Formation and Evolution of Silicate Inclusions in Molten Steel by Magnesium Treatment

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(Received on August 3, 2018; accepted on October 29, 2018; J-STAGE Advance published date: December 19, 2018)

The effect of magnesium addition on the formation and evolution of inclusions in Mn–Si killed steel is studied by laboratory experiments and thermodynamic calculation. Samples were taken at different holding time after magnesium addition to study the transient evolution of inclusions. The morphology, composition, number and diameter of inclusions were thoroughly analyzed by SEM-EDS. The results show that four types of inclusions (MgO–SiO₂–MnO liquid inclusion, MgO–SiO₂–MnO complex inclusion, MgO–SiO₂ and MgO solid inclusion) form with different amount of magnesium addition. Liquid inclusion of MnO–SiO₂ is promptly modified to MgO–SiO₂–MnO liquid inclusion with 0.0005% magnesium addition. As the amount of magnesium is increased to 0.0011%, intermediate product MgO forms immediately and then gradually transforms to MgO–SiO₂ solid inclusion with holding time. While MgO solid inclusion keeps stable throughout with 0.0019% magnesium addition.

KEY WORDS: magnesium treatment; silicate inclusions; thermodynamics.

1. Introduction

The presence of inclusion in steel has an adverse influence on the plasticity, toughness and fatigue life of steel. Beside, inclusion would deteriorate the castability of molten steel and severely affect the production process.^{1,2)} In order to improve the performance of steel, it is necessary to control the composition, number and size of the residual inclusion in steel.

Calcium is generally used in steelworks to modify non-deformable Al₂O₃ inclusion to calcium aluminate system inclusion with low melting point.^{3,4)} However, there are still some limitations for the application of calcium treatment. For instance, calcium treatment is prohibited in bearing steel production process due to the adverse effect of calcium aluminate inclusion on the fatigue life of steel.⁵⁾ During the production of high sulfur steel, the problem of nozzle clogging is still serious owing to the precipitation of CaS.⁶⁾ Thence, magnesium treatment has gained more and more attentions as the replacement of calcium treatment.

Similar to calcium, magnesium also has strong affinity to oxygen in steel at the steelmaking temperature. In recent years, many investigations have focused on the modification of Al₂O₃ based inclusion by magnesium treatment.^{7–10)} A number of thermodynamic studies on the formation of MgO·Al₂O₃ were carried out.^{11,12)} Zhang *et al.*¹³⁾ reviewed the reported calculation for the stability diagram of Al–Mg–O system inclusion at steelmaking temperature.

Kimura *et al.*¹⁴⁾ reported that MgO–Al₂O₃ complex inclusion had a much weaker tendency to aggregate and form clusters than Al₂O₃ inclusion by the in-situ observation with a confocal scanning laser microscope. Zhang *et al.*¹⁵⁾ studied the effect of magnesium addition on the evolution of inclusion in Al–Ca deoxidized melts, and found that the size of oxide inclusion could be controlled well with a certain amount of magnesium addition. Similar results were also reported by Zhang *et al.*¹⁶⁾ in Mn–Si–Al deoxidized molten steel. Kim *et al.*¹⁷⁾ and Chang *et al.*¹⁸⁾ investigated the effect of magnesium on the evolution of inclusion in Mn–Si–Ti deoxidized low carbon steel using induction melting furnace. It is found that the phase of inclusion changed sequentially in the path of Ti₂O₃→Ti–Mg–O→MgTiO₃→MgO with the increase of magnesium content. Wen *et al.*¹⁹⁾ observed the effect of Si–Mg alloy on inclusion and microstructure of 16 Mn steel. The result indicated that inclusion transformed into MgAl₂O₄ and MgO after treated by Si–Mg alloy. The research of magnesium treatment is mainly concentrated on Al killed steel, however few studies have been carried out for Mn–Si killed steel. In the production of semi-killed steel, Mn–Si deoxidization is usually adopted to avoid the precipitation of high melting point inclusion, however, the formation and evolution mechanism of silicate inclusion by magnesium treatment has not been elucidated yet.

In the current study, laboratory experiments were carried out to study the effect of magnesium addition on inclusions in Mn–Si killed molten steel. The type, composition, number and diameter of inclusions at different holding time were investigated comprehensively. The results from present work are significant for understanding and controlling

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DOI: <https://doi.org/10.2355/isijinternational.ISIJINT-2018-543>

silicate inclusions by magnesium treatment.

2. Experimental Methods

2.1. Experimental Procedures

The experiments were carried out in a tube furnace, which was heated by MoSi₂ rods with two B-type thermocouples, as shown in Fig. 1. Approximately 450 g industrial pure iron was melted in MgO crucible under high pure argon atmosphere (99.99%) at 1 873 K. After 30 min stabilization of the melt, the initial dissolved oxygen ([O]₁) was detected by electrolyte oxygen probe. Then Mn–Fe alloy and pure silicon were successively added to the molten steel to deoxidize. 5 min later, first sample (S0) was sucked out by a quartz tube and immediately quenched in ice-water bath. Subsequently, Ni–Mg alloy was quickly inserted to the melt and three samples (S1, S2 and S3) were taken at 1 min, 5 min and 10 min after magnesium addition, respectively. The final dissolved oxygen ([O]₂) was then determined after magnesium addition. Thereafter, the melt cooled to the room temperature by cutting off the power supply to the furnace. Three sets of experiments (A, B and C) with different amount of magnesium were performed. The detailed procedures of present experiments are provided in Fig. 2. The compositions of raw material used in the experiments are listed in Table 1.

2.2. Detection Methods for Steel Composition and Inclusions

The residual steel samples in MgO crucible were chosen to analyze the contents of silicon, manganese and magnesium by the inductively coupled plasma optical emission

spectrometer (ICP-OES). Oxygen activities in the molten steel were directly measured by solid electrolyte concentration cell method in 8–15 s without sampling. Figure 3 shows the working principle of the oxygen concentration cell. Due to the difference in oxygen partial pressure between the two half cells, O^{2–} migrates between the two half cells, thereby generating an electromotive force. The electromotive force is subject to Nernst's Equation, as shown in Eq. (1). Based on Eq. (1), the general function of oxygen concentration and the electromotive force is given in Eq. (2).²⁰⁾

$$E = \frac{RT}{nF} \ln \frac{a_{[O]}}{P_{O_2}^{1/2}} \dots\dots\dots (1)$$

Where E - electromotive force, mV; R -ideal gas constant; T -temperature, K; n - reference electrode moles; F - Coulomb constant; $a_{[O]}$ -oxygen concentration, ppm; P_{O_2} -oxygen partial pressure, Pa.

$$a_{[O]} = 10^{-(a_0+b_0/T)} \\ \left\{ \frac{10^{(a+b/T)/4} + 10^{(a_1-b_1/T)/4}}{10^{5.04(E+a_2-b_2t)/T}} - 10^{(a_1-b_1/T)/4} \right\}^2 \times 10^4 \dots\dots\dots (2)$$

Where t -temperature, °C; a_0 , b_0 -measured medium coefficient; a , b -reference material coefficient; a_1 , b_1 -solid electrolyte coefficient; a_2 , b_2 -conductor coefficient.

After all the experiments, the molten steel samples were

Fig. 1. Schematic diagram of tube furnace. (Online version in color.)

Fig. 2. Procedure of the experiments. (Online version in color.)

Fig. 3. Working principle of the oxygen concentration cell.

Table 1. Chemical compositions of raw material, wt.%.

Raw material	Fe	Ni	Al	Mn	C	Si	Mg	S	Balance
Industrial pure iron	99.90	0.01	0.018	0.03	0.0021	0.01	–	0.003	0.035
Mn–Fe alloy	12.57			84.20	1.50	1.50	–	0.03	
Pure silicon						99.90			0.10
Ni–Mg alloy	0.93	80.12					17.98		0.97

grinded on abrasive papers and then polished on polishing machine. Afterwards, the two-dimensional morphology and internal composition of inclusions were analysed by the field emission scanning electron microscope (FE-SEM) and energy dispersive spectrometer (EDS).

Image analysis software Image Pro Plus 6.0 was used to count the number and diameter of inclusions. The diameter of inclusion was estimated as the diameter of a circle with the same area.²¹⁾ The total observed area of each sample was 1.2 mm², which corresponded to 108 observation areas at the magnification of 2 000 obtained by FE-SEM.

3. Results and Discussion

3.1. Chemical Composition of Steel

Table 2 lists the measured compositions of magnesium, silicon and manganese in steel. It is obviously seen that the mass fraction of manganese and silicon in three melts are at the same level, which is about 1.2% and 0.2%, respectively. In order to investigate the effect of magnesium content on the evolution of inclusion, different quantity of Ni–Mg alloy was added to the molten steel. The analysis results

show that magnesium content in different melt are at three different levels in the range of 0.0005% to 0.0019%. Ni in the Ni–Mg alloy does not affect the experimental results. On the one hand, when the amount of Ni introduced is low ($w_{Ni} < 0.3\%$), the oxidation of Ni does not occur in the molten steel according to the thermodynamic calculation. On the other hand, the influence of Ni on the formation and evolution of inclusions can be neglected because of the small interaction coefficients between Ni and other elements such as Si and Mg. The initial dissolved oxygen in molten steel is 0.016–0.017% and the final dissolved oxygen decreases to below 0.0035%.

3.2. Characteristics of Inclusions

3.2.1. Types of Inclusions in Steel

There are five types of inclusions observed in Melt A to Melt C. The typical morphology and EDS spectra of each type of inclusion are presented in Figs. 4 to 8.

The typical inclusion found in the sample S0 after silicon addition is Type 1 SiO₂–MnO system inclusion. Figure 4 presents the typical morphology of Type 1, which is in spherical shape. The composition analysis results and SiO₂–MnO phase diagram²²⁾ indicate that Type 1 inclusion is in liquid phase.

Type 2 inclusion is MgO–SiO₂–MnO system, as shown in Fig. 5. Type 2 inclusion is mainly detected in S1, S2 and S3 of Melt A with trace amount of magnesium addition. The EDS analysis results show that Type 2 inclusion contains a small amount of magnesium and the mass fraction is 5% with the atomic ratio of Mg/Si about 0.35. The uniform element distributions of Mn, Si, Mg and O indicate that this

Table 2. Chemical compositions in different melts, wt.%.

Melt	Mn	Si	Mg	[O] ₁	[O] ₂
A	1.19	0.203	0.0005	0.0163	0.0033
B	1.31	0.194	0.0011	0.0160	0.0035
C	1.22	0.187	0.0019	0.0167	0.0018

[O]₁ the initial dissolved oxygen, [O]₂ the final dissolved oxygen

Fig. 4. Type 1 SiO₂–MnO system inclusion. (Online version in color.)

Fig. 5. Type 2 MgO–SiO₂–MnO system homogeneous inclusion. (Online version in color.)

Fig. 6. Type 3 MgO-SiO₂ system inclusion. (Online version in color.)

Fig. 7. Type 4 MgO-SiO₂-MnO system complex inclusion. (Online version in color.)

Fig. 8. Type 5 MgO system inclusion. (Online version in color.)

type of inclusion is homogeneous.

Type 3 inclusion is MgO–SiO₂ system and its typical morphology and composition are given in Fig. 6. The results show that the appearances of Type 3 inclusion are rectangular or spherical. The elemental mappings reveal that Type 3 inclusion is homogeneous and mainly composed of Mg, Si and O. The EDS analysis results indicate that the mass fraction of magnesium in Type 3 inclusion increases to more than 16% with the atomic ratio of Mg/Si between 1–2. Type 3 inclusion is mainly observed in S2 and S3 of Melt B with medium amount of magnesium addition.

Type 4 inclusion presented in Fig. 7 is a combination of Type 2 and Type 3. The elemental mappings show that the core of Type 4 is MgO–SiO₂ and surrounded by MgO–SiO₂–MnO. Type 4 inclusion is globular and mainly detected in S3 of Melt B.

Type 5 inclusion given in Fig. 8 is MgO system. Both rectangle and sphere shapes of Type 5 were observed. The spherical Type 5 inclusion is mainly found in S1 of Melt B, while the rectangular Type 5 inclusion is detected in Melt C with excess magnesium addition. Moreover, the EDS analysis results show that the spherical MgO system inclusion contains trace amount of silicon.

The distributions of various inclusions in different samples are summarized in **Table 3**. The number in Table 3 represents the type of inclusion. The results show that SiO₂–MnO liquid inclusions are modified to MgO–SiO₂–MnO and MgO respectively in Met A and Melt C. In Melt B, MgO forms firstly and then transforms to SiO₂–MgO with the prolongation of holding time.

3.2.2. Composition Evolution of Inclusions

To assess the evolution process of inclusions with holding time after magnesium addition, the EDS analysis results of inclusions were converted to mass percentage of MgO, SiO₂ and MnO, which could be projected into MgO–SiO₂–MnO ternary system phase diagram,²³⁾ as shown in **Fig. 9**. In Melt A, MgO–SiO₂–MnO is the main type of inclusions and the compositions are all in the region of liquid, which is shown in Fig. 9(a). The composition distribution of inclusions in Melt B is given in Fig. 9(b). It can be seen that most inclusions distribute in the composition region of 2MgO·SiO₂ saturation. (Mg, Mn)O solid solutions form immediately at 1 min after magnesium addition. 5 min later, the mass percentage of SiO₂ in inclusions increases and the compositions of inclusions distribute in the region of 2MgO·SiO₂ saturation. 10 min later, the content of SiO₂ in inclusions continues to increase and Type 3 inclusion forms. In Melt C, the inclusions of (Mg, Mn)O solid solutions precipitate and remain stable with the increase of holding time, as shown in Fig. 9(c). Based on the experimental results, it

can be concluded that the evolution process of inclusion is MgO–SiO₂–MnO(l) → MgO–SiO₂(s) → MgO(s) with the increase of magnesium addition.

3.2.3. Number and Diameter of Inclusions

Figure 10 shows the effect of magnesium addition on the number and diameter of inclusions, which is plotted against holding time after magnesium addition. The type of inclusion before magnesium addition is SiO₂–MnO liquid oxide and the average diameter of inclusion is 1.4 μm in the sample S0. After magnesium addition, the average diameter of inclusion decreases firstly and then increases with the prolongation of holding time. The similar results were also reported in other studies.^{16,24,25)} It can be clearly seen that the number of inclusions below 2.0 μm increases rapidly in the sample S1. With prolonging holding time, the number of inclusions above 2.0 μm increases gradually in the sample S2 and S3. One of the possible reason is that inclusion collides and grows during holding time. Moreover, it is noticed that the number of inclusions above 2.0 μm in Melt B is more than that in Melt A and Melt C. The reason is that MgO formed in Melt B is unstable and then reacts with molten steel. With the diffusion of Si from molten steel, inclusion grows continuously in Melt B.

According to the results in Mn–Si killed steel, it can be summarized that appropriate magnesium addition is necessary. In the present magnesium treatment level, a medium amount of magnesium addition would lead to the precipitation of more large size inclusions.

3.3. Thermodynamic Calculation and Formation Mechanism of Inclusions

In order to explain the modification mechanism of inclusions with magnesium addition, thermodynamic calculation was carried out at 1 873 K using Fact Sage 7.1 with databases of FactPS, FToxide and FTmisc.^{26,27)} **Figure 11** shows the effect of magnesium addition on the equilibrium precipitations in Fe–1.2Mn–0.016O–0.2Si molten steel system. According to the characteristics of precipitations in steel, the evolution process of inclusions can be divided into 5 zones and the related reactions are given in **Table 4**.^{28–30)}

At zone I, the mass fraction of magnesium addition is low and only MgO–SiO₂–MnO exists in the molten steel. The formation of MgO–SiO₂–MnO can be given by Eq. (1).

At zone II, both MgO–SiO₂–MnO and 2MgO·SiO₂ are the equilibrium precipitations. Part of MgO–SiO₂–MnO is modified to 2MgO·SiO₂ by Eq. (2), which leads to a drop in the mass fraction of MgO–SiO₂–MnO.

At zone III, MgO–SiO₂–MnO is completely modified to 2MgO·SiO₂ and only 2MgO·SiO₂ system inclusions exist in the molten steel. With the increase of magnesium addition in steel, the mass fraction of 2MgO·SiO₂ continues to increase through Eq. (3).

At zone IV, MgO and 2MgO·SiO₂ are the equilibrium precipitations. The mass fraction of MgO increases with the decrease of 2MgO·SiO₂, which indicates that the equilibrium precipitation transfers from 2MgO·SiO₂ to MgO via Eq. (4).

At zone V, the mass fraction of magnesium addition is high and the equilibrium precipitation is MgO. The mass fraction of MgO slightly increases by Eq. (5).

Table 3. Types of inclusions in different samples.

Melt	S0	S1	S2	S3
	5 min after Si addition	1 min after Mg addition	5 min after Mg addition	10 min after Mg addition
A	1	2	2	2
B	1	5	3	3/4
C	1	5	5	5

Fig. 9. Composition distribution of inclusions with holding time after magnesium addition. (Online version in color.)

Fig. 10. Number and diameter of inclusions observed in all samples. (Online version in color.)

Fig. 11. Effect of magnesium content on the equilibrium precipitation of inclusions at 1 873 K. (Online version in color.)

Based on the analysis mentioned above, the evolution process of equilibrium precipitations is $\text{MnO-SiO}_2(l) \rightarrow \text{MgO-SiO}_2\text{-MnO}(l) \rightarrow 2\text{MgO} \cdot \text{SiO}_2(s) \rightarrow \text{MgO}(s)$ with the increase of magnesium addition in Mn-Si killed molten steel, which is in good agreement with the experimental results. Similar findings were reported in Ti-Mg killed melts.^{17,18)}

Based on the experimental results and thermodynamics of inclusions, the evolution mechanism is proposed in Fig. 12

and the details are described as followings.

In route 1, a small amount of magnesium is added to the molten steel and the equilibrium precipitation is $\text{MgO-SiO}_2\text{-MnO}$ liquid inclusion. Mg dissolves into the molten steel and then partly substitute for Mn and Si in $\text{SiO}_2\text{-MnO}$ deoxidization product. The modification of $\text{SiO}_2\text{-MnO}$ to $\text{MgO-SiO}_2\text{-MnO}$ is given by Eq. (1).

Table 4. Reactions at different zones.

Zones	Reaction	$\Delta G^\circ/\text{J}\cdot\text{mol}^{-1}$	Equation
I	$\text{MnO}\cdot\text{SiO}_2(\text{l}) + [\text{Mg}] = \text{MgO}\cdot\text{SiO}_2(\text{l}) + [\text{Mn}]$	$-444\,094 + 106.29T$	(1)
II	$2\text{MgO}\cdot\text{SiO}_2(\text{s}) + 1/3[\text{Si}] = 4/3\text{MgO}\cdot\text{SiO}_2(\text{l}) + 2/3[\text{Mg}]$	$404\,544 - 135.52T$	(2)
III	$2[\text{Mg}] + [\text{Si}] + 4[\text{O}] = 2\text{MgO}\cdot\text{SiO}_2(\text{s})$	$-2\,106\,300 + 702.14T$	(3)
IV	$4\text{MgO}(\text{s}) + [\text{Si}] = 2\text{MgO}\cdot\text{SiO}_2(\text{s}) + 2[\text{Mg}]$	$808\,100 - 251.46T$	(4)
V	$[\text{Mg}] + [\text{O}] = \text{MgO}(\text{s})$	$-728\,600 + 238.4T$	(5)

Fig. 12. Formation and evolution of inclusions by magnesium treatment. (Online version in color.)

In route 2, a medium amount of magnesium is added to the molten steel and the equilibrium precipitation is $2\text{MgO}\cdot\text{SiO}_2$ solid inclusion. Different from route 1, spherical MgO forms as intermediate product immediately after magnesium addition in route 2. As MgO is unstable according to thermodynamics, MgO continues to react with the molten steel through Eq. (4) and eventually converts to $2\text{MgO}\cdot\text{SiO}_2$ solid inclusion with holding time.

In route 3, an excessive amount of magnesium is added to the molten steel and the equilibrium precipitation is MgO solid inclusion. Rectangular MgO forms immediately after magnesium addition and keeps stable with holding time.

4. Conclusions

The effect of magnesium addition on the evolution of inclusions in Mn–Si killed molten steel has been studied by the laboratory experiments and thermodynamic calculation at 1 873 K. The main findings can be summarized as followings.

(1) Four types of inclusions are detected after magnesium addition, namely $\text{MgO}\cdot\text{SiO}_2\text{--MnO}$ liquid inclusion, $\text{MgO}\cdot\text{SiO}_2\text{--MnO}$ complex inclusion, $\text{MgO}\cdot\text{SiO}_2$ and MgO system solid inclusion, which are in accordance with the result of thermodynamic calculation.

(2) The amount of magnesium added to the molten steel significantly influences the evolution of inclusions. Liquid inclusion of $\text{MnO}\cdot\text{SiO}_2$ is promptly modified to $\text{MgO}\cdot\text{SiO}_2\text{--MnO}$ liquid inclusion with 0.0005% magnesium addition. As the amount of magnesium is increased to 0.0011%, intermediate product MgO forms immediately and then gradually transforms to $\text{MgO}\cdot\text{SiO}_2$ solid inclusion with holding time. While MgO solid inclusion keeps stable

throughout with magnesium amount further increased to 0.0019%.

(3) In the present magnesium treatment level, a medium amount of magnesium addition would lead to the precipitation of more large size inclusions.

Acknowledgements

The authors gratefully acknowledge the support from the National Natural Science Foundation of China (Grant No. NSFC 51674069) and the National Key R & D Program of China (Grant No. 2017YFC0805100).

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