Formation and Evolution of Non-metallic Inclusions in Medium Mn Steel during Secondary Refining Process

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Industrial and laboratory experiments were carried out to understand the formation and evolution mechanism of non-metallic inclusions in medium Mn steel during secondary steelmaking process. In industrial experiments, with the generation of dissolved Mg and Ca in liquid steel, the inclusions in liquid steel would transform along with the route of “Al2O3 inclusions → MgO·Al2O3 spinel inclusions → (Mn, Mg)O·Al2O3 spinel inclusions → CaO–MgO–MnO–Al2O3 system calcium aluminate inclusions”. (Mn, Mg)O·Al2O3 spinel with a high MnO content was found as a different type of inclusions compared with conventional Al-killed steel grades, and finally, the MnO content in calcium aluminate inclusions became very low. Laboratory experiments were employed to explain the generation of (Mn, Mg)O·Al2O3 spinel inclusions. It is found that the crystal structure of MgO·Al2O3 spinel phase would help the formation of (Mn, Mg)O·Al2O3 inclusions, while Al2O3 inclusions can not react with dissolved Mn in steel to form (Mn, Mg)O·Al2O3 spinel inclusions, even the Mn content was around 5 mass% in steel. Consequently, (Mn, Mg)O·Al2O3 spinel inclusions formed after the formation of MgO·Al2O3 spinel inclusions in industrial practice.

KEY WORDS: non-metallic inclusions; MgO·Al2O3 spinel; MnO·Al2O3 spinel; medium Mn steel; secondary refining.

1. Introduction

MgO·Al2O3 spinel inclusions are mainly found in Al-killed steel.1–7) Due to their high hardness and irregular shape, this kind of inclusions tend to induce microcosmic cracks and lead to fatigue failure of final product, and they are usually considered as harmful inclusions for steel.

In order to control these inclusions, a lot of researchers1–4,7–30) have studied the formation and evolution mechanism of MgO·Al2O3 spinel inclusions in steel. Some of them7–10,12,21,29) thought that the formation of MgO·Al2O3 spinel inclusions depends on the concentration of dissolved Mg and Ca in liquid steel. Meanwhile, some researchers18,19,21) found that MgO·Al2O3 spinel could still precipitate from CaO–SiO2–Al2O3–MgO system inclusions during the cooling of liquid steel, although the composition of Mg, Al and O in liquid steel was not in the stable region of MgO·Al2O3. Additionally, Todoroki et al.16) and Wang et al.20) also proposed SiO2 in slag would hinder the formation of MgO·Al2O3 inclusions. Moreover, many researchers7–7) believed that when a trace of dissolved Ca is formed in liquid steel, the MgO·Al2O3 inclusions in steel are not stable, and could be easily modified into CaO–MgO–Al2O3 inclusions and even CaO–Al2O3 with a low melting temperature.

The studies mentioned above were mainly based on conventional Al-killed steel or silicon-killed stainless steel. Recently, more and more attention is paid to Mn steel due to its advantages in auto mobile industry. Many studies aim to improve the performances of steel by the addition of Mn.31,32) The Mn content in Mn steel is much higher than that in conventional steel grades. Since the steel grades are still new, the inclusion behaviors of medium Mn steel grades in refining process are rarely studied, and the formation and evolution of inclusions in medium Mn steel is not well understood. Besides, in industrial practice, the present authors found many (Mn, Mg)O·Al2O3 spinel inclusions in medium Mn steel during secondary refining process. In fact, this kind of inclusions is seldom reported33,34) and their formation mechanism is not clear as well. Therefore, some investigations need to be conducted to clarify the behavior of non-metallic inclusions in medium Mn steel.

In the present work, industrial and laboratory experiments were carried out to study the formation and evolution mechanism of non-metallic inclusions in medium Mn steel. Some steel samples were taken at different stages in industrial refining process to identify the types of inclusions in liquid steel. Laboratory experiments were also designed to explain the formation mechanism of MnO·Al2O3 spinel inclusions. Based on the results of industrial and laboratory experiments, the evolution behaviors of inclusions in medium Mn steel during refining process were discussed.
2. Experimental

2.1. Industrial Experiment

The experimental medium Mn steel was produced in a steel plant by the process of "hot metal pre-treatment → 100 t BOF steelmaking → 100 t ladle furnace (LF) refining → 100 t VD refining → slab continuous casting". The chemical composition of the steel is listed in Table 1. After hot metal pre-treatment, the S content in hot metal was less than 0.0020%. The C content was lower than 0.03%, while the activity of dissolved oxygen was in the range of 700–1 000 ppm at the end of BOF. Before tapping, about 3.8 t metal manganese was added into ladle. Thereafter, during tapping, 1.5 t metal manganese, around 380 kg FeMnAl alloy (Mn 25–30%, Al 16–22%) and other alloys as well as 300–400 kg lime were added into ladle for deoxidation and pre-sludging. In LF refining process, slagging and alloying were carried out by the addition of approximate 1 t synthetic slag, 110 kg Al and other alloys. The argon bottom blowing flow rate was 350–500 NL/min. After 50–60 min treatment, the activity of dissolved oxygen was measured as 2–4 ppm in steel using oxygen probe, and the composition of refining slag is given in Table 2. During VD treatment, the vacuum pressure was controlled smaller than 67 Pa, and the treatment time was around 20 min.

Some steel samples were taken at different stages, namely before LF refining (Sample 1), at the middle stage of LF refining (Sample 2), after LF refining (Sample 3) and after VD refining (Sample 4), respectively. These steel samples were prepared for chemical analysis and inclusion investigation. The contents of Al, Mg, and Ca in the samples were analyzed by ICP-AES method, while the morphology, size and composition of the inclusions were determined by a scanning electron microscope (SEM, Zeiss Ultra Plus) with an energy-dispersive X-ray spectrometer (EDS).

2.2. Laboratory Experiment

Laboratory experiments were designed to study the formation mechanism of MnO·Al2O3 inclusions in medium Mn steel. The experimental setup is shown in Fig. 1. Since it is very difficult to find the same specific inclusion in the steel samples, some Al2O3 and MgO·Al2O3 oxide sticks were used to simulate Al2O3 and MgO·Al2O3 inclusions in steel, respectively. These oxide sticks were made from analytical reagents, and the detailed preparation description was given in Ref. 29. Note that the spinel stick is not the same dense reagents, and the detailed preparation description was given in Ref. 29. Note that before LF refining, the Ca content is significantly low, while the Mg content is even around 40 times higher than Ca. The increase trend in Table 3 is in line with our previous study7) while in Table 1 the Ca content is significantly low, while the Mg content is even around 40 times higher than Ca. The increase trend in Table 3 is in line with our previous study7) while in Table 1 the Ca content is significantly low, while the Mg content is even around 40 times higher than Ca.

Some steel samples were taken at different stages, namely before LF refining (Sample 1), at the middle stage of LF refining (Sample 2), after LF refining (Sample 3) and after VD refining (Sample 4), respectively. These steel samples were prepared for chemical analysis and inclusion investigation. The contents of Al, Mg, and Ca in the samples were analyzed by ICP-AES method, while the morphology, size and composition of the inclusions were determined by a scanning electron microscope (SEM, Zeiss Ultra Plus) with an energy-dispersive X-ray spectrometer (EDS).

### Table 1. Chemical composition of medium steel (mass%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Al</th>
<th>*Mg</th>
<th>*Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.04–0.06</td>
<td>0.15–0.25</td>
<td>4.85–5.55</td>
<td>0.38–0.42</td>
<td>0.28–0.35</td>
<td>0.18–0.30</td>
<td>0.02–0.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Composition of LF refining slag (mass%).

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>MgO</th>
<th>FeO + MnO</th>
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<tr>
<td></td>
<td>45–52</td>
<td>8–10</td>
<td>25–30</td>
<td>6–8</td>
<td>≤2</td>
</tr>
</tbody>
</table>

### Table 3. Chemical compositions of steel samples (mass%, *ppm).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Al</th>
<th>*Mg</th>
<th>*Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.043</td>
<td>0.018</td>
<td>4.86</td>
<td>0.29</td>
<td>0.31</td>
<td>0.18</td>
<td>0.018</td>
<td>3.7</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.054</td>
<td>0.021</td>
<td>5.48</td>
<td>0.35</td>
<td>0.30</td>
<td>0.20</td>
<td>0.032</td>
<td>4.0</td>
<td>0.7</td>
</tr>
<tr>
<td>3</td>
<td>0.057</td>
<td>0.021</td>
<td>5.70</td>
<td>0.39</td>
<td>0.30</td>
<td>0.21</td>
<td>0.031</td>
<td>5.8</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>0.057</td>
<td>0.020</td>
<td>5.45</td>
<td>0.40</td>
<td>0.30</td>
<td>0.21</td>
<td>0.022</td>
<td>5.9</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of experimental setup. (Online version in color.)
the results of Yoshioka et al. the decrease of Mg and Ca has been seen after RH treatment. This difference might be related to the different experimental conditions.

3.1.2. Inclusions in Industrial Steel Samples

The types and the specification of each type of inclusions are shown in Table 4 and Figs. 2 to 7, and the composition range of each type of inclusions is listed in Table 5.

Seven different types of inclusions are found in these industrial samples. Type 1 and Type 2 inclusions are singular and cluster Al$_2$O$_3$ inclusions as shown in Figs. 2(a) and 2(b), respectively. The size of Type 1 inclusions is usually smaller than 15 μm, while the alumina clusters are normally bigger than 10 μm. Both of them are mainly found before LF refining. Since Al$_2$O$_3$ inclusions are common inclusions in Al-killed steel, no elemental mappings are given in Fig. 2.

Figure 3 shows the elemental mappings of Type 3 inclusions. It can be seen that Type 3 inclusions are MgO·Al$_2$O$_3$ spinel inclusions in a small size (<10 μm). As shown in Table 5 and Fig. 3, almost no Mn is distributed in this type of inclusions, and the shape of these inclusions is irregular.

The elemental mappings of Type 4 inclusions are given in Fig. 4. As shown in Fig. 4 and Table 5, this type of inclusions contains a large amount of MnO and a small amount of MgO. Since MnO·Al$_2$O$_3$ spinel and MgO·Al$_2$O$_3$ spinel could form a solid solution at steelmaking temperature, the structure of these inclusions would be spinel as well. As shown in the figure, the size of (Mn, Mg)O·Al$_2$O$_3$ spinel inclusions is still very small, and usually they are irregular in shape and smaller than 10 μm in size. Note that compared with the inclusions in conventional Al-killed steel grades, this type of inclusions is a different type of inclusions, since it is rarely reported in literature.

Type 5 inclusions are a combination of Type 3 and Type 4 inclusions, namely a MgO·Al$_2$O$_3$ spinel core surrounded by a (Mn, Mg)O·Al$_2$O$_3$ spinel out layer. The elemental mappings of a typical Type 5 inclusion are shown in Fig. 5. As shown in this figure, Mn element is only distributed in the out layer. Similar to Type 3 and Type 4 inclusions, the shape of Type 5 is also irregular, and the size is less than 10 μm. As given in Table 5, the inclusions of Type 3, Type 4 and Type 5 are mainly detected at the middle stage of LF refining, while very small amounts of Type 4 and Type 5

Table 4. Types of inclusions at different stages.

<table>
<thead>
<tr>
<th>Type</th>
<th>Specification of Inclusions</th>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Singular Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Al$_2$O$_3$ cluster</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>MgO·Al$_2$O$_3$ spinel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(Mn, Mg)O·Al$_2$O$_3$ spinel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>MgO·Al$_2$O$_3$ spinel + (Mn, Mg)O·Al$_2$O$_3$ spinel (outer layer)</td>
<td>1–10</td>
<td>××</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Calcium aluminate with low MgO, MnO, and SiO$_2$ contents</td>
<td>1–10</td>
<td>××</td>
<td>×</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(Mn, Mg)O·Al$_2$O$_3$ spinel + calcium aluminate with low MgO, MnO, and SiO$_2$ contents</td>
<td>1–10</td>
<td>××</td>
<td>××</td>
<td>×</td>
<td></td>
</tr>
</tbody>
</table>

“××” main type of inclusions at the stage, “×” small amount of inclusions at the stage.
inclusions are also found at the end of LF refining.

The inclusions of Type 6 are calcium aluminate inclusions with a small amount of MgO, MnO, and SiO2. Figure 6 shows the elemental mappings of a typical Type 6 inclusion. In order to keep brief, the elemental mapping of oxygen is not given in this figure, but it is still one of the elements of these inclusions. As can be seen from Fig. 6, this type of inclusions is globular with a size less than 10 μm. According to CaO–Al2O3 phase diagram,35 the shape and the composition given in Table 5 also indicate that this type of inclusions is mainly in liquid phase.

Type 7 is a combination of Type 5 and Type 6. Figure 7 gives an example of a Type 7 inclusion. As shown in Fig. 7, there is an irregular (Mn, Mg)O·Al2O3 spinel surrounded by a calcium aluminate layer. In the (Mn, Mg)O·Al2O3 spinel phase, the amount of MnO is still high, while the content of MnO in calcium aluminate layer is much lower as shown in Table 5. Besides, the amounts of SiO2 and MgO in calcium aluminate are also very low. Similar to Type 6, the inclusions of Type 7 are also globular and small in size. Note that Type 6 inclusions are mainly found after LF and VD treatment, while Type 7 is presented as a main type of inclusions after LF refining.

3.2. Laboratory Results

3.2.1. Composition of Laboratory Steel Samples

After laboratory experiments, the steel composition is given in Table 6. It is seen that the composition after experiment is almost the same as the one shown in Table 1. Especially, the Al content is still higher than 200 ppm, and this means that the dissolved oxygen in liquid steel is very low at experimental temperature.

3.2.2. Boundary between Steel and Oxide Stick

The elemental mappings of the boundary between steel and the Al2O3 stick are shown in Fig. 8. As shown in this figure, no evident change can be seen at the boundary after 100 min of reaction. Mn element is only distributed in steel side, while no obvious Mn element can be seen in the Al2O3 stick. In contrast, Fig. 9 gives the elemental mappings of the boundary between steel and the MgO·Al2O3 stick. As shown in Fig. 9, after 100 min of reaction, a large amount of Mn element is distributed in the MgO·Al2O3 stick, leading to the formation of (Mn, Mg)O·Al2O3 spinel. On the other hand, as shown in the upper part of Fig. 9, there is a small region without Mn element. This in fact proves the stick used in the present study is in MgO·Al2O3 spinel phase before
experiments. In addition, steel particles are also found in the pores of the oxide stick, since the stick is not very dense as mentioned in the experimental section. It is very necessary to mention that in Fig. 9, the intensity of Mn in steel and the stick is different, even though the intensity looks quite close due to the contrast of the figure. A line scanning of the boundary between steel and the MgO·Al2O3 stick shown in Fig. 10 proves that the concentration of Mn in steel is higher than that in the stick, indicating that the Mn element in stick is from liquid steel. The results in Figs. 8 to 10 imply that MgO·Al2O3 spinel inclusions tend to transform into (Mn, Mg)O·Al2O3 spinel in medium Mn steel, while Al2O3 inclusions are very difficult to react with medium Mn steel to form MnO·Al2O3 phase, even the content of dissolved Mn is higher than 5 mass%.

4. Discussion

4.1. Evolution of Inclusions in Medium Mn Steel

Before tapping, metal manganese has been added into ladle. Since the dissolved oxygen in crude steel is very high (700–1 000 ppm) at the end of BOF, when the liquid steel is tapped into ladle, the dissolved oxygen will react with manganese as shown in Eq. (1). However, due to the weak deoxidation capacity of Mn, the equilibrium dissolved oxygen in liquid steel would still be high. According to the thermodynamic data in Eqs. (1) and (2), the calculated equilibrium dissolved oxygen after 5 mass% Mn deoxidation is around 350 ppm at 1 873 K, if the activity of MnO is considered as unity. In fact, the dissolved Mn is much lower than 5 mass% at the beginning of tapping, because a certain amount of metal manganese is still solid, not melted. It means the dissolved oxygen in this case is much higher than the calculated value. When the deoxidizer FeMnAl alloy is added, dissolved Al would react with the rest of dissolved O to form Al2O3 by the reaction of Eq. (3). Due to Al’s strong affinity to oxygen, the dissolved oxygen would decrease to several ppm immediately. At the same time, the deoxidation product (Mn, Fe)O could also be reduced by dissolved Al to generate alumina inclusions (see Eq. (5)). Similar results are also reported in an earlier study by the present authors. Therefore, the main type of inclusions are alumina inclusions before LF refining (Type 1 and Type 2) as given in Table 4 and Fig. 2.

\[
[Mn] + [O] = MnO(s) \quad \text{......................... (1)}
\]

\[
\log K_1 = -6.43 + \frac{13 450}{T} \quad \text{......................... (2)}
\]

\[
2[Al] + 3[O] = Al_2O_3(s) \quad \text{......................... (3)}
\]

\[
\log K_2 = -20.57 + \frac{64 000}{T} \quad \text{......................... (4)}
\]

\[
3MnO(s) + 2[Al] = Al_2O_3(s) + 3[Mn] \quad \text{......................... (5)}
\]

\[
\log K_3 = -1.28 + \frac{23 650}{T} \quad \text{......................... (6)}
\]

At the middle stage of LF refining, MgO·Al2O3 spinel (Type 3), (Mn, Mg)O·Al2O3 spinel (Type 4 and Type 5) inclusions become the main types of inclusions as shown in Table 4. Type 3 is almost pure MgO·Al2O3 spinel, and no obvious Mn is distributed in the inclusions as shown in Fig. 3. The inclusions of Type 4 contain a high MnO content with a small amount of MgO, while Type 5 is a combination of Type 3 and Type 4, since it has a MgO·Al2O3 core surrounded by a (Mn, Mg)O·Al2O3 out layer. These three types of inclusions in fact indicate that Type 5 inclusions are the intermediate product between Type 3 and Type 4 inclusions. According to the element distribution in Type 5 inclusions (see Fig. 5), it can be concluded that MgO·Al2O3 spinel should be the inclusion before evolution, while (Mn, Mg)O·Al2O3 spinel would be the evolution product. In other words, during the refining process of medium Mn steel, MgO·Al2O3 spinel inclusions will transform into (Mn, Mg)O·Al2O3 spinel inclusions with a high MnO content and a
The formation of \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) spinel in Al-killed steel has been studied by many researchers.\(^7,9,10,21\) Most of them believed that if there is a trace of dissolved Mg in steel, alumina inclusions tend to transform into spinel inclusions. In the present study, as shown in Table 3, before LF refining and at the middle of LF, several ppm dissolved Mg has been generated. A phase stability diagram of \( \text{MgO}/\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 \) can be obtained according to Refs. 4), 7) and 8). In the calculation, pure solid state and infinite dilute solution states for the oxides and the dissolved elements in the liquid steel are taken as the standard states for the oxides and the dissolved elements in the liquid steel, respectively. The dissolved oxygen content was measured as 2–4 ppm, so 4 ppm is taken for the calculation, while the interaction coefficients of the dissolved elements are listed in Table 7. The results are shown in Fig. 11. The manner to have the dashed line corresponding to the boundary between \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) and \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) will be described in the following text in detail. The contents of \( \text{Al} \) and \( \text{Mg} \) listed in Table 3 are located at the stable region of \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \). It means that \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) spinel (Type 3) would form at the early stage of LF refining.

After the formation of \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) spinel inclusions, these inclusions will transform into \( \text{(Mn, Mg)} \cdot \text{Al}_2\text{O}_3 \) spinel inclusions. As shown in Fig. 5, it is seen that Mn diffuses into \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) spinel inclusions, while in the center, there is almost no Mn element. Note that no MnO inclusions are found at this stage, so it rules out the possibility that the Mn element in Type 5 inclusions is from MnO inclusions. As shown in Fig. 5, it is seen that MnO diffuses into MgO·Al2O3 spinel inclusions, while in the center, there is almost no Mn element. This can include, for example, \( \text{(Mn}_{0.001}, \text{Mg}_{0.999}) \cdot \text{Al}_2\text{O}_3 \) that Mn is very trace in the solid solution with the consideration of an extreme case. In this view, in order to draw the boundary in Fig. 11, it is necessary to assume that the boundary is calculated based on the data in Ref. 37. The Gibbs free energy of Eq. (7) at standard state can be obtained based on the thermodynamic data of MgO·Al2O3,\(^7\) MnO·Al2O3,\(^37\) MgO,\(^7\) and \( \text{MnO} \cdot \text{Al}_2\text{O}_3 \).

\[
\Delta G_f = -235 \, 312 + 231.58 T \text{ J/mol} \quad (8)
\]

On the basis of the phase stability diagram of \( \text{MgO}/\text{MgO} \cdot \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 \) (see Fig. 11), the present authors have attempted to calculate the boundary of \( \text{MgO} \cdot \text{Al}_2\text{O}_3/(\text{Mn}, \text{Mg}) \cdot \text{Al}_2\text{O}_3 \) (the dashed line in Fig. 11) considering Eq. (7). In fact, thermodynamically, it is quite difficult to draw a line, because \( \text{(Mn, Mg)} \cdot \text{Al}_2\text{O}_3 \) is a solid solution that is able to take arbitrarily any compositions. This can include, for example, \( \text{(Mn}_{0.001}, \text{Mg}_{0.999}) \cdot \text{Al}_2\text{O}_3 \) that Mn is very trace in the solid solution with the consideration of an extreme case. In this view, in order to draw the boundary in Fig. 11, it is necessary to assume that the boundary is calculated according to the measured inclusion compositions in Table 5.

The boundaries of \( \text{MgO} \cdot \text{Al}_2\text{O}_3/(\text{Mn}, \text{Mg}) \cdot \text{Al}_2\text{O}_3 \) in Al-killed steel are determined by Eqs. (7) and (8). Accounting for the measured inclusion compositions at the \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) enriched side, the activities of \( \text{MnO} \cdot \text{Al}_2\text{O}_3 \) and \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) in the solid solution \( \text{(Mn, Mg)} \cdot \text{Al}_2\text{O}_3 \) are taken as 0.05 and 0.85, respectively, on the basis of the study results of Zhao et al.\(^7\) Meanwhile, at the \( \text{MnO} \cdot \text{Al}_2\text{O}_3 \) enriched side where it is a virtually extreme case, the activities of \( \text{MnO} \cdot \text{Al}_2\text{O}_3 \) and \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) are read as 0.9 and 0.05, respectively.

Thereby, it is found that \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) is stable above 4.2 ppm Mg. Thus, the boundary between \( \text{(Mn, Mg)} \cdot \text{Al}_2\text{O}_3 \) and \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) is presented by a dashed line in Fig. 11. The experimental data are plotted in Fig. 11. In the figure, alumina is observed in the Sample 1 though plotted in the sample 1.

![Fig. 11. Stability phase diagram of MgO/(Mn, Mg)O·Al2O3/Al2O3.](image)

<table>
<thead>
<tr>
<th>Researchers</th>
<th>( \Delta G^\circ ) at 1873 K</th>
<th>References</th>
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<tbody>
<tr>
<td>Zhao et al.</td>
<td>(-56 , 000 +14.98T)</td>
<td>37</td>
</tr>
<tr>
<td>Kim et al.</td>
<td>(-5 , 030 +0.09T)</td>
<td>38</td>
</tr>
<tr>
<td>Belic et al.</td>
<td>(-2 , 105 +558 +105.49T)</td>
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<td>Pandit et al.</td>
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<td>Timucin et al.</td>
<td>(-15.87T)</td>
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<td>Barin et al.</td>
<td>(-43 , 776 -18.8T)</td>
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<td>Ogasawara et al.</td>
<td>(-45 , 370 +10.40T)</td>
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<td>Knacke et al.</td>
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<td>(-10 , 466)</td>
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</tbody>
</table>
region where (Mn, Mg)O·Al2O3 is stable. It is considered that the inclusions do not reach an equilibrium state with the liquid steel. On the other hand, (Mn, Mg)O·Al2O3 and MgO·Al2O3 inclusions can coexist in Sample 2. It is obviously seen that the plot is located at the boundary, proving that this coexistence is quite consistent. Therefore, MgO·Al2O3 will transform into (Mn, Mg)O·Al2O3. With the reaction, Mg element in MgO·Al2O3 inclusions is continually replaced by Mn element, leading to a layer of (Mn, Mg)O·Al2O3, namely Type 5 inclusions. The thickness of the layer would increase with time and finally generate (Mn, Mg)O·Al2O3 inclusions completely, namely Type 4 inclusions. Detailed discussion on the formation of (Mn, Mg)O·Al2O3 inclusions is given in the following section.

In Table 3, a trace of dissolved Ca is formed during the refining process in the present study, and some calcium aluminate inclusions (Type 6 and Type 7) are found after LF refining and VD treatment. Many studies1,2,4,6,17) pointed out that MgO·Al2O3 spinel inclusions are not stable and would transform into calcium aluminate inclusions, when there is a trace of dissolved Ca in liquid steel. Note that these study results are mainly based on conventional Al-killed steel grades. In fact, in the present study similar results are also obtained. After VD refining, those (Mn, Mg)O·Al2O3 inclusions have been vanished, and calcium aluminate inclusions with a small amount of MgO, MnO, and SiO2 (Type 7), are the main type of inclusions. It implies that (Mn, Mg)O·Al2O3 inclusions are not stable as well, when trace of dissolved Ca exists in liquid steel. As a result, those (Mn, Mg)O·Al2O3 inclusions will transform into calcium aluminate inclusions. Since the contents of MnO and MgO in calcium aluminates are really low (see Table 5), during the evolution of (Mn, Mg)O·Al2O3 inclusions into calcium aluminates, the MnO and MgO in spinel inclusions would be replaced by CaO, and then form a Type 7 inclusion. With the increase of evolution time, the calcium aluminate layer in a Type 7 inclusion will occupy the entire inclusion and result in a Type 6 inclusion. Furthermore, trace of SiO2 is observed in Type 6 and Type 7 inclusions. In fact, in order to reach thermodynamic equilibrium, little amount of silicon would be oxidized and dissolved into oxide solution, resulting in the small amount of SiO2 in the inclusions. Similar results are also reported by Beskow et al.24)

On the basis of previous studies,4,7) a stability phase diagram of (Mn, Mg)O·Al2O3/calcium aluminate/Al2O3, viz. Figure 12 can also be calculated based on Fig. 11. It should be noted that CaO and Al2O3 are dominated in the calcium aluminate inclusions though small amounts of MgO, MnO and SiO2 are contained as understood in Table 5. It is still reasonable to choose CaO·Al2O3 as calcium aluminate specie in the calculation the same as the previous study.7)

In Fig. 12, as for Sample 1, as explained above, it is considered that the reactions between liquid steel and the inclusions do not reach an equilibrium state. It can be realized that Sample 2 is plotted in the (Mn, Mg)O·Al2O3 region and it is close to the boundary between (Mn, Mg)O·Al2O3 and CaO·Al2O3. It is emphasized that Sample 2 is plotted on the boundary of the three: (Mn, Mg)O·Al2O3, MgO·Al2O3 and calcium aluminate. As listed in Table 5, (Mn, Mg)O·Al2O3 and MgO·Al2O3 inclusions are dominated with coexistence of a small amount of calcium aluminate with a (Mn, Mg)O·Al2O3 core in Sample 2. This is very consistent with each other, which proves that the calculation is quite reasonable. It can also be seen that Sample 3 and 4 are quite consistently plotted on the region where CaO·Al2O3 is stable merely with 2–3 ppm Ca contained in the steel. It is considered that the inclusions of CaO·Al2O3 with a (Mn, Mg)O·Al2O3 core are the phase transforming toward the most stable CaO·Al2O3 phases.

The agreement of the measured inclusion compositions with the stability diagrams proves that the following fact. Inclusion composition can be determined on the basis of thermodynamic equilibrium, and it also implies that the kinetic consideration of the reactions between inclusions and molten steel can be ignored during the period of the sampling interval of this study.

To show a full picture of the evolution route, Fig. 13 gives a sketch of the evolution of inclusions during the refining process of medium Mn steel. In this figure, the related reactions are listed. As shown, during the refining process in the present study, it is seen that the main evolution route of the inclusions in medium Mn steel is “Al2O3 inclusions → MgO·Al2O3 spinel inclusions → (Mn, Mg)O·Al2O3 spinel inclusions → CaO·MnO·MgO·Al2O3 calcium aluminate inclusions”. During evolution, alumina and spinel inclusions are all solid inclusions and irregular in shape, while calcium aluminate inclusions are globular and usually in liquid phase. (Mn, Mg)O·Al2O3 spinel inclusions have a high MnO content and a low MgO content, while the contents of MgO, MnO, and SiO2 in calcium aluminates are all very low.

The evolution route of the inclusions in medium Mn steel has an obvious character, viz. the formation of (Mn,
MgO·Al2O3 spinel inclusions, which is different from conventional Al-killed steel grades. In conventional Al-killed steel grades, no (Mn, Mg)O·Al2O3 spinel inclusions can be found. Due to the similar spinel structure, the effect of (Mn, Mg)O·Al2O3 spinel inclusions on the properties of medium Mn steel is probably close to that of MgO·Al2O3 spinel inclusions. However, there is lack of studies in this field, so it is hard to draw an exact conclusion, and will be a new study topic in the near future. Meanwhile, if the refining time is long enough, the final inclusions are all calcium aluminate inclusions in both conventional Al-killed steel and Al-killed medium Mn steel grades. Although they contain MnO in medium Mn steel, these calcium aluminate inclusions in medium Mn steel will present almost the same effect on the properties of final products, since the MnO content is very small.

4.2. Formation of (Mn, Mg)O·Al2O3 Spinel Inclusions

As mentioned above, (Mn, Mg)O·Al2O3 spinel inclusions are formed during refining process. In fact, it seems that the beginning of deoxidation is a good moment for the formation of MnO·Al2O3 spinel inclusions, since there is already a large amount of dissolved Mn in liquid steel before deoxidation, and the reactions of Eqs. (9), (10), (12), (13) and (15) are all possible to happen during deoxidation.

\[
\text{Al}_2\text{O}_3(s) + [\text{Mn}] + [\text{O}] = \text{MnO} \cdot \text{Al}_2\text{O}_3(s) \quad \text{......... (9)}
\]

\[
4\text{Al}_2\text{O}_3(s) + 3[\text{Mn}] = 3\text{MnO} \cdot \text{Al}_2\text{O}_3(s) + 2[\text{Al}] \quad \text{......... (10)}
\]

\[
\log K_{10} = -1.9 - \frac{10078}{T} \quad \text{......... (11)}
\]

\[
4\text{MnO}(s) + 2[\text{Al}] = \text{MnO} \cdot \text{Al}_2\text{O}_3(s) + 3[\text{Mn}] \quad \text{......... (13)}
\]

\[
\log K_{13} = -1.26 + \frac{21778}{T} \quad \text{......... (14)}
\]

\[
2[\text{Al}] + [\text{Mn}] + 4[\text{O}] = \text{MnO} \cdot \text{Al}_2\text{O}_3(s) \quad \text{......... (15)}
\]

In the laboratory experiments, Al2O3 and MgO·Al2O3 sticks are used to model the inclusions in medium Mn steel. Although the sticks are much larger than a real inclusion, the boundary reaction could still present the reaction between an inclusion and liquid steel. On the other hand, the experimental steel is the same as industrial steel grade (see Tables 1 and 6), and the experimental temperature is also the same. As shown in Table 6, the Al content in steel is about 0.02%. According to Eq. (3), the dissolved oxygen activity in liquid steel can be evaluated as 4 ppm, which is in line with the industrial situation. As a result, the experimental condition is almost the same as the industrial experimental condition, then the laboratory results should be reasonable.

As shown in Fig. 8, no evident change is seen at the boundary between liquid steel and the Al2O3 stick, while in Fig. 9, the Mn element has already diffused into the MgO·Al2O3 stick. The experimental results rule out the possibility of Eqs. (9) and (10), and indicate that alumina inclusions could not generate MnO·Al2O3 directly during deoxidation. Meanwhile, Fig. 9 also implies that MgO·Al2O3 spinel inclusions tend to transform into (Mn, Mg)O·Al2O3 spinel in medium Mn steel.

Besides, no MnO containing inclusions but alumina inclusions (Type 1 and Type 2) are found before LF refining as shown in Table 4. As mentioned above, during deoxidation the deoxidation product of Mn would be reduced by dissolved Al to form alumina inclusions. Therefore, the reactions in Eqs. (12), (13) and (15) are also difficult to take place. Otherwise, MnO·Al2O3 system inclusions could be seen before LF refining.

A stability phase diagram of MnO/MnO·Al2O3/Al2O3 (see Fig. 14) can be calculated based on the Eqs. (10) and (13). The activities of Al2O3 and MnO are considered as unity, while the activity of MnO·Al2O3 in Al2O3 and MnO is calculated as 0.97 and 0.45 using FactSage, respectively. At the same time, the steel composition after deoxidation (Sample 1) is plotted in Fig. 14.

As shown in Fig. 14, the content of Sample 1 does not stay in the region of MnO·Al2O3, but the region of Al2O3. It indicates that alumina should be the stable phase if there is no Mg, so Al2O3 can not directly react with Mn to generate MnO·Al2O3. The calculation is in line with the present experimental results and the results of Paek et al. 47 Besides, Fig. 14 also proves that pure MnO·Al2O3 can not be generated, and the spinel phase should be the solid solution of (Mn, Mg)O·Al2O3, which is confirmed by the compositions listed in Table 5.

After 100 min of reaction, dissolved Mn could transfer into MgO·Al2O3 stick, but not in Al2O3 stick. This can be used to explain the formation of (Mn, Mg)O·Al2O3 spinel inclusions after MgO·Al2O3 spinel inclusions. It is likely that the spinel crystal structure helps the transfer of Mn element from liquid steel into inclusions. It is well known that the structure of Al2O3 inclusions is corundum at liquid steel temperature, while the structure of MnO·Al2O3 inclusions is spinel. The reaction between Al2O3 inclusions and dissolved Mn to form MnO·Al2O3 inclusions needs a huge activation energy to decompose the Al2O3 corundum structure, and then form a new spinel structure. On the other hand, because the structure of both MnO·Al2O3 and MgO·Al2O3 is spinel, the evolution of MgO·Al2O3 into MnO·Al2O3 does not need a huge energy to build a new structure, and consequently
the reaction is much easier. As mentioned above, the possibility of reactions in Eqs. (9)-(12) and (14) are excluded, the reaction of Eq. (7) therefore should be the formation mechanism of (Mn, Mg)O·Al2O3 spinel inclusions during refining process.

Note that precaution is needed when these thermodynamic calculations are carried out, because the scattered thermodynamic data, e.g. the data of Mg23,29) and MnO·Al2O3 (see Table 8), would influence the calculation results. However, both the reaction trend in the calculation and the present experimental results strongly prove that Eq. (7) is the mechanism of the formation of (Mn, Mg)O·Al2O3 spinel inclusions.

5. Summary

In order to understand the mechanism of formation and evolution of non-metallic inclusions in medium Mn steel, industrial experiments were carried out during refining steelmaking process, while laboratory experiments were employed to explain the generation of MnO·Al2O3 spinel inclusions. Some conclusions are drawn as follows:

(1) With the generation of dissolved Mg and Ca in liquid steel, the inclusions in liquid medium Mn steel would transform along with the route of “Al2O3 inclusions → MgO·Al2O3 spinel inclusions → (Mn, Mg)O·Al2O3 spinel inclusions → CaO–MgO–MnO–Al2O3 calcium aluminate inclusions”. (Mn, Mg)O·Al2O3 spinel is found as a different type of inclusions compared with conventional Al–killed steel grades, and it contains a high MnO content and a low MgO content. Finally, the MnO and MgO contents in calcium aluminate inclusions become very low at the end of refining process.

(2) The crystal structure of MgO·Al2O3 spinel phase would help the formation of (Mn, Mg)O·Al2O3 spinel inclusions, while Al2O3 inclusions can not react with dissolved Mn in steel to form MnO·Al2O3 spinel inclusions, even the Mn content is around 5 mass% in steel. Consequently, (Mn, Mg)O·Al2O3 spinel inclusions forms after the formation of MgO·Al2O3 spinel inclusions in industrial practice.

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