relatively similar to that of the measured results shown in Fig. 7. When the C/A ratio of the slag is lower than 1.2, the spinel inclusion increases with the reaction time at the early stage of the reaction (until 15–20 min) at the expense of alumina inclusion, after which the spinel inclusion decreases while the liquid oxide inclusion increases. After 40 min, the fraction of spinel and liquid oxide inclusions are kept almost constant.

In case of the C/A ratio of the slag is 1.8–2.3, the alumina inclusion rapidly transforms to the spinel inclusion within 10 min. Afterward, the spinel is continuously modified to the liquid oxide and is entirely modified to the liquid inclusion at about 30–35 min. Finally, when the C/A ratio of the slag is 3.3, the transformation from alumina to spinel is completed within approx. 5 min, followed by a modification to liquid oxide within 20 min. Afterward, the MgO inclusion drastically increases at the expense of liquid inclusion,

Fig. 13. Calculated results using ReSMI multiphase reaction model for the change in the relative fraction (population) of the inclusions in molten steel at 1 873 K.

Fig. 14. The schematic summary of the formation behavior of inclusions at different ranges of C/A ratio of the slag.

which is finished at about 25 min.

From the results of ReSMI multiphase reaction model and experiments, the formation behavior of the inclusion can be

divided into three cases according to the C/A ratio of the slag as shown in **Fig. 14**.

Case 1) $(\text{CaO}/\text{Al}_2\text{O}_3)_{\text{slag}} < 1.5$.

Since the initial activity of MgO and CaO in the slag are relatively low and Al_2O_3 activity is relatively high, the transfer of Mg and Ca from slag to molten steel is small at the early stage of the reaction. However, the dissolution of MgO is highly occurred due to chemical reaction between refractory and molten slag. Therefore, the spinel inclusion is formed in molten steel. Afterward, although the spinel inclusion is partly modified to liquid oxide inclusion by Ca and Si, the spinel cannot be completely modified into liquid oxide inclusions because the transferred content of Ca is relatively small (less than 1.5 ppm).

Case 2) $1.5 < (\text{CaO}/\text{Al}_2\text{O}_3)_{\text{slag}} < 2.5$

MgO dissolution from refractory to slag occurs relatively little, and Mg and Ca transferred into molten steel about 8 ppm and 2 ppm, respectively. As a result, even the spinel inclusion is formed at the early stage of the reaction, all the spinel inclusions are modified to liquid oxide inclusions during the reaction.

Case 3) $(\text{CaO}/\text{Al}_2\text{O}_3)_{\text{slag}} > 3.0$.

MgO dissolution does not occur because the MgO is already saturated in the initial slag. Since the initial activities of MgO and CaO in the slag are relatively high and Al_2O_3 activity is relatively low, the transfer of Mg and Ca from slag to molten steel drastically occurs at the early stage of the reaction. Thus, the modification from alumina to spinel and then to liquid oxide is completed within 20 minutes. Magnesium is also dissolved up to about 11 ppm into the steel melt due to low activity of Al_2O_3 in the slag. As a result, although the Ca increases to about 4 ppm, MgO inclusion is formed in molten steel at the final stage of the reaction.

Therefore, it is recommended that the C/A ratio of the ladle slag should be controlled from about 1.5 to 2.5 in order to suppress the harmful solid inclusion such as spinel during the ladle refining process.

4. Conclusions

The multiphase reactions among the Mn-V-alloyed specialty steel melt, the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{MgO}-\text{CaF}_2$ slag, and the MgO refractory were investigated to understand the evolution mechanism of the inclusions by employing high temperature experiments in conjunction with the ReSMI multiphase reactions simulation. The $\text{CaO}/\text{Al}_2\text{O}_3$ ($=C/A$) ratio of the ladle slag was varied to understand the effect of slag basicity on the formation behavior of inclusions. The major findings of the present study are as follows.

(1) The driving force of the formation of spinel inclusion was strongly affected by the activity of MgO in the initial slag at the early stage of the reaction.

(2) The activity of MgO converged to unity during the reaction. Therefore, the formation behavior of inclusion was affected by the activity of CaO and Al_2O_3 in the slag rather than that of MgO at the final stage of the refining reaction. The driving force of the modification reaction from spinel to liquid oxide inclusion was higher as the C/A ratio of the slag increased. However, if the C/A ratio of the slag was greater than critical limit (e.g., 3.0 in the present study),

MgO inclusion was formed in the molten steel.

(3) The formation behavior of the inclusion could be divided into three cases with the C/A ratio of the slag as follows.

a. $C/A < 1.5$; Alumina $\rightarrow$ Spinel $\rightarrow$ Spinel and Liquid inclusion.

b. $1.5 < C/A < 3.0$; Alumina $\rightarrow$ Spinel $\rightarrow$ Liquid inclusion,

c. $C/A > 3.0$; Alumina $\rightarrow$ Spinel $\rightarrow$ Liquid inclusion $\rightarrow$ MgO.

(4) It was recommended that the C/A ratio of the ladle slag should be controlled from about 1.5 to 2.5 in order to suppress the harmful solid inclusion such as spinel during the ladle refining process.

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