Evolution Mechanism of Non-metallic Inclusions in Al-Killed Alloyed Steel during Secondary Refining Process

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The evolution mechanism of inclusions in Al-killed alloyed steel during secondary refining process was studied by industrial experiments and thermodynamic calculations. It is found that during the tapping process, Al–O deoxidization reaction is very close to equilibrium with the formation of many Al₂O₃ clusters. With the slag/steel reaction, inclusions vary with the route as Al₂O₃ inclusions $\rightarrow$ MgO–Al₂O₃ system inclusions $\rightarrow$ CaO–MgO–Al₂O₃ system inclusions, and finally change into globular inclusions surrounded by CaO–Al₂O₃ outer layer, of which the melting point is lower than liquid steel temperature. Since MgO is less stable than CaO and it is easier to be reduced by Al, dissolved Mg is generated earlier and faster than Ca before LF refining, thus the MgO–Al₂O₃ system inclusions form at first. The mapping photos of inclusions show that the evolution mechanism of MgO–Al₂O₃ system inclusions into CaO–MgO–Al₂O₃ system inclusions is Ca element substitution for Mg element in MgO–Al₂O₃ inclusions. The line scanning shows that there is also the reaction of Ca element substitution for Al element in the outer CaO–Al₂O₃ layer without MgO.

KEY WORDS: non-metallic inclusions; spinel; calcium aluminate; thermodynamic calculation; evolution mechanism; secondary refining.

1. Introduction

Alloyed steels are widely applied in producing special products such as bolts, springs and bearings. During the past decades, a series of high-quality alloyed steels with high cleanliness have been developed by steel companies to meet the increasing needs of the market. Large, hard and angular inclusions are harmful to steel performance, such as cold-forming ability, fatigue resistance and delayed fracture resistance. Because spinel (MgO–Al₂O₃ system) inclusions are hard, irregular and non-deformable, it is commonly very harmful to the final products. Calcium aluminate inclusions are usually globular with low melting points, so performing calcium treatment is very common in steelworks in order to have such inclusions, but there is still lack of agreement about the harmness of these inclusions. Spinel and calcium aluminate inclusions are mainly found in Al-killed steel, and many scholars have contributed to research the formation and evolution mechanism of these inclusions, such as Itoh et al., Park et al., Kang et al., Seo et al., and Wang et al. The proposed mechanism was commonly mentioned that the dissolved Mg and Ca were supplied from the slag and refractory, and the MgO–Al₂O₃ system inclusions formed by the reaction between alumina inclusions and dissolved Mg. Besides, Kang et al. and Wang et al. indicated that MgO–Al₂O₃ system was not stable when there was a trace of dissolved Ca, would transfer into CaO–MgO–Al₂O₃ system. Although these mechanisms could explain the evolution process to a certain extent, there are still some points to be concerned.

Firstly, most of these studies were carried out in laboratory that differs from the actual secondary refining process. For instance, the steel of industrial product, which may already contain Mg and Ca, was commonly used as raw material with the contents of Mg and Ca different from real refining process, while the Mg and Ca contents are often considered as zero because of the high content of dissolved oxygen after BOF blowing. Therefore, it is hard to study the formation process of dissolved Ca and Mg in laboratory. Moreover, there was no argon stirring in laboratory experiments, and it would lead elements enrichment in part of steel and result in some inclusions hardly formed in the practice, taking MgO inclusions as an example. In these studies, MgO–Al₂O₃ system inclusions formed before CaO–Al₂O₃ system inclusions, and the Mg activity higher than that of Ca was commonly considered as the main reason. Without concerning the formation process of dissolved Ca and Mg, this phenomenon could not be well explained because several ppm dissolved Ca has already coexisted with Mg in liquid steel, which is conflict with that MgO–Al₂O₃ system inclusions are unstable in that case. Meanwhile, there are different views about the evolution process of MgO–Al₂O₃ system into CaO–MgO–Al₂O₃ system. Some believed that Ca element substitutes for Al element of MgO–Al₂O₃ system inclusions in the evolution process, while most scholars obtained the result that Mg element was substituted.
by Ca element.\textsuperscript{6,12,14–16,18,19} Theoretic analysis for the evolution of inclusions is still lack.

In present work, the formation process of dissolved Ca and Mg, the evolution of inclusions and theoretic analysis for the evolution were mainly considered with industrial experiments, which were carried out in a smelting process of Al-killed alloyed steel. Based on the formation process of dissolved Ca and Mg, the phase stability diagram of MgO-Al\textsubscript{2}O\textsubscript{3} was calculated to investigate the formation of MgO–Al\textsubscript{2}O\textsubscript{3} system inclusions in refining process. Moreover, the formation of CaO–MgO–Al\textsubscript{2}O\textsubscript{3} system inclusions was also studied by SEM mapping and line scanning and phase stability diagram. The evolution mechanisms of non-metallic inclusions in refining process were proposed.

2. Experiments

2.1. Experimental Procedure and Sampling

The industrial experiment was made in a steel plant, and the steel grade SCM435 with chemical composition listed in Table 1 was produced by the process of “hot metal pre-desulfurization → 80 ton BOF steelmaking → 80 ton LF refining → 80 ton RH refining → Bloom continuous casting”. After hot metal pre-desulfurization, the S content was less than 0.006%, and at the blowing end of BOF the C content of the steel was less than 0.006%, and at the blowing end of BOF the C content of the steel was 0.07–0.12% with dissolved oxygen activity of 250–400 ppm. During the tapping of BOF, most alloys, refining fluxes and about 100 kg Al were added into the ladle for composition adjustment, deoxidation and early slag formation. In LF refining, some fluxes and about 40 kg Al were also added to keep high basicity refining slag with low FeO content shown in Table 2, and the slag amount was about 1.6 ton. Argon was used for agitation with the flow rate of 200–400 NL/min, and the time for LF refining was about 40 min. In RH refining, there were no more alloys and fluxes added, and the treat time was about 25 min with vacuum pressure less than 133 Pa.

In the experimental procedure, five liquid steel samples were taken with barrel type samplers namely, after BOF tapping (Sample 1), before LF reining (Sample 2), during LF reining (Sample 3), after LF refining (Sample 4) and after RH refining (Sample 5).

2.2. Analysis of Samples

The activity of dissolved oxygen in liquid steel was measured by oxygen probe. Steel and slag samples were prepared for chemical analysis, and the acid-soluble Al, Ca and Mg contents in steel were analyzed by ICP-AES method. Total oxygen contents of these samples were measured by fusion and the infrared absorption method. Steel samples for inclusions were analyzed by SEM-EDS to obtain the morphology, size and chemical compositions. When an inclusion was analyzed by EDS, the composition in the center was considered as the composition of the entire inclusion.

3. Results and Discussion

3.1. Activity of Dissolved Oxygen and Chemical Compositions of Samples

After tapping of BOF, the activities of dissolved oxygen were measured as soon as possible, and the thermodynamic calculation of Al–O equilibrium was presented in Fig. 1. The standard states in this article were chosen for the both activities of elements in the liquid steel and the oxides in the slag and the inclusions, and the former was taken relative to a dilute solution taking unit as mass percent while the latter to pure solid taking unit as molar fraction. In the calculation, the activity of Al\textsubscript{2}O\textsubscript{3} was considered as unity, and the equilibrium constant and interaction coefficients used in thermodynamic calculations are listed in Tables 3 and 4, and the activity of element \(i\) can be calculated from Eq. (1). Meanwhile, the activity of dissolved oxygen content at RH station was also measured as shown in Fig. 1. Due to the systematic

![Fig. 1. Calculated and measured activities of dissolved oxygen.](image)

<table>
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<tr>
<th>Table 1. Chemical composition of SCM435, mass%.</th>
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<td>C</td>
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<td>0.33–0.38</td>
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<th>Table 2. Composition of refining slag, mass%.</th>
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<tr>
<td>CaO</td>
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<td>47.61</td>
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<th>Table 3. Equilibrium constants used in the thermodynamic calculations.</th>
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<td>Reactions</td>
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<tr>
<td>2[Al] + 3[O] = Al\textsubscript{2}O\textsubscript{3}</td>
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<tr>
<td>[Mg] + [O] = MgO</td>
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<tr>
<td>[Ca] + [O] = CaO</td>
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<tr>
<td>MgO + Al\textsubscript{2}O\textsubscript{3} = MgO·Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>CaO + Al\textsubscript{2}O\textsubscript{3} = CaO·Al\textsubscript{2}O\textsubscript{3}</td>
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<th>Table 4. Interaction coefficients used in thermodynamic calculations at 1 873 K.\textsuperscript{25}</th>
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<td>(i)</td>
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<tr>
<td>Al</td>
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<tr>
<td>O</td>
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<tr>
<td>Mg\textsuperscript{11}</td>
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<td>Ca</td>
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errors of oxygen probe and deviation of thermodynamic data, the measured plots tend to be positioned slightly above the calculated equilibrium lines. However, it also can be seen from Fig. 1 that the activities of dissolved oxygen in liquid steel after Al addition are very close to the equilibrium. It implies the AlO\textsubscript{3} deoxidization reaction occurs so fast in the tapping process that the dissolved oxygen content would be very low in the refining process and the dissolved oxygen content was considered as 3 ppm in the following calculations.

\[
\lg a_j = \sum c_j [\text{mass}\%] + \lg [\text{mass}\%] \quad \ldots \ldots (1)
\]

**Figure 2** shows the total oxygen contents in smelting process. It can be seen from this figure that the total oxygen content decreases from several hundred ppm to about 23 ppm after Al deoxidation during the tapping, and it indicates most of Al\textsubscript{2}O\textsubscript{3} cluster inclusions have floated into slag quickly and only a small amount of inclusions remain in liquid steel. According to LF refining and RH refining, the total oxygen content is just several ppm in final products.

The chemical compositions of samples were given in **Table 5**. The contents of C, Si, Mn and Cr increase because of the composition adjustment. With the steel/slag interface reactions, the contents of Ca and Mg in liquid steel increase, and the Mg content is much higher than Ca content all the time. There is an interesting phenomenon that the Mg content is already around 4 ppm just after tapping (Sample 1) while the Ca content before LF refining (Sample 1 and 2) is very low and almost close to zero. It implies that the formation of dissolved Mg in liquid steel is very fast and there is almost no Ca generated before LF refining process.

At the end of BOF blowing, the oxygen activity is so high that the content of dissolved Mg and Ca can be considered as zero. After strong deoxidation by Al addition, MgO and CaO in the slag and refractory may be reduced by Al as Eqs. (2) and (3) to generate dissolved Mg and Ca in liquid steel, and the results shown in Table 5 have proven these two reduction reactions with the increase of Mg and Ca content.

\[
3(\text{MgO}) + 2[\text{Al}] = 3[\text{Mg}] + (\text{Al}_2\text{O}_3) \quad \ldots \ldots (2)
\]

\[
3(\text{CaO}) + 2[\text{Al}] = 3[\text{Ca}] + (\text{Al}_2\text{O}_3) \quad \ldots \ldots (3)
\]

Equations (4) and (5) reflect the stability of MgO and CaO with thermodynamic data from Table 3. In the temperature range of steelmaking (1 500–1 700°C), Eq. (4) could occur at standard state because of the Gibbs free energy \(\Delta G\) \textsuperscript{θ} is minus, and MgO is less stable than CaO and easier to be reduced by Al. Therefore, Mg has been generated without Ca in the process of tapping. As a trace of Mg generated, Al\textsubscript{2}O\textsubscript{3} would react with dissolved Mg to form MgO-\textsubscript{Al}2O\textsubscript{3}. It is the main reason why MgO-\textsubscript{Al}2O\textsubscript{3} system inclusions are formed before CaO-\textsubscript{Al}2O\textsubscript{3} system inclusions. Although Mg activity higher than that of Ca was commonly considered as the main reason, \(\text{11,15}\) the present authors believe that the generation process of dissolved Mg in tapping process could be used to explain this phenomenon rather than that reason in the references.

\[
\text{MgO} + [\text{Ca}] = [\text{Mg}] + \text{CaO} \quad \ldots \ldots \ldots (4)
\]

\[
\Delta G\textsuperscript{θ}_1 = -48 242 + 18.914T \text{ J/mol} \quad \ldots \ldots (5)
\]

### 3.2. Evolution of Inclusions during Secondary Refining Process

#### 3.2.1. Morphologies of Inclusions

The typical morphologies and EDS spectra of inclusions in the smelting process are presented in **Figs. 3** to **5**. In the smelting process, there are mainly three types of inclusions, namely Al\textsubscript{2}O\textsubscript{3} inclusions shown in **Fig. 3**, MgO-\textsubscript{Al}2O\textsubscript{3} system inclusions shown in **Fig. 4** and CaO-MgO-\textsubscript{Al}2O\textsubscript{3} system inclusions shown in **Fig. 5**.

Typical Al\textsubscript{2}O\textsubscript{3} inclusions mainly observed after tapping and before LF refining at LF station show two kinds of appearances. One is completely Al\textsubscript{2}O\textsubscript{3} inclusion clusters with relatively large size shown in **Fig. 3(a)**, and the other is single particle Al\textsubscript{2}O\textsubscript{3} inclusions containing small amount of MgO as shown in **Fig. 3(b)**. Al\textsubscript{2}O\textsubscript{3} inclusions have begun to react with dissolved Mg.

Typical MgO-\textsubscript{Al}2O\textsubscript{3} system inclusions shown in **Fig. 4** are blocky or rectangular and mainly observed in the middle of LF refining. Some of them also can still be found at the end of LF refining.

Typical CaO-MgO-\textsubscript{Al}2O\textsubscript{3} system inclusions are globular as shown in **Fig. 5**. Many of these inclusions can be found both at the ends of LF refining and RH refining. Since sulfur will be precipitated during the solidification process of the steel, there is a small amount of CaS precipitated at the inclusion surface, and finally the inclusions contain sulfur as shown in **Figs. 5(a)** and **5(c)**. In addition, the Mg peak for some inclusions is very low and some inclusions contain trace of Si as shown in **Fig. 5(c)**. It indicates that calcium can help to change the MgO-\textsubscript{Al}2O\textsubscript{3} system into globular.
3.2.2. Compositions of Inclusions

CaO–MgO–Al2O3 ternary system is considered in Fig. 6, and the distribution of inclusions is marked in these ternary phase diagrams. Since the temperature in the refining process is above 1,550°C, the liquid region (melting point of inclusions below 1,550°C) surrounded by blue solid line is calculated by software FactSage 6.1.

Al2O3 inclusions containing a trace of MgO shown in Fig. 6(a) are the main inclusions after tapping at BOF station. With the slag/steel interface reaction, the MgO content increases with MgO–Al2O3 system inclusions formed in the LF refining process as shown in Figs. 6(b)–6(c). In the later stage of LF refining, most MgO–Al2O3 system inclusions change into CaO–MgO–Al2O3 system inclusions as shown in Fig. 6(d), and part of them are already in the composition region of liquid. After RH treatment, most inclusions are in liquid region with very low MgO content shown in Fig. 6(e).

The average compositions of inclusion in the smelting process are given in Fig. 6(f), and it shows that the Al2O3 content of inclusions decreases from 100 mass% to about 60 mass%, the MgO content increases at first and then decreases with the maximum value about 20 mass%, while the CaO content increases all the time. Finally, the inclusions are very close to calcium aluminate with low melting point.

3.2.3. Element Distribution in Inclusions

Figure 7 shows the mapping photos of typical CaO–MgO–Al2O3 system inclusion after LF refining. As can been seen,
Fig. 6. Composition distribution of inclusions in different samples.

Fig. 7. Mapping photos of typical CaO–MgO–Al₂O₃ system inclusion.
Ca element is mainly distributed in the edge of inclusion with an MgO–Al2O3 core, and the Ca and Mg elements present complementary as MgO–Al2O3 inclusion surrounded by an outer CaO–Al2O3 layer. This result was also obtained by Wang et al.,6,14–16) Pistorius et al.,18) Verma et al.19) and Yang et al.32) Therefore, based on Figs. 6 and 7, it is concluded that CaO–MgO–Al2O3 system inclusions are formed by Ca element substitution for Mg element in MgO–Al2O3 inclusions.

Figure 8 shows the line scanning of typical CaO–MgO–Al2O3 system inclusion after LF refining. It can be seen from Fig. 8 that the complementary between Ca and Mg elements is also presented like that shown in Fig. 7, and the Al content increases from outer part to inner part of the CaO–Al2O3 layer. Therefore, there is also a reaction of Ca element substitution for Al element just in the outer CaO–Al2O3 layer without MgO. This is very similar to the evolution mechanism of Al2O3 inclusions into calcium aluminate developed by Ye et al.33)

Above all, in the entire inclusions, there are reactions of Ca element substitution for not only Mg element but also Al element, which are different from that shown in the previous studies.6,14–16)

3.2.4. Thermodynamics of Inclusion Evolution

(1) Formation of MgO·Al2O3 System Inclusions

Thermodynamic calculations were carried out to explain the evolution of the inclusions in steel. When a trace of Mg is generated in liquid steel, Al2O3 would react with dissolved Mg to form MgO·Al2O3 as shown in Eq. (6)34)

\[
4(\text{Al}_2\text{O}_3) + 3[\text{Mg}] = 3(\text{MgO} \cdot \text{Al}_2\text{O}_3) + 2[\text{Al}] \quad \text{...... (6)}
\]

\[
\log K_6 = 34.37 - \frac{46950}{T} \quad \text{................ (7)}
\]

\[
K_6 = \frac{a^4_{\text{Al}_2\text{O}_3}a^3_{\text{MgO} \cdot \text{Al}_2\text{O}_3}}{a^4_{\text{Al}_2\text{O}_3}a^3_{[\text{Mg}]}} \quad \text{................ (8)}
\]

When the Mg content is high enough, MgO·Al2O3 would react with dissolved Mg to form MgO as shown in Eq. (9)34)

\[
(\text{MgO} \cdot \text{Al}_2\text{O}_3) + 3[\text{Mg}] = 4(\text{MgO}) + 2[\text{Al}] \quad \text{...... (9)}
\]

\[
\log K_9 = 33.09 - \frac{50880}{T} \quad \text{................ (10)}
\]

\[
K_9 = \frac{a^4_{\text{MgO}}a^2_{\text{Al}_2\text{O}_3}}{a^3_{[\text{Mg}]a^3_{\text{MgO} \cdot \text{Al}_2\text{O}_3}}} \quad \text{................ (11)}
\]

Therefore, Eqs. (6)–(11) can be used to calculate the stability diagram of MgO/MgO·Al2O3/Al2O3. In the calculation, the activities of MgO·Al2O3 in MgO and Al2O3 are 0.8 and 0.47 respectively, and the activities of MgO and Al2O3 at saturated state are 0.99 and 1 respectively.35)

Figure 9 shows the calculated phase stability diagram of MgO/MgO·Al2O3/Al2O3. As there is little Ca generated before LF refining (Sample 1 and 2) and during LF refining (Sample 3), the contents of dissolved Al and Mg in liquid steel are mainly considered at these stages. This figure indicates that contents of dissolved Al and Mg in liquid steel are in the region of MgO·Al2O3 formation, which can explain the observation of MgO·Al2O3 inclusions in steel as shown in Figs. 3(b), 4 and 6(a)–6(c).

(2) Formation of CaO–MgO–Al2O3 System Inclusions

As seen from Fig. 6, if there is a trace of dissolved Ca in liquid steel, the MgO–Al2O3 system inclusions will be unstable and change into CaO–MgO–Al2O3 system inclusions, finally tend to form calcium alumina inclusions. Among the calcium alumina inclusions, the CaO·Al2O3, 12CaO·7Al2O3 and 3CaO·Al2O3 are all in liquid phase at 1,873 K. With the evolution route of CaO·Al2O3 \(\rightarrow\) 12CaO·7Al2O3 \(\rightarrow\) 3CaO·Al2O3 described in Ref.33, the CaO·Al2O3 is chosen as the liquid phase for the calculation of phase stability between MgO·Al2O3 and liquid, and the boundary between these two phases is calculated from Eqs. (12)–(14).

\[
[\text{Ca}] + \text{MgO} \cdot \text{Al}_2\text{O}_3 = \text{CaO} \cdot \text{Al}_2\text{O}_3 + [\text{Mg}] \quad \text{...... (12)}
\]

\[
\log K_{12} = -0.40 + \frac{2476}{T} \quad \text{................ (13)}
\]

\[
K_{12} = \frac{a^4_{\text{CaO} \cdot \text{Al}_2\text{O}_3}a^3_{[\text{Mg}]}}{a^4_{\text{MgO} \cdot \text{Al}_2\text{O}_3}a^3_{[\text{Ca}]}} \quad \text{................ (14)}
\]

Besides, according to Eqs. (6)–(8) the boundary between MgO·Al2O3 and Al2O3 can be calculated like above, and the boundary between CaO·Al2O3 and Al2O3 can be calculated from Eqs. (15)–(17).

\[
4(\text{Al}_2\text{O}_3) + 3[\text{Ca}] = 3(\text{CaO} \cdot \text{Al}_2\text{O}_3) + 2[\text{Al}] \quad \text{...... (15)}
\]

\[
\log K_{15} = 33.17 - \frac{39532}{T} \quad \text{................ (16)}
\]
3.3. Evolution Mechanism of Inclusions

According to the above analysis, there are two stages for evolution of inclusions: (I) Al2O3 inclusions → MgO–Al2O3 system inclusions; (II) MgO–Al2O3 system inclusions → CaO–MgO–Al2O3 system inclusions. Although these two stages are very similar to the previous studies,11,14–16 there are also some differences in present work because of the different conditions, and the evolution of inclusions in present work can be illustrated in Fig. 11. The evolution mechanism is described as follows.

(1) When Al is added in the tapping process, a lot of Al2O3 clusters are formed quickly, and most of them float into slag while a small amount of them remain in liquid steel with very low dissolved oxygen content as shown in Fig. 11(a).

(2) Because MgO is less stable than CaO, MgO in slag and refractory is firstly reduced by Al to form dissolved Mg as shown in Eq. (2), and then MgO–Al2O3 system inclusions are generated by the reaction of Eq. (18) between Al2O3 inclusions and dissolved Mg as shown in Fig. 11(b).

\[ \text{MgO} + x\text{Al}_2\text{O}_3 = \text{MgO} \cdot x\text{Al}_2\text{O}_3 \quad (x = 1/3) \quad \text{Eq. (18)} \]

(3) When the slag/steel reaction goes to a certain extent, CaO in slag and refractory also starts to be reduced by Al, and dissolved Ca is generated as shown in Eq. (3), then the dissolved Ca and Mg coexist in liquid steel. If there is a trace of Ca, MgO–Al2O3 inclusions would become unstable and transform into CaO–MgO–Al2O3 system inclusions. The melting points of inclusions become lower, and at the temperature of liquid steel, liquid phase starts to appear on the inclusions with the shape of globular shown in Fig. 11(c). With the continuous reaction, the MgO content of inclusions decreases until the inclusions totally transfer into calcium aluminate.

Compared with the previous studies,11,14–16 the formation process of Mg and Ca in the tapping of BOF was concerned for the first time in present work, and the reduction sequence of MgO and CaO can be easily used to explain why MgO–Al2O3 system inclusions are formed before CaO–Al2O3 system inclusions. Besides, with the sequence of reduction by Al, the illustration of inclusions evolution shown in Fig. 11 is different from that of the references,11,15 in which the CaO and MgO are usually considered to be reduced by Al at the same time, due to the different experimental conditions.

The detail of evolution of MgO–Al2O3 system into CaO–Al2O3 system has already been described by Wang et al.14–16 The evolution of the outer CaO–Al2O3 layer was not concerned in their description, while the CaO–Al2O3 layer surrounding the MgO–Al2O3 core was obviously presented in their experimental results. Based on the previous studies and the results from the present work, the model of evolution of MgO–Al2O3 system into CaO–Al2O3 system is newly illustrated in Fig. 12, and the detail of this model is described as follows.

1) At first, a layer of CaO–MgO–Al2O3 system is formed at the surface of MgO–Al2O3 system inclusion by Eq. (19).

\[ x[Ca] + y\text{MgO} \cdot z\text{Al}_2\text{O}_3 \]

\[ = x\text{CaO} \cdot (y - x)\text{MgO} \cdot z\text{Al}_2\text{O}_3 + x[Mg] \quad \text{Eq. (19)} \]

2) With the diffusion of Ca element, the layer becomes thicker and thicker, and with increasing CaO and decreasing
MgO contents, the edge of the inclusion will change into liquid CaO–MgO–Al2O3 system whose melting temperature is lower than liquid steel temperature. Therefore, the shape of inclusion would change into globular because of liquid edges. Meanwhile, the content gradients of CaO and MgO are formed in this layer, and the CaO content decreases with increase of MgO content from outer part to inner part of the layer. MgO diffuses from inside to outside of the inclusion while CaO diffuses to the opposite direction. The reaction in the layer can be expressed as Eq. (20), and the reaction between the layer and the MgO–Al2O3 system core is shown in Eq. (21).

\[
\text{CaO} + x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{MgO} = (x+1)\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot (z-1)\text{MgO} + \text{MgO} \quad (20)
\]

\[
\text{CaO} + x\text{MgO} \cdot y\text{Al}_2\text{O}_3 = \text{CaO} \cdot (x-1)\text{MgO} \cdot y\text{Al}_2\text{O}_3 + \text{MgO} \quad (21)
\]

3) Calcium aluminate is formed when MgO diffuses to the outer surface of the inclusion and reduced by dissolved Ca as expressed by Eq. (22).

\[
[\text{Ca}] + x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot 2\text{MgO} = (x+1)\text{CaO} \cdot y\text{Al}_2\text{O}_3 + [\text{Mg}] \quad (22)
\]

Especially, in the description of Refs. 14–16), the liquid phase was considered to appear as the calcium aluminate formed. The present authors believe that when the edge of inclusions transformed into CaO–MgO–Al2O3 whose melting point is lower than steel temperature, the liquid phase would appear as the above description of 2) before calcium aluminate formed.

4) Because the diffusion coefficients of CaO and MgO in liquid phase are larger than those in solid phase, the diffusion of MgO to outer of liquid phase and the diffusion of CaO to inner are so fast with lack of MgO and surplus of CaO. Therefore, a CaO–Al2O3 system layer would be easily generated surrounding the CaO–MgO–Al2O3 system layer. According to the evolution mechanism of Al2O3 inclusions into calcium aluminate developed by Ye et al.33 and Ito et al.,37 calcium aluminate could change into another state with lower melting point as Eq. (23). The reaction between calcium aluminate layer and CaO–MgO–Al2O3 system layer is expressed as Eq. (24), and the product of MgO is quickly diffused to outer of inclusion and reduced into dissolved Mg. Based on the description and compared with the MgO–Al2O3 core and the outer CaO–MgO–Al2O3 layer in Refs. 14–16), the MgO–Al2O3 core, the middle CaO–MgO–Al2O3 layer and outer CaO–Al2O3 layer are presented in Fig. 12, which is accord with the experimental results.

\[
[\text{Ca}] + x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot (z-1)\text{MgO} + \frac{2}{3}[\text{Al}] \quad (23)
\]

\[
\text{CaO} + x\text{CaO} = (x+1)\text{CaO} \cdot y\text{Al}_2\text{O}_3 + 2\text{MgO} \quad (24)
\]

5) The MgO–Al2O3 system core becomes smaller and smaller, and MgO content of inclusions decreases continuously. With long enough time of reaction, the inclusions will be transferred into CaO–MgO–Al2O3 system inclusions containing a very small amount of MgO or into CaO–Al2O3 system inclusions totally.

4. Conclusions

The evolution mechanism of inclusions in Al-killed alloyed steel during secondary refining process was studied by industrial experiments and thermodynamic calculations, and the following conclusions were obtained.

1) During the tapping process, Al–O deoxidization reaction is very close to equilibrium with a lot of Al2O3 clusters formed. With the slag/steel reaction, inclusions vary with the route as Al2O3 inclusions→MgO–Al2O3 system inclusions→CaO–MgO–Al2O3 system inclusions, and finally change into globular inclusions surrounded by CaO–Al2O3 outer layer with the melting points lower than liquid steel temperature.

2) Since MgO is less stable than CaO and it is easier to be reduced by Al, dissolved Mg is generated earlier and faster than Ca before LF refining, thus the MgO–Al2O3 system inclusions form at first.

3) The mapping photos of inclusions show that the evolution mechanism of MgO–Al2O3 system inclusions into CaO–MgO–Al2O3 system inclusions is Ca element substitution for Mg element in MgO–Al2O3 inclusions. Meanwhile, the line scanning shows that in the outer CaO–Al2O3 layer without MgO, there is also the reaction of Ca element substitution for Al element.

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