Effect of Slag Composition on MgO·Al₂O₃ Spinel-Type Inclusions in Molten Steel

Akifumi HARADA,¹* Akitoshi MATSUI,¹) Seiji NABESHIMA,²) Naoki KIKUCHI¹) and Yuji MIKI¹)

1) Steel Research Laboratory, JFE Steel Corporation, 1 Kokan-cho, Fukuyama, Hiroshima, 721-8510 Japan.
2) Steel Research Laboratory, JFE Steel Corporation. Now at Mizushima Ferroalloy Corporation, 1-1 Kawasakidori, Mizushima, Kurashiki, Okayama, 712-8513 Japan.

(Received on March 31, 2017; accepted on May 11, 2017)

It is well known that the formation of MgO·Al₂O₃ spinel-type inclusions is affected by the slag composition. To clarify the effect of the slag composition on the formation of spinel-type inclusions, laboratory-scale experiments were carried out in 30 kg-scale induction furnace. Changes in the composition of inclusions were investigated with different slag compositions. As the CaO/SiO₂ and CaO/Al₂O₃ of the slag increased, spinel-type inclusions were observed, and the total Mg content and average composition of MgO in the inclusions were also higher. On the other hand, the total Mg content and average composition of MgO in inclusions decreased with decreasing CaO/SiO₂ and CaO/Al₂O₃ of the slag, and most inclusions were Al₂O₃-type inclusions including a small amount of MgO. Based on the experimental results, a kinetic analysis was carried out using a calculation model to simulate the reactions between the molten steel, slag, refractory and inclusions in order to evaluate the effect of the slag composition on inclusions. The calculated results of the inclusion composition were in good agreement with the experimental results. In this experimental system, the total Mg content and spinel-type inclusions were suppressed due to a decrease in the activity of MgO in the slag and an increase in the oxygen activity at the interface between the molten steel and slag when the CaO/SiO₂ and CaO/Al₂O₃ of the slag were lower. Therefore, the formation of spinel-type inclusions can be determined by the relationship between the MgO activity of the slag and the interfacial activity of oxygen.

KEY WORDS: inclusion; spinel; slag composition; kinetic calculation.

1. Introduction

It is well known that MgO·Al₂O₃ spinel-type inclusions in steel products often cause cracking and surface flaws because of their high melting temperature and low deformability.¹ In addition, they raise a serious problem for operation by causing nozzle clogging.¹ Thus, it is necessary to control the composition of inclusions in steel in order to suppress the formation of spinel-type inclusions.

Many researchers have studied the formation mechanism of spinel-type inclusions. Spinel-type inclusions are thought to be formed by the reaction between alumina-type inclusions and Mg, which is formed in the molten steel through the reduction of MgO in the slag or refractory by Al.²⁻⁸ Some researchers have pointed out that changes in the slag composition affected the formation of spinel-type inclusions.²,³,⁹⁻¹¹ When the slag basicity CaO/SiO₂ and CaO/Al₂O₃ is lower, reduction of MgO in the slag is suppressed. This means that decreasing the slag basicity is effective for suppressing the formation of spinel-type inclusions. Although the qualitative method for controlling the formation of spinel-type inclusions is understood, few studies have mentioned a quantitative control method.

Most previous studies evaluated the formation of spinel-type inclusions on the basis of thermodynamic calculations.⁴⁻⁷,⁸,¹⁰ However, when considering the actual process, a kinetic analysis is necessary because the compositions of the molten steel, slag and inclusions change with time. Okuyama et al.¹¹ and Galindo et al.¹² analyzed experimental and operational results by using a coupled reaction model which considers the reaction between molten steel and slag, and simulated the changes in the MgO content in Al₂O₃–MgO type inclusions by using the changes in the composition of the molten steel. Actually, however, the reactions which occur simultaneously between the molten steel, slag, inclusions and refractory should be considered in calculations of the inclusion composition. Harada et al.¹³,¹⁴ reported a kinetic model for simulating the reactions between the molten steel, slag, refractory and inclusions, and it is considered possible to calculate the composition change of inclusions more precisely by that model.

In this study, laboratory-scale experiments were carried out to evaluate the effect of the slag composition on the formation of spinel-type inclusions. Then, based on the experimental results, the slag composition for suppressing spinel-type inclusions was evaluated by using a kinetic model which considers the reactions between the molten
steel, slag, refractory and inclusions.

2. Experimental Method

Laboratory-scale experiments were conducted to investigate the effect of the slag composition on the inclusion composition. Figure 1 shows a schematic diagram of the 30 kg induction furnace used in these experiments. First, the crucible was set in the chamber, and a porous plug was set in the bottom of the crucible to stir the molten metal by injection of Ar gas at a rate of 2.0 Nl/min. Then, electrolytic iron was inserted into the crucible. After the iron melted, Fe–Si alloy, metallic Mn, metallic Cr, Fe–S alloy and carbon were added to the molten iron as alloying elements. The target composition of the steel in this study is shown in Table 1. During the experiments, Ar gas was injected to maintain an Ar atmosphere in the chamber. After adjusting the composition of the molten steel, 2.0 kg of an oxide mixture was added on the steel surface. The mixture was composed of reagents of CaO, SiO₂, Al₂O₃ and MgO in an appropriate mixing ratio. The compositions of the initial slags are listed in Table 2.

3. Experimental Results

3.1. Composition Change of Molten Steel

Figure 2 shows the composition change of the molten steel. The Al content in the steel increased slightly before Al addition because the Al₂O₃ in the slag was reduced by the Si of the steel. The Al content in the steel increased largely shortly after Al addition, and the Al content then decreased gradually. With all the slags, the total Mg content increased after Al addition. Here, the total Mg content means the sum of soluble Mg and insoluble Mg. However, the increase rate of total Mg was different with the composition of slags. These results showed that the total Mg content became lower as the CaO/SiO₂ and CaO/Al₂O₃ of the slag decreased. This experimental result was the same tendency as that in

\[
\text{Fig. 2.} \quad \text{Composition change of (a) Al and (b) total Mg in steel.}
\]
3.2. Composition Change of Inclusions

The composition change of the inclusions in the steel is shown in Fig. 3. In all the slags, the composition of the inclusions was Al₂O₃-type inclusions including a small amount of MgO before the Al was added because the Al was present in the molten steel before Al addition as mentioned above. In slag A, MgO·Al₂O₃ spinel-type and MgO-type inclusions were observed soon after Al addition. In slags B and C, MgO·Al₂O₃ spinel-type inclusions were observed soon after Al addition. In contrast, in slag D, Al₂O₃ type inclusions with a small amount of MgO were observed soon after Al addition, and the content of spinel-type inclusions was small. Around 20 min after Al addition, the significant change of the inclusion composition was not observed from 3 min in all the slags. Thus, the change rate of the inclusion composition is considered to be very fast. The change in the average composition of MgO in the observed inclusions is shown in Fig. 4. As with the change in total Mg, the average composition of MgO in the observed inclusions became lower as the CaO/SiO₂ and CaO/Al₂O₃ of the slag decreased. The size of the observed inclusions was around
4. Discussion

4.1. Outline of Calculation Model

As mentioned in the previous chapter, the behavior of the changes in the average composition of MgO in the inclusions was different depending on the composition of the slag. To evaluate the effect of the slag composition on the inclusion composition, a kinetic model was applied to the experimental results. In order to analyze the compositions of the inclusions, it is necessary to consider the reactions among the refractory and inclusions in addition to the reaction between the molten steel and slag. Therefore, in this study, a kinetic model which makes it possible to consider the reactions among the molten steel, slag, refractory and inclusions was used in the analysis. The outline of the model is shown in Fig. 6. The reactions considered in the model were as follows:

① Dissolution of refractory into slag
② Reaction between molten steel and slag
③ Reaction between molten steel and inclusions originating from slag
④ Deoxidation reaction
⑤ a. Entrapment of top slag into molten steel (formation of inclusions originating from slag)
   b. Agglomeration of deoxidation products with inclusions originating from slag
   c. Floatation of deoxidation products and inclusions originating from slag into the slag

In the model, two sources of inclusions were considered: (i) entrapment of slag in the molten steel and (ii) deoxidation products resulting from addition of the deoxidizer. The composition changes in the molten steel, slag and inclusions were obtained by calculating reactions ① to ⑤. When the activity of each component in the slag phase was calculated in reactions ② and ③, FactSage7.0 was linked to the calculation model.

In this case, it is necessary to determine certain parameters (slag entrapment, flotation of inclusions and agglomeration of inclusions) in the model. The parameters used in this study were determined by fitting with the experimental results, as shown in Table 3. The values of the parameters were different from those used in the previous reports. The difference of the parameters can be caused by the difference of the experimental conditions. Especially, it is thought that the parameters are influenced by the difference of temperature condition of molten steel, composition of molten steel and slag and stirring condition. Thus, as these experimental factors can affect the flow of molten steel, the interfacial properties and physical characteristics of molten steel, slag and inclusions, the parameters are changed in every experiment. However, since the relationship between the parameters and experimental factors has not been clarified, it is necessary to make a match with more experimental data and perform systematic evaluation in the future.

The size of the inclusions was set to be 2 μm in the model because the average size of the inclusions observed in the experiments was 2 μm.

The calculation flow of the model is shown in Fig. 7.
After inputting the initial data, the composition changes in the molten steel, slag and inclusions are obtained as the output data. The formation amounts of deoxidation products and inclusions originating from the slag are also calculated.

4.2. Calculation Results
The changes in the inclusions under the experimental conditions were calculated by using the kinetic model mentioned in the previous section.

According to the model calculation, spinel-type inclusions were formed after Al was added in the case of slags A, B and C. However, in the case of slag D, only a minimal amount of spinel-type inclusions formed after Al addition. Based on the calculation results, the changes of the average compositions of CaO, Al₂O₃ and MgO in the inclusions in slags A and D were calculated, as shown in Fig. 8. The calculated changes in the average compositions of the inclusions were in good agreement with the experimental results. Figure 9 shows the calculation results of the mass ratio of each inclusion type to the total in slag A and D. In slag A, the ratio of Al₂O₃ type and spinel type was almost same before Al addition. Then, the ratio of spinel type was very high shortly after Al addition. In slag D, the ratio of Al₂O₃ type was very high before and after Al addition. Although the ratio of spinel type increased slightly shortly after Al addition, it was lower during the experiment in slag D. In both experiments, the ratio of slag originating from slag increased gradually, but it was lower than that of deoxidation products.

Therefore, the applicability of this calculation model to this experiment was confirmed. As the formation of MgO-
type inclusions was not considered in this model, the model will need to be improved in this regard in the future in order to understand the phenomena more precisely.

4.3. Effect of Slag Composition

By using this model, the effect of the slag composition on the total Mg content and formation of spinel-type inclusions 20 min after Al addition was calculated when the CaO/SiO₂ and CaO/Al₂O₃ of slag were changed. The amount of spinel-type inclusions decreased with the decrease in the CaO/SiO₂ and CaO/Al₂O₃ of the slag, as shown in Fig. 10. In this calculation, formation of spinel-type inclusions was minimal when the CaO/Al₂O₃ of the slag was less than 1.0. The relationships between the MgO activity of the slag and the oxygen activity at the interface between the molten steel and slag are shown in Fig. 11. As the CaO/SiO₂ and CaO/Al₂O₃ of the slag decreased, the MgO activity of the slag decreased and the interfacial activity of oxygen increased. Therefore, reaction (1) at the interface between the molten steel and slag was suppressed and the total Mg content and the formation of spinel-type inclusions were suppressed with the decrease in the CaO/SiO₂ and CaO/Al₂O₃ of the slag.

\[
(MgO)_{slag} = [Mg] + [O] \quad \cdots (1)
\]

Figure 12 shows the relationships between the amount of

![Fig. 10](image)

Calculation results of relationships between slag composition and amount of spinel-type inclusions 20 min after Al addition.

![Fig. 11](image)

Calculation results of relationships between (a) slag composition/MgO activity in slag and (b) slag composition/interfacial oxygen activity 20 min after Al addition.

![Fig. 12](image)

Calculation results of relationships among slag composition, activity of MgO in slag and amount of spinel-type inclusions 20 min after Al addition.
spinel-type inclusions, the slag composition and the MgO activity of the slag. According to the calculated result, in this experimental system, spinel-type inclusions can be suppressed when the MgO activity of the slag is less than around 0.6. The summarized results of this model calculation are shown in Fig. 13. In this figure, the hatched area shows the formation area of spinel-type inclusions of more than 0.1 mass ppm. This experimental result is also in good agreement with the calculated results by the model. Thus, in this experimental system, spinel-type inclusions can be avoided by controlling the slag composition so as to be outside of the hatched area.

However, in the actual process, the slag is sometimes saturated with MgO due to dissolution from MgO-type refractory into the slag. As the activity of MgO becomes closer to 1.0 in that case, the effect of the slag composition on inclusions can change compared with the case of this study. Therefore, the effect of the slag composition on the composition of inclusions was calculated by setting the initial content of MgO in the slag to 10 mass%. Figure 14 shows the relationship between the slag composition and the formation of spinel-type inclusions 20 min after Al addition with these higher MgO contents. Compared with Fig. 13, although the area of formation of spinel-type inclusions is wider, the spinel-type inclusions are suppressed with the decrease in the CaO/SiO₂ and CaO/Al₂O₃ of slag. Thus, even though the activity of MgO is higher, the reaction shown in Eq. (1) can be suppressed because interfacial oxygen activity increases when the CaO/SiO₂ and CaO/Al₂O₃ of the slag decreases.

From the above, the slag composition has a significant influence on the formation of spinel-type inclusions. This study has shown that the formation of spinel-type inclusions can be determined by the dependence on the MgO activity of the slag and interfacial oxygen activity. However, a countermeasure to reduce the dissolution of MgO-type refractory into the slag is required, as it becomes more difficult to suppress spinel-type inclusions if the MgO content of the slag increases due to dissolution of the refractory.

5. Conclusions

In order to clarify the effect of the slag composition on the formation of spinel-type inclusions, laboratory-scale experiments and a model calculation based on the experimental results were carried out.

(1) According to the experimental results, when the CaO/SiO₂ and CaO/Al₂O₃ of the slag was higher, the total Mg content in the steel and the MgO content in the inclusions increased with time after Al addition. On the other hand, when the CaO/SiO₂ and CaO/Al₂O₃ of the slag were lower, the formation of spinel-type inclusions was suppressed and the average content of MgO in the inclusions also decreased.

(2) A kinetic calculation to simulate the reactions between the molten steel, slag, refractory and inclusions was carried out based on the experimental results. The calculation results were in good agreement with the experimental results. Using this model, the effect of the slag composition on the formation of spinel-type inclusions was evaluated. The calculation results indicated that spinel-type inclusions decreased with a decrease in the CaO/SiO₂ and CaO/Al₂O₃ of the slag. Therefore, in this experimental system, the formation of spinel-type inclusions can be determined by the dependence on the MgO activity of the slag and the oxygen activity at the interface between the molten steel and slag.

REFERENCES