Evolution of Mg–Al-based Inclusions with Changes in Mg Content during Ladle Treatment Based on a Coupled Reaction Model

Jeong-In KIM and Sun-Joong KIM*

Department of Material Science & Engineering, Chosun University, 309, Pilmun-daero, Dong-gu, Gwangju, 61452 Republic of Korea.

(Received on August 16, 2019; accepted on September 24, 2019)

In the steelmaking process, MgAl_2O_4 spinel inclusions diminish steel qualities and cause nozzle clogging based on the high melting point and low deformation of MgAl_2O_4 . Typically, MgAl_2O_4 spinel inclusions are generated from Al_2O_3 inclusions with increasing MgO content, meaning ladle treatment does not represent an equilibrium state. However, complex reactions simultaneously occur between molten steel, slag, inclusions, refractory, and alloying elements during ladle treatment. Therefore, it is necessary to develop a kinetic model to predict compositional changes in molten steel, slag, and the inclusions during ladle treatment. Such a kinetic model must be able to simulate the generation of MgAl_2O_4 spinel inclusions from Al_2O_3 to control such inclusions. Additionally, MgAl_2O_4 spinel inclusions can evolve into MgO-rich inclusions with gradually increasing MgO content in Mg–Al-based inclusions. In this study, we developed an enhanced kinetic model based on a coupled reaction model with the compositional changes in Mg–Al-based inclusions. We also investigated the influence of the CaO/SiO₂ ratio in slag on the generation of spinel inclusions under industrial conditions for a 210-ton steel sample.

KEY WORDS: ladle treatment; coupled reaction model; slag basicity; MgAl_2O_4 spinel inclusions; MgO inclusions.

1. Introduction

In the steelmaking process, non-metallic inclusions weaken the physicochemical properties of steel products. In particular, MgAl_2O_4 spinel inclusions are harmful inclusions because they can lower the quality of final steel products based on the high melting point and low deformation of MgAl_2O_4 .^{1,2)} Furthermore, MgAl_2O_4 has a stronger adhesive tendency with nozzle materials compared to Al_2O_3 and MgO.³⁾ Therefore, spinel inclusions influence nozzle clogging, which can lead to operational problems, meaning spinel inclusions must be controlled and suppressed during ladle treatment.

Many previous studies have analyzed spinel formation mechanisms experimentally. Nishi and Shinme⁴⁾ forced spinel generation from Al_2O_3 inclusions using 15 kg of SUS 304 under an Ar gas flow in a high-frequency induction furnace. They reported that even with an Mg content in steel of less than 1 ppm by mass, the MgO content in Al_2O_3 inclusions increased after Al de-oxidation based on reactions with Mg. This indicates that Al_2O_3 inclusions evolve into spinel inclusions with increasing MgO content, which is supplied by the Mg in steel. Okuyama *et al.*⁵⁾ investigated the influence of MgO in slag on spinel generation using 20 kg of molten steel containing 16%Cr-0.1%Al under an Ar gas flow in a high-frequency vacuum induction furnace.

They discovered that the increasing MgO content in Al_2O_3 inclusions is supplied by the Mg in steel based on the reduction of MgO in slag. Additionally, they evaluated the influence of the CaO/SiO₂ ratio in slag on spinel generation. They reported that the MgO content in Al_2O_3 inclusions increased when the CaO/SiO₂ ratio increased. Harada *et al.*⁶⁾ analyzed the influence of the CaO/SiO₂ ratio in slag on spinel generation using 30 kg of molten steel under an Ar gas flow. According to their results, the MgO content in Al_2O_3 inclusions increased following Al addition and spinel inclusions were observed. Furthermore, when the CaO/SiO₂ ratio in slag increased, the activity of MgO in the slag and the diffusivity rate of Mg in the steel also increased. Park and Kim⁷⁾ studied the effects of CaO– Al_2O_3 –MgO system slag on spinel generation using Fe-16%Cr ferritic stainless steel. MgO-rich inclusions were observed in their research, indicating that MgO-rich inclusions can be generated in addition to spinel inclusion. Todoroki and Mizuno⁸⁾ investigated the influence of MgO-containing slag with Al content on spinel generation in the steelmaking process. They also analyzed the morphology of inclusions, including spinel and MgO-rich inclusions. Harada *et al.*⁹⁾ evaluated the dissolution of MgO in a crucible in terms of spinel generation. They observed the formation of spinel inclusions without the addition of Mg or MgO-containing slag. Liu *et al.*¹⁰⁾ reported the influence of MgO-based refractory on spinel generation based on an experiment on the rotation of a MgO rod. They discovered that MgO-based refractory can supply the Mg content in steel, resulting in spinel generation.

* Corresponding author: E-mail: ksjoong@chosun.ac.kr
DOI: <https://doi.org/10.2355/isijinternational.ISIJINT-2019-488>

Furthermore, in another study,¹¹⁾ it was concluded that the diffusivity of MgO led to spinel generation on the surface of an Al₂O₃ rod.

Based on the studies above, Eq. (1) represents the formation mechanism of spinel generation. First, Al₂O₃ inclusions are generated by Al de-oxidation. Al₂O₃ inclusions evolve into MgAl₂O₄ spinel inclusions through reactions with the Mg content in steel, which is supplied by the reduction of slag and dissolution of MgO-based refractory. Additionally, if the MgO content in spinel inclusions increases gradually, MgO-rich inclusions can be generated from spinel inclusions. Therefore, the evolution of Mg–Al-based inclusions indicates that ladle treatment does not represent an equilibrium state.

However, during ladle treatment, complex reactions simultaneously occur between molten steel, slag, inclusions, refractory, and alloying additions. Therefore, it is nontrivial to control and suppress the behaviors of spinel generation during ladle treatment. Therefore, a kinetic model is required to predict compositional changes in molten steel, slag, and inclusions during ladle treatment. Previous studies have developed such kinetic models. For example, Peter *et al.*¹²⁾ presented the *Metsim* model, which can simulate industrial-scale samples sizes of 123 tons and 151 tons. This model can calculate compositional changes in molten steel and slag based on the mass transfer determined by Ar flow rate. Shu *et al.*^{13,14)} developed a ladle tank recirculation model called the *Inclusion Composition in Steel* (ICS) model. In this model, the ladle furnace is divided into several tanks that are circulated using the stirring energy generated by an Ar flow. This model can predict compositional changes in molten steel, slag, and inclusions, such as Al₂O₃, MgAl₂O₄, CaO·6Al₂O₃, and CaO–MgO–Al₂O₃, based on a 210-ton sample size. Van Ende *et al.*¹⁵⁾ presented the *Effective Equilibrium Reaction Zone* (EERZ) model. In the EERZ model, the volume of the reaction interface area is considered for reactions between steel and slag. The volume of the reaction interface area can also be applied as the mass transfer. This model is reliable for a sample size of 165 tons and can simulate the generation of Al₂O₃, MgAl₂O₄, CaO·3Al₂O₃, and CaO·6Al₂O₃ inclusions, as well compositional changes in steel and slag. Ren *et al.*^{16–19)} developed a kinetic model based on *FactSage macro processing* to predict the formation of inclusions using Al-killed steel and Al–Ti-killed steel. The reactions between steel and inclusions were assumed to be equilibrated, and the reactions between bulk area and interface area in steel and slag were simulated by mass transfer. In the case of Ca treatment, the molten steel zone was divided into the Ca-rich zone and the bulk steel zone, and their model showed the reliability to simulate the formation of CaO–Al₂O₃ and CaS inclusions based on the data of 311-ton scale. Furthermore, the amounts of Al₂O₃, Al₂O₃–TiO_x and SiO₂–MnO–FeO inclusions can be calculated with their model. The kinetic model can be applied for the tundish process based on 25-ton scale, then the compositions of Al₂O₃, CaO, MgO and CaS in inclusions were evaluated.¹⁹⁾ Harada *et al.*^{20–22)} developed a kinetic model called the *LF* model based on coupled reactions. This model considers the complex reac-

tions between molten steel, slag, inclusions, refractory, and alloying elements. Reactions between molten steel and slag, and between molten steel and inclusions originating from slag are calculated using the double-film theory.^{23,24)} This model can simulate compositional changes in steel, slag, and inclusions, such as Al₂O₃, MgAl₂O₄, CaO·Al₂O₃, and MnO·SiO₂, based on three inclusion behaviors using a sample size of 165 tons. However, a kinetic model considering the compositional changes in Mg–Al-based inclusions has not been reported.

In this study, we enhanced a kinetic model based on coupled reactions to predict compositional changes in steel, slag, and inclusions during ladle treatment. In the enhanced model, compositional changes in Mg–Al-based inclusions resulting from Al₂O₃ and MgO inclusions are considered. We investigated the kinetic model to clarify the influence of the CaO/SiO₂ ratio in slag on spinel generation under industrial conditions with a 210-ton sample size.

2. Model Description

Figure 1 presents a schematic diagram of the enhanced kinetic model based on coupled reactions (also referred to as the coupled reaction model) for simulating the reactions between molten steel, molten slag, inclusions, refractory, and alloying additions. The details of reactions and inclusion behaviors in the model have been described in previous publications.^{20–22)} In the coupled reaction model, the following four main types of reactions and three types of inclusion behaviors were considered:

- (a) Reactions between molten steel and slag
- (b) Reactions between slag and inclusions originating from slag
- (c) Dissolution of refractory material into the molten steel and slag phase
- (d) De-oxidation reactions based on the addition of alloying elements
- (e) Inclusion behaviors
 - A. Flotation of de-oxidation products and inclusion originating from slag
 - B. Entrapment of slag
 - C. Agglomeration of inclusions

Fig. 1. Schematic diagram of the enhanced kinetic model (coupled reaction model).

In this paper, the original coupled reaction model and the improvements implemented in this study are described. Reactions (a) and (b) were calculated based on the double-film theory.^{23,24} A phase can be divided into a bulk zone and interface zone, such as the steel phase and slag phase in Fig. 1, and reactions in the interface zones of adjacent phases are assumed to be equilibrated. The reactions between the bulk zone and interface zone in each phase are considered as flux density in terms of mass transfer. The mass transfer coefficient of each component is calculated based on stirring energy using the Ar flow rate and conditions of the ladle furnace.

In previous models, the components in the slag were CaO, SiO₂, MgO, Al₂O₃, MnO, and CaS. In the enhanced model, the slag phase also includes a CaF₂ component. Typically, CaF₂ is included in slag during ladle treatment because CaF₂ is able to influence the melting point and viscosity of slag, as well as the desulfurization of molten steel.²⁵ In the enhanced model, for calculating the activities of slag components, including CaF₂, the thermodynamic data from *Factsage 7.1*²⁶ were incorporated via *Chemapp*.²⁷ The activity coefficients of components in the metal phase were calculated using data from the Japan Society for the Promotion of Science.²⁸

2.1. Generation of MgAl₂O₄ and MgO Inclusions through Reactions between Al₂O₃ Inclusions and Mg in Steel

To simulate the generation of MgAl₂O₄ and MgO inclusions, the compositions of Al₂O₃ inclusions were changed based on reactions with the Mg in steel using a stability diagram²⁹ of Mg–Al–O in steel. First, for the generation of spinel inclusions, the concept of a stability diagram between [Al] and [Mg] was applied based on the following equations:

$$\log K_{(1)} = 34.37 - 46\,950/T \dots\dots\dots (2)$$

$$[\text{Mg}]^{\text{spinel*}} = \left(\frac{1}{K_{(1)}} \cdot \frac{a_{\text{MgAl}_2\text{O}_4}^3}{a_{\text{Al}_2\text{O}_3}^4} \cdot \frac{f_{[\text{Al}]}^2}{f_{[\text{Mg}]}^3} \cdot [\text{Al}]^2 \right)^{1/3} \dots\dots (3)$$

Equation (1) can be converted into Eq. (3) using $[\text{Mg}]^{\text{spinel*}}$, which represents the equilibrated content of [Mg] between Al₂O₃ and MgAl₂O₄ spinel. In Eq. (3), K is the equilibrium constant calculated using Eq. (2).²⁾ T is the temperature, a_i and f_i are the activity and activity coefficient of element i , respectively. $[i]$ and (i) are the concentrations of element i in the molten steel and slag (or inclusions), respectively.

Figure 2 presents an Al–Mg–O-based stability diagram considering previous results.³⁰⁾ Regarding the previous results in Fig. 2, the stable state of inclusions transitions into the formation of spinel with increasing reaction time. It is well known that Al₂O₃ inclusions are converted into MgAl₂O₄ spinel inclusions with increasing [Mg] content in Al₂O₃ inclusions.

Based on the equilibrium state of inclusions with changing steel compositions, the formation of spinel was simulated using the enhanced model. When $[\text{Mg}]^{\text{bulk}}$ is smaller

Fig. 2. Stability diagram of a Mg–Al–O system considering previous results.

Fig. 3. Activity changes of Al₂O₃, MgO, and spinel in MgAl₂O₄ with changing spinel composition.

than $[\text{Mg}]^{\text{spinel*}}$, Al₂O₃ is stable, where $[\text{Mg}]^{\text{bulk}}$ is the concentration of Mg in the molten steel. In contrast, when $[\text{Mg}]^{\text{spinel*}}$ is greater than $[\text{Mg}]^{\text{bulk}}$, the generation of spinel inclusions begins. Based on Eq. (3), the activities of Al₂O₃ and MgAl₂O₄ spinel were calculated in the enhanced model using reported data,²⁹⁾ as shown in **Fig. 3**.

Next, the generation of MgO inclusions was simulated using the following equations:

$$\log K_{(4)} = 33.09 - 50\,880/T \dots\dots\dots (5)$$

$$[\text{Mg}]^{\text{MgO sat.}} = \left(\frac{1}{K_{(4)}} \cdot \frac{a_{\text{MgO}}^4}{a_{\text{MgAl}_2\text{O}_4}} \cdot \frac{f_{[\text{Al}]}^2}{f_{[\text{Mg}]}^3} \cdot [\text{Al}]^2 \right)^{1/3} \dots\dots (6)$$

Equation (4) represents the generation of MgO inclusions from spinel, and can be transformed into Eq. (6) using the activity terms and equilibrium constant $K_{(4)}$.²⁾ Based on Eq. (6), the equilibrium concentration of Mg in the steel between spinel and MgO, denoted $[\text{Mg}]^{\text{MgO sat.}}$, can be calculated in the enhanced model. Consequently, MgO inclusions

are generated when $[Mg]^{bulk}$ is greater than $[Mg]^{MgO sat.}$

Fujii *et al.*²⁹⁾ investigated the activity changes in spinel with varying spinel compositions. Figure 3 presents the activity changes in Al_2O_3 , MgO , and spinel with compositional changes in $MgAl_2O_4$ spinel.²⁹⁾ In Eq. (3), $[Mg]^{spinel*}$ is affected by each activity in spinel. In previous models, the generation of spinel was simulated when the mole fraction of MgO and Al_2O_3 in the spinel was halved and the activity in the spinel was fixed.^{12–22)} However, in the proposed enhanced model, the activities of Al_2O_3 , MgO , and spinel change with increasing MgO content in Mg – Al -based inclusions.

Compositional changes in spinel were simulated using the following equation.

$$\frac{d[Mg]^{Mg-Al inc.}}{dt} = k_{[Mg]}^{spinel} \cdot \frac{A}{V} \cdot ([Mg]^{bulk} - [Mg]^{eq*}) \cdot \frac{N_{MgO}}{N_{Mg}} \dots (7)$$

where $[Mg]^{Mg-Al inc.}$ is the concentration of Mg in Mg – Al -based inclusions, t is the time (s), $k_{[Mg]}^{spinel}$ is the mass transfer coefficient of Mg into spinel (m/s), A is the total interfacial area between inclusions and molten steel (m^2), V is the volume of molten steel (m^3), and N_i is the molar weight of species i . The mass transfer coefficient of Mg into Mg – Al -based inclusions was assumed to equal $k_{[Mg]}^{spinel}$. A is calculated as (number of inclusions) $\times$ (area of inclusions). In this study, the average diameter of a single Al_2O_3 inclusion was assumed to be $10 \mu m$. $[Mg]^{bulk}$ and $[Mg]^{eq*}$ can be calculated using the double-film theory with Eqs. (3) and (6), respectively. $[Mg]^{eq*}$ is determined based on the inclusion stable state in the stability diagram of Mg – Al – O . For example, Eq. (3) is equal to $[Mg]^{eq*}$ when the spinel inclusions are stable. Eq. (6) is used for the stable state of MgO inclusions. The mass transfer coefficient of Mg into spinel ($k_{[Mg]}^{spinel}$) can be calculated as follows:³¹⁾

$$k_{[Mg]}^{spinel} = \frac{Sh \cdot D_{(MgO)}^{spinel}}{d} \dots \dots \dots (8)$$

where $D_{(MgO)}^{spinel}$ represents the diffusivity of MgO into spinel (m^2/s) based on reported data.¹¹⁾ d is the average diameter of inclusions (m). In Eq. (9), Sh is the Sherwood number,³²⁾ which can be obtained from the Reynolds number and Schmidt number as follows:

$$Sh = 2 + 0.6 \cdot Re^{1/2} \cdot Sc^{1/3}, 0 \leq Re < 200, 0 \leq Sc < 250 \dots \dots (9)$$

$$Re = \frac{\rho u L}{\mu} \dots \dots \dots (10)$$

$$Sc = \frac{\mu}{\rho D} \dots \dots \dots (11)$$

The Reynolds number (Re) and Schmidt number (Sc) are defined by Eqs. (10) and (11), respectively. ρ , u , and μ are the density (kg/m^3), slip velocity (m/s), and dynamic viscosity ($N \cdot s/m^2$) of the molten steel, respectively. L is the average diameter of inclusions (m) and D is the diffusivity of Mg in molten steel (m^2/s). The slip velocity of molten steel can be calculated by the enhanced model.²⁰⁾ The dynamic viscosity of the molten steel was calculated using a standard viscosity formula.³³⁾ Using Eqs. (7) to (11), the compositional changes in Mg – Al -based inclusions can be calculated by the enhanced model.

Table 1. Calculation conditions at the initial state based on industrial data for a 210-ton sample.

Mass of steel and slag	Steel: 210 ton, Slag: 2.5 ton
Initial composition of steel (before 2nd de-oxidation reaction)	C: 0.11%; Mn: 0.90%; Cr: 0.24%; Si: 0.38%; Al: 0.01%; O: 13 ppm
Initial composition of slag (before 2nd de-oxidation reaction)	CaO: 54%; SiO ₂ : 12%; Al ₂ O ₃ : 22%; MgO: 8%; MnO: 0.5%; FeO: 0.5%; CaF ₂ : 4%
De-oxidation alloying	Al 0.13 ton at 10 s
Gas flow rate (recirculation)	Ar soft blowing, 133 Nl/min
Temperature (°C)	1 600
Mass transfer coefficient ratio (Metal/Slag)	2
Area of furnace (cm ²)	80 384
Calculation step (sec)	2
Calculation time (sec)	1 200

2.2. Calculation Conditions

Table 1 lists the calculation conditions at the initial state based on industrial data¹³⁾ for a 210-ton sample. Inclusion behavior parameters were set to optimized values based on our previous work by comparing the total composition changes of inclusions in the ICS model to those of inclusions in our current results.³⁰⁾ In our previous work, we investigated the effects of inclusion behavior parameters on overall compositional changes and the number of inclusions.

3. Results & Discussion

3.1. Compositional Changes in $MgAl_2O_4$ Spinel Inclusions

Figures 4 and **5** present the results of model reliability based on compositional changes in the molten steel and slag. In Fig. 4(a), the Al content in the steel increases to 0.07% at the start of calculation, then decreases based on de-oxidation. In Fig. 4(b), the concentration of O decreases based on Al de-oxidation. Both results are in good agreement with measured results at 1 200 s. In Fig. 5, the compositions of CaO, Al_2O_3 , SiO₂, and MgO in slag are compared between the ICS model,^{13,14)} enhanced model, and measured results. The enhanced model shows closer agreement with the measured results at 1 200 s.

Figure 6 presents the concentration changes of $[Mg]^{bulk}$, $[Mg]^{spinel*}$, and $[Mg]^{MgO sat.}$ in steel. For the previous model, after 210 s, spinel inclusions are formed when the Gibbs free energy of the spinel inclusions is stable. Therefore, after 210 s, the growth of $[Mg]^{bulk}$ slows based on spinel generation. Regarding the results of the enhanced model, the spinel becomes the stable after 150 s because $[Mg]^{bulk}$ is close to $[Mg]^{spinel*}$. $[Mg]^{bulk}$ is greater than $[Mg]^{spinel*}$ after 310 s. The reason for the decrease in $[Mg]^{bulk}$ between 150 s and 310 s is that the Mg in steel transforms into MgO content in Al_2O_3 inclusions based on Eq. (7). However, $[Mg]^{MgO sat.}$ is much greater than $[Mg]^{bulk}$ at the right-side y axis. **Figures 7** and **8** present compositional changes in Al_2O_3 and spinel inclusions, and a phase diagram³⁴⁾ of Al_2O_3 and MgO , respectively. In Fig. 7, one can see that the MgO content

Fig. 4. Concentration changes of [Al] (a) and [O] (b) in the molten steel.

Fig. 5. Compositional changes of CaO, Al₂O₃, SiO₂, and MgO in the slag.

in Al₂O₃ inclusions increases significantly with increasing $[Mg]^{bulk}$ up to 150 s, reaching a level of 18 mass% at 150 s. The composition of Mg–Al-based inclusions at 150 s is close to the equilibrium composition between Al₂O₃ and

Fig. 6. Concentration changes in $[Mg]^{bulk}$, $[Mg]^{spinel*}$, and $[Mg]^{MgO sat.}$ from previous results to enhanced results.

Fig. 7. Compositional changes of Al₂O₃ and MgO in Mg–Al-based inclusions.

Fig. 8. Phase diagram of an Al₂O₃ and MgO system.³⁰⁾

MgAl₂O₄ spinel in the phase diagram, as shown in Fig. 8.³⁴⁾ Therefore, the kinetic model accurately simulated spinel generation according to the phase diagram. After 150 s, spinel inclusions are generated and a decreasing gradient of

MgO content is caused by the difference driving force of the spinel inclusion in Eq. (3). Additionally, in Fig. 8, when the MgO content in the MgO–Al₂O₃ system is greater than 18 mass%, the spinel is stable. Following spinel generation, the MgO content in the spinel inclusions gradually increases up to 22 mass% at 1 200 s. However, the MgO content in MgO generation is much greater than the MgO content of spinel inclusions. Furthermore, if $[Mg]^{bulk}$ increases further, spinel inclusions can evolve into MgO-rich inclusions.

Figures 9 and 10 present the compositional changes in all inclusions. In Fig. 9, the MgO content in the enhanced results decreases compared to the previous results. The mole fraction of MgO in the spinel inclusions is assumed to be halved in the previous results, so its value is much larger than the enhanced results. Figure 10 presents a ternary phase diagram of a CaO–MgO–Al₂O₃ system based on our calculation results. The increase in CaO content in the inclusions is influenced by the inclusions originating from slag. However, when considering the curved line in the ternary phase diagram, one can see that the calculation results bend significantly following Ca-treatment. It is well known that spinel is a very harmful inclusion based on its

Fig. 9. Compositional changes of Al₂O₃, MgO, and CaO in total inclusions.

Fig. 10. Ternary phase diagram of an Al₂O₃–MgO–CaO system based on calculation results.

low deformation and high melting point. The purpose of inclusion control is to generate softer inclusions, such as liquid calcium-aluminate.

Figure 11 presents the changes in Al₂O₃ inclusion and spinel inclusion content. The amount of Al₂O₃ is the same between the previous results and enhanced results because the method of forming Al₂O₃ inclusions did not change between the previous model and enhanced model. However, the amount of spinel inclusion in the enhanced results is decreased compared to the previous results. In the previous model, the activity of MgO in spinel inclusions was fixed as 0.8 with a halved mole fraction. The activity value for the enhanced model is much smaller than that for the previous model, as shown in Fig. 3. In the enhanced results, spinel inclusions form after 150 s when $[Mg]^{bulk}$ is close to $[Mg]^{spinel*}$. The content increases significantly after 310 s based on the increasing value of $[Mg]^{bulk}$ in Fig. 6. The local maximum amount of spinel inclusions is approximately 10 kg at 580 s. Then the amount decreases gradually based on the flotation of inclusions into the slag phase.

3.2. Influence of Slag Composition

Many previous studies have contained experiments to clarify the influence of the CaO/SiO₂ ratio in slag on spinel generation, as referenced in Section 1. These studies discovered that when the CaO/SiO₂ ratio in slag increases, the MgO content in Al₂O₃ inclusions increases and the diffusivity rate of Mg in steel increases.^{4–6} These results indicate that the generation of spinel inclusions can be suppressed by a low CaO/SiO₂ ratio in slag. Therefore, the influence of the initial CaO/SiO₂ ratio in slag on the generation of spinel inclusions was evaluated using the enhanced model, as shown in Fig. 12. The CaO/SiO₂ ratio in slag was varied in the range of 2–4.5. When the CaO/SiO₂ ratio in slag decreases, the local maximum amount of spinel inclusions decreases and the initiation time of spinel generation is delayed. To investigate the influence of the CaO/SiO₂ ratio in slag, the equilibrium distribution ratio of Mg between the reactions of Mg/MgO and Al/Al₂O₃ was calculated as follows:

Fig. 11. Content changes for Al₂O₃ inclusions and MgAl₂O₄ spinel inclusions between the enhanced model, previous model, and ICS model.

$$\log K_{(12)} = -24.46 + 31\,200/T \quad \dots\dots\dots (13)$$

$$L_{Mg} = \frac{(MgO\%)}{[Mg\%]} = \frac{1}{K_{(12)}^{1/3}} \cdot \frac{f_{[Mg]}}{\gamma_{(MgO)}} \cdot \frac{a_{(Al_2O_3)}^{1/3}}{a_{[Al]}^{2/3}} \cdot N_{MgO} \quad \dots (14)$$

Equation (12) can be converted into Eq. (14) to derive L_{Mg} , which denotes the equilibrium distribution ratio of Mg. The equilibrium constant $K_{(12)}$ in Eq. (14) is calculated using Eq. (13).²⁸⁾ **Figure 13** illustrates the value of L_{Mg} and ratio of f_{Mg}/γ_{MgO} calculated using Eq. (14). The ratio of f_{Mg}/γ_{MgO} is almost constant as the CaO/SiO₂ ratio in slag changes, but the activities of Al in steel and Al₂O₃ in slag become dominant parameters for the value of L_{Mg} . When the CaO/SiO₂ ratio decreases, the value of L_{Mg} increases. This indicates that the CaO/SiO₂ ratio in slag influences the activity of Al₂O₃ in Eq. (14). Additionally, the component of MgO in slag at a higher value of L_{Mg} is much more stable than that at a lower value (*i.e.*, the reduction tendency of MgO in slag decreases at a higher value of L_{Mg}). Therefore, $[Mg]^{bulk}$ decreases with a lower CaO/SiO₂ ratio in slag based on a higher value of L_{Mg} . The Mg content in steel is related to the driving force of spinel generation based on Eq. (7).

Therefore, the driving force of spinel generation decreases at a lower CaO/SiO₂ ratio in slag. These calculation results show good agreement with previous experimental results.⁴⁻⁶⁾ Therefore, we can conclude that when the CaO/SiO₂ ratio in slag decreases, the local maximum amount and initiation time of spinel generation decrease based on a greater value of L_{Mg} .

3.3. Evolution of MgAl₂O₄ Spinel Inclusions into MgO Inclusions

Typically, the Mg content in molten steel increases during ladle treatment without the addition of Mg based on the reduction of MgO in slag and dissolution of refractory-based MgO. Therefore, in Fig. 6, if $[Mg]^{bulk}$ is greater than $[Mg]^{MgO\ sat.}$, then MgO-rich inclusions can be generated from spinel inclusions. To simulate the generation of MgO-rich inclusions, the calculation time set to 7 200 s for the enhanced model. **Figure 14** presents the concentration changes of $[Mg]$ in the molten steel. $[Mg]^{bulk}$ exceeds than $[Mg]^{MgO\ sat.}$ after 3 680 s. Therefore, MgO-rich inclusions become thermodynamically stable state after 3 680 s. In **Fig. 15**, one can see that the MgO content in Mg–Al-based inclu-

Fig. 12. Content changes of Al₂O₃ inclusions and MgAl₂O₄ spinel inclusions with variations of the CaO/SiO₂ ratio in slag (2 to 4.5).

Fig. 14. Concentration changes of $[Mg]^{bulk}$ over 7 200 s.

Fig. 13. Equilibrium distribution ratio of Mg, and the ratio of f_{Mg}/γ_{MgO} in Eq. (14) by variation of the CaO/SiO₂ ratio in slag (2 to 4.5).

Fig. 15. Compositional changes of Al₂O₃ and MgO in Mg–Al-based inclusions over 7 200 s.

Fig. 16. Content changes of Al_2O_3 , MgAl_2O_4 spinel, MgO -rich inclusions, as well as the inclusions originating from slag.

sions is 30.8 mass% at 3 680 s, indicating compositional changes in Mg – Al -based inclusions. The MgO content nears the equilibrium composition between MgO and MgAl_2O_4 spinel in Fig. 8, which presents a phase diagram of MgO – Al_2O_3 system. **Figure 16** presents the content changes of Mg – Al -based inclusions and inclusions originating from slag. A small amount of MgO -rich inclusions is generated after 3 680 s. However, after 3 680 sec, the decreasing trend in spinel inclusions is similar to the increasing trend in MgO -rich inclusions. The flotation of inclusions into slag is considered in the enhanced model, but flotation rarely occurs after 3 000 s, as shown by the content changes of the inclusions. This indicates that MgO -rich inclusions were evolved from spinel inclusions with increasing MgO content in Mg – Al -based inclusions. MgO -rich inclusions have been observed in previous studies.^{7,8)} Therefore, proposed kinetic model can accurately model the inclusion evolution from Al_2O_3 inclusions to MgO -rich inclusions and the associated changes in composition.

4. Conclusion

In this study, we enhanced an existing kinetic model to predict the compositional changes of molten steel, slag, and inclusions during ladle treatment.

(1) We discussed how to apply the compositional changes in Mg – Al -based inclusions by considering stability diagrams and activity changes.

(2) The enhanced kinetic model provides reliable predictions of compositional changes in molten steel, slag, and inclusions using industrial data from a 210-ton sample.

(3) When the CaO/SiO_2 ratio in slag decreases, the local maximum amount of MgAl_2O_4 spinel inclusions and the initiation time of spinel generation decrease based on a greater equilibrium partition ratio of Mg . Therefore, Mg content in molten steel is the dominant factor for spinel generation.

(4) MgAl_2O_4 spinel inclusions can evolve into MgO -rich inclusions with a gradual increase in MgO content in Mg – Al -based inclusions supplied by molten steel.

Acknowledgments

The authors would like to thank Prof. Shin-ya Kitamura in Tohoku University for his valuable comments about the kinetic reaction and thermodynamics. We appreciate the financial support by the Iron & Steel Institute of Japan (ISIJ) from the research group on “Refining of Cr Steel by slag and inclusion control”. This work was supported by the Korea Institute of Energy Technology Evaluation and Planning and the Ministry of Trade, Industry, & Energy of the Republic of Korea (No. 20185210100030).

REFERENCES

- 1) J. H. Park and Y. Kang: *Steel Res. Int.*, **88** (2017), 1700130.
- 2) J. H. Park and H. Todoroki: *ISIJ Int.*, **50** (2010), 1333.
- 3) H. Todoroki, F. Kirihara, Y. Kanbe and Y. Miyazaki: *Tetsu-to-Hagane*, **100** (2014), 539 (in Japanese).
- 4) T. Nishi and K. Shinme: *Tetsu-to-Hagane*, **84** (1998), 837 (in Japanese).
- 5) G. Okuyama, K. Yamaguchi, S. Takeuchi and K. Sorimachi: *ISIJ Int.*, **40** (2000), 121.
- 6) A. Harada, A. Matsui, S. Nabeshima, N. Kikuchi and Y. Miki: *ISIJ Int.*, **57** (2017), 1546.
- 7) J. H. Park and D. S. Kim: *Metall. Mater. Trans. B*, **36** (2005), 495.
- 8) H. Todoroki and K. Mizuno: *Iron Steelmaker*, **30** (2003), No. 3, 60.
- 9) A. Harada, G. Miyano, N. Maruoka, H. Shibata and S. Kitamura: *ISIJ Int.*, **54** (2014), 2230.
- 10) C. Liu, F. Huang and X. Wang: *Metall. Mater. Trans. B*, **47** (2016), 999.
- 11) C. Liu, M. Yagi, X. Gao, S.-J. Kim, F. Huang, S. Ueda and S. Kitamura: *Metall. Mater. Trans. B*, **49** (2018), 113.
- 12) J. Peter, K. D. Peaslee, D. G. C. Robertson and B. G. Thomas: *Proc. Iron & Steel Technology Conf. (AISTech 2005)*, Vol. 1, AISTech, Charlotte, (2005), 959.
- 13) Q. Shu, O. Volkova, S. Lachmann and P. R. Scheller: *Proc. Iron & Steel Technology Conf. (AISTech 2011)*, Vol. 2, AISTech, Indianapolis, (2011), 537.
- 14) T. Dubberstein, O. Volkova, S. Lachmann and P. R. Scheller: *Proc. Int. Conf. on Clean Steel, OMBKE, Budapest*, (2012), 1.
- 15) M.-A. Van Ende and I.-H. Jung: *Metall. Mater. Trans. B*, **48** (2017), 28.
- 16) Y. Ren, Y. Zhang and L. Zhang: *Ironmaking Steelmaking*, **44** (2017), 497.
- 17) Y. Ren, L. Zhang, H. Ling, Y. Wang, D. Pan, Q. Ren and X. Wang: *Metall. Mater. Trans. B*, **48** (2017), 1433.
- 18) Y. Ren and L. Zhang: *Ironmaking Steelmaking*, **45** (2018), 585.
- 19) Y. Ren, L. Zhang and Y. Zhang: *J. Iron Steel Res. Int.*, **25** (2018), 146.
- 20) A. Harada, N. Maruoka, H. Shibata and S. Kitamura: *ISIJ Int.*, **53** (2013), 2110.
- 21) A. Harada, N. Maruoka, H. Shibata and S. Kitamura: *ISIJ Int.*, **53** (2013), 2118.
- 22) S.-J. Kim, A. Harada, S. Kitamura: *Proc. Iron & Steel Technology Conf. (AISTech 2015)*, Vol. 3, AISTech, Cleveland, (2015), 3261.
- 23) D. G. C. Robertson, B. Deo and S. Ohguchi: *Ironmaking Steelmaking*, **11** (1984), 41.
- 24) S. Ohguchi, D. G. C. Robertson, B. Deo, P. Grieveson and J. H. E. Jeffes: *Ironmaking Steelmaking*, **11** (1984), 202.
- 25) J. H. Park, D. J. Min and H. S. Song: *Metall. Mater. Trans. B*, **33** (2002), 723.
- 26) Factsage 7.1, Thermfact/CRCT and GTT-Technologies, 1976-2019.
- 27) ChemApp, GTT-Technologies, 2003-2019.
- 28) M. Hino and K. Ito: *Thermodynamic Data for Steelmaking*, Tohoku University Press, Sendai, (2010), 10.
- 29) K. Fujii, T. Nagasaka and M. Hino: *ISIJ Int.*, **40** (2000), 1059.
- 30) J.-I. Kim, S.-J. Kim and S. Kitamura: *7th Int. Congr. on Science and Technology of Steelmaking (ICS2018)*, AIM, Venice, (2018), CD-ROM.
- 31) A. Galindo: Ms. thesis, McMaster University, (2015), <https://macsphere.mcmaster.ca/handle/11375/18449>, (accessed 2015-10-21).
- 32) W. R. Paterson and A. N. Hayhurst: *Chem. Eng. Sci.*, **55** (2000), 1925.
- 33) M. Hirai: *ISIJ Int.*, **33** (1993), 251.
- 34) Verein Deutscher Eisenhüttenleute: *Slag Atlas*, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 44.