Research Article

Fu-bin Gao, Xinbo Yan, Fuming Wang*, Xinhua Wang, and Jianli Li*

Effect of ladle-lining materials on inclusion evolution in Al-killed steel during LF refining

https://doi.org/10.1515/htmp-2022-0317
received September 27, 2023; accepted January 23, 2024

Abstract: The effect of lining materials (Al2O3 and Al2O3–MgO–Al2O3) of ladle on evolution of non-metallic inclusions in aluminum-killed (Al-killed) steel during ladle furnace refining without Ca treatment was investigated through industrial experiments. The results showed that non-metallic inclusions experienced the changes from Al2O3→MgO–Al2O3→CaO–Al2O3. During the refining process using either of the two ladle lining materials, for all non-metallic inclusions, the vast majority are distributed in the high Al2O3 area of the CaO–Al2O3–MgO phase diagram, with very little or none in the low melting point zone. Non-metallic inclusions are mainly smaller than 3 μm, while those larger than 3 μm consisted primarily of MgO–Al2O3 and CaO–Al2O3 inclusions. The use of an Al2O3–MgO-Al2O3-lining ladle is more effective in reducing the number density of inclusions in the steel. However, during the refining process, the Al2O3-lining ladle does not have a significant influence on the presence of MgO–Al2O3 and CaO–Al2O3 inclusions in the molten steel. The Al2O3–MgO–Al2O3-lining ladle does not have a significant effect on MgO–Al2O3 inclusions, but it does promote the formation of CaO–Al2O3 and CaS inclusions in the molten steel.

Keywords: Al2O3 lining, Al2O3, MgO-Al2O3 lining, LF refining, Al-killed steel, inclusions

1 Introduction

In the process of refining aluminum-killed (Al-killed) steel, various types of inclusions are commonly encountered, including Al2O3, MgO–Al2O3, and CaO–Al2O3 [1–4]. During the refining process of Al-killed steel, Al2O3 inclusions are inevitably formed in the molten steel due to the use of aluminum for deoxidation [5,6]. As the refining progresses, MgO–Al2O3 and CaO–Al2O3 inclusions gradually appear in the steel. Some studies have confirmed [7–10] that even without the addition of Mg and Ca, MgO–Al2O3 and CaO–Al2O3 inclusions can still be formed in the molten steel. MgO–Al2O3 inclusions, owing to their high melting point and sharp geometric structure, can seriously damage the fatigue performance of steel products [2,3]. CaO–Al2O3 inclusions, typically larger in size, are also considered to have the potential to cause defects in the products [11,12]. The control of non-metallic inclusions has become imperative for achieving higher steel product quality. However, the nature of inclusions is primarily determined by the chemical composition of the steel, which, in turn, is directly influenced by the ladle lining and the refining slag. Hence, the choice of ladle-lining refractory and refining slag indirectly impacts the inclusions [13]. During refining process of Al-killed steel, the refractory used in the ladle lining come into extensive real-time contact with the molten steel. Therefore, the influence of ladle material on inclusions in the steel has gained increasing attention. Harada [14,15] investigated the reaction mechanism between MgO–C refractory and Al-killed steel, and observed the presence of MgO and MgO–Al2O3 inclusions in the steel and the formation of a spinel layer at the steel–refractory interface. Liu [7,13] discovered that [Al] in the molten steel could reduce MgO in the MgO–C refractory, leading to an increase in dissolved [Mg] in the steel and the formation of MgO-Al2O3 inclusions. Similar results were obtained by Chi et al. [16], Brabie [17], Jansson et al. [18], and others who studied the interaction between MgO-based refractories and molten steel. Huang et al. [19], through research on the dissolution kinetics of MgO-based refractories in steel, found that the reaction of MgO with [Al] in the steel occurs concurrently with the
decomposition of MgO refractories, contributing to an increase in Mg in the steel. Deng et al. [20] studied the effect of spinel refractories on inclusions in Al-killed steel, and found that there is no transformation of Al2O3 inclusions in the molten steel. This is due to relatively low activity of MgO in spinel refractories, which is not easily reduced by [Al]. The studies in these literature have mainly focused on MgO–C refractory, while the study of the effect of other refractory on inclusions in steel is still incomplete. Therefore, it is necessary to systematically study the effect of ladles with different refractories on inclusions in steel.

In this article, industrial sampling was carried out during the refining and continuous casting process of Al-killed steel with Al2O3-lined ladle and Al2O3–MgO–Al2O3-lined ladle. The effect of two different lined refractories on various inclusions is also analyzed.

2 Methods

2.1 Industrial production and sampling

The production process of Al-killed steel in this study was basic oxygen furnace (BOF) → ladle furnace refining (LF) → continuous casting (CC). The operations of the refining process included: (1) After tapping from BOF, aluminum and lime were added to the ladle for deoxidation and slag making. (2) The steel was heated using electrodes and alloyed with aluminum, lime, and ferromanganese alloy. The molten steel is heated for 20 min. The slag basicity ([CaO]/[SiO2]) was greater than 11. (3) Argon was blown to stir the steel for 6 min before LF departure. (4) Continuous casting was started after LF departure, and the basicity of the flux in tundish was 2.3–2.6.

Samples of steel and slag were collected at various points in the production process. The sampling nodes were LF arrival (LF1), end of electrode heating (LF2), LF departure (LF3), and casting tundish (CC1) (about 100 tons of molten steel was poured), as shown in Figure 1.

2.2 Analysis methods

Steel samples were analyzed and detected for inclusions with an equivalent diameter greater than 1 μm, including their size, morphology, and composition, using a field-emission electron probe microanalyzer (Shimadzu/EPMA 8050G). The scanning area for each sample was set to 15 mm².

The content of carbon [C] and sulfur [S] in the steel samples was determined using a high-frequency infrared ray carbon sulfur analyzer (LECO CS744). The content of [Si], [Mn], [P], [Ca], and [Al] were measured using an inductively coupled plasma mass spectrometer (ICP-MS/NexION 1000G). The oxide composition of the refining slag and tundish flux was determined through inductively coupled plasma-atomic emission spectrometry (ICP-MS/NexION 1000G).

3 Results

3.1 Composition of samples from refining and casting processes

The composition of the molten steel refined using different lined ladles is shown in Table 1. It is clear that when an Al2O3-lining ladle is used, the [Al] content in the molten steel initially increases due to the addition of aluminum for deoxygenation. As the refining process proceeds, the [Al] content gradually decreases. At the same time, the contents of [Si] and [Mn] tend to increase. The reason for this phenomenon is that [Mn] in the molten steel participates in steel–slag reactions, resulting in the formation of MnO (as shown in equation (1)). In addition, the [Al] in the molten steel reacts with MnO in the slag (equation (2)). These two reactions lead to an increase in [Si] and [Mn] content in the molten steel. Since calcium treatment is not carried out during the refining process, the [Ca] content in the molten steel remains very low throughout the process [21,22].
Table 1: Molten steel composition at various sampling points (wt%)

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Al</th>
<th>Als</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>LF1</td>
<td>0.040</td>
<td>0.004</td>
<td>0.128</td>
<td>0.011</td>
<td>0.033</td>
<td>0.0001</td>
<td>0.061</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>LF2</td>
<td>0.032</td>
<td>0.005</td>
<td>0.137</td>
<td>0.011</td>
<td>0.022</td>
<td>0.0001</td>
<td>0.076</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>LF3</td>
<td>0.060</td>
<td>0.013</td>
<td>0.290</td>
<td>0.011</td>
<td>0.011</td>
<td>0.0001</td>
<td>0.050</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>CC1</td>
<td>0.068</td>
<td>0.013</td>
<td>0.281</td>
<td>0.012</td>
<td>0.011</td>
<td>0.0004</td>
<td>0.039</td>
<td>0.034</td>
</tr>
<tr>
<td>Al₂O₃–MgO·Al₂O₃</td>
<td>LF1</td>
<td>0.041</td>
<td>0.004</td>
<td>0.095</td>
<td>0.009</td>
<td>0.029</td>
<td>0.0001</td>
<td>0.055</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>LF2</td>
<td>0.042</td>
<td>0.012</td>
<td>0.216</td>
<td>0.010</td>
<td>0.015</td>
<td>0.0001</td>
<td>0.098</td>
<td>0.096</td>
</tr>
<tr>
<td></td>
<td>LF3</td>
<td>0.065</td>
<td>0.021</td>
<td>0.280</td>
<td>0.009</td>
<td>0.006</td>
<td>0.0001</td>
<td>0.055</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>CC1</td>
<td>0.073</td>
<td>0.020</td>
<td>0.279</td>
<td>0.010</td>
<td>0.006</td>
<td>0.0002</td>
<td>0.052</td>
<td>0.050</td>
</tr>
</tbody>
</table>
| Als: acid soluble aluminum in molten steel.

\[
(SiO_2) + 2[Mn] = 2(MnO) + [Si] \tag{1}
\]
\[
\Delta G \theta = 129200 - 23.1T \text{ J mol}^{-1}
\]

\[
2[Al] + 3[MnO] = (Al₂O₃) + 3[Mn] \tag{2}
\]
\[
\Delta G \theta = -337980 + 1.5T \text{ J mol}^{-1}
\]

As shown in Table 1, it can be observed that the composition changes in the molten steel during LF refining are consistent when using both ladles. The decrease in [S] content in the molten steel during refining, indicates that the refining slag has some desulfurization capacity. However, the key difference lies in the removal rate of [S] in the molten steel. The removal rate of [S] was 66% when using an Al₂O₃-lined ladle, while it was 79% when using an Al₂O₃–MgO·Al₂O₃-lined ladle. (desulfurization rate: ratio of sulfur removal to initial sulfur content). This suggests that the use of an Al₂O₃–MgO·Al₂O₃-lining ladle is more effective in desulfurizing the molten steel.

The chemical compositions of the refining slag and tundish flux are shown in Table 2. The basicity (w(CaO)/w(SiO₂)) of the refining slag during the refining process ranges from 11.38 to 37.42, while the basicity of the tundish flux ranges from 2.35 to 2.60. The sulfur content in the slag gradually increases during LF refining. Conversely, the content of MnO and SiO₂ in the slag decreases as the refining process progresses.

### 3.2 Transformation of non-metallic inclusions

#### 3.2.1 Types and number ratio of non-metallic inclusions

In the refining of Al-killed steel, the addition of aluminum blocks during steel tapping promotes strong deoxidation, as shown in equation (3). However, when a large quantity of aluminum blocks is added at once, it leads to the rapid formation of clustered Al₂O₃ inclusions in the molten steel, as depicted in Figure 2(a). These Al₂O₃ clusters have poor wettability with the molten steel, causing them to float upward into the slag during the refining process [23]. Consequently, small-sized block-shaped Al₂O₃ inclusions are left behind in the molten steel. As the steel interacts with the slag and ladle lining, the content of [Mg] and [Ca] in the molten steel increases, resulting in the transformation of Al₂O₃ inclusions, as shown in equations (4) and (5). This leads to the formation of MgO–Al₂O₃ and CaO–Al₂O₃ series inclusions, which exhibit irregular or spherical shapes, as observed in Figures 2 and 3 [24,25].

\[
2[Al] + 3[O] = (Al₂O₃), \tag{3}
\]
\[
4(Al₂O₃) + 3[Mg] = 3(MgO·Al₂O₃) + 2[Al], \tag{4}
\]

Table 2: Composition of refining slag and tundish flux at various sampling points (wt%)

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>T.Fe</th>
<th>S</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>LF1</td>
<td>3.71</td>
<td>42.21</td>
<td>4.55</td>
<td>41.86</td>
<td>1.33</td>
<td>0.22</td>
<td>4.47</td>
<td>0.14</td>
<td>11.38</td>
</tr>
<tr>
<td></td>
<td>LF2</td>
<td>1.95</td>
<td>57.22</td>
<td>8.30</td>
<td>32.72</td>
<td>0.13</td>
<td>0.01</td>
<td>0.15</td>
<td>0.51</td>
<td>29.34</td>
</tr>
<tr>
<td></td>
<td>LF3</td>
<td>1.50</td>
<td>56.13</td>
<td>8.74</td>
<td>34.23</td>
<td>0.07</td>
<td>/</td>
<td>0.25</td>
<td>0.48</td>
<td>37.42</td>
</tr>
<tr>
<td></td>
<td>CC1</td>
<td>15.81</td>
<td>37.12</td>
<td>11.20</td>
<td>30.78</td>
<td>0.95</td>
<td>0.06</td>
<td>1.41</td>
<td>0.08</td>
<td>2.35</td>
</tr>
<tr>
<td>Al₂O₃–MgO·Al₂O₃</td>
<td>LF1</td>
<td>3.09</td>
<td>42.45</td>
<td>4.23</td>
<td>43.65</td>
<td>1.56</td>
<td>0.07</td>
<td>2.61</td>
<td>0.19</td>
<td>13.74</td>
</tr>
<tr>
<td></td>
<td>LF2</td>
<td>2.57</td>
<td>51.91</td>
<td>4.65</td>
<td>31.56</td>
<td>0.92</td>
<td>/</td>
<td>2.90</td>
<td>0.44</td>
<td>20.20</td>
</tr>
<tr>
<td></td>
<td>LF3</td>
<td>2.17</td>
<td>52.86</td>
<td>5.01</td>
<td>34.90</td>
<td>0.15</td>
<td>/</td>
<td>0.40</td>
<td>0.62</td>
<td>24.36</td>
</tr>
<tr>
<td></td>
<td>CC1</td>
<td>14.97</td>
<td>38.98</td>
<td>5.28</td>
<td>29.60</td>
<td>0.82</td>
<td>0.033</td>
<td>0.75</td>
<td>0.14</td>
<td>2.60</td>
</tr>
</tbody>
</table>

\[ R = \frac{w(CaO)}{w(SiO₂)} \]
Figure 2: Morphology and composition of inclusions (Al$_2$O$_3$-lining ladle: (a) LF1, 10,000×, (b) LF2, 5,000×, (c) LF3, 10,000×, and (d) CC1, 5,000×). (The morphology and composition of typical inclusions in steel at different process stages when using Al$_2$O$_3$-lining ladle during LF refining of Al-killed steel. The inclusion composition is the mass fraction).

Figure 3: Morphology and composition of inclusions (Al$_2$O$_3$–MgO·Al$_2$O$_3$-lining ladle: (a) LF1, 5,000×, (b) LF2, 2,000×, (c) LF3, 10,000×, and (d) CC1, 10,000×). (The morphology and composition of typical inclusions in steel at different process stages when using Al$_2$O$_3$–MgO·Al$_2$O$_3$-lining ladle during LF refining of Al-killed steel. The inclusion composition is the mass fraction).
\[ [\text{Ca}] + \left( X + \frac{1}{3} \right) [\text{Al}_2\text{O}_3] = (\text{CaO} \cdot x \text{Al}_2\text{O}_3) + \frac{2}{3} [\text{Al}] \]  

Figure 4 shows information on the number ratio of different types of non-metallic inclusions at various sampling points during two industrial experiments. It was evident that non-metallic oxide inclusions in the molten steel can be classified into three types: \( \text{Al}_2\text{O}_3 \), \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \), and \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \).

In the case of refining with an \( \text{Al}_2\text{O}_3 \)-lining ladle, the number ratio of non-metallic inclusions changed as shown in Figure 4(a). When LF arrived, 87% of the inclusions were \( \text{Al}_2\text{O}_3 \), while 13% were \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) inclusions. As the LF refining progressed, the ratio of \( \text{Al}_2\text{O}_3 \) inclusions decreased to 49%, \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions were 22%, and \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) inclusions increased to 29%. During casting, the ratio of \( \text{Al}_2\text{O}_3 \) inclusions decreased to 38%, \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions increased to 48%, and \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) inclusions decreased to 13%.

For the refining of ladle-lining with \( \text{Al}_2\text{O}_3 \)-\( \text{MgO} \cdot \text{Al}_2\text{O}_3 \)-lining ladle, the variation of the number ratio of non-metallic inclusions is shown in Figure 4(b). The ratio of \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) inclusions remains relatively stable during LF refining, ranging between 35 and 46%. In contrast, \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions exhibit almost opposite trends. The ratio of \( \text{Al}_2\text{O}_3 \) inclusions increased toward the end of electrode heating, decreased at LF departure, and then rose again. Meanwhile, the ratio of \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions decreased initially and then increased. During the casting, the ratio of \( \text{Al}_2\text{O}_3 \) inclusions increased significantly, which could be attributed to the secondary oxidation of molten steel. Consequently, the ratio of \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) and \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) decreased during the casting.

### 3.2.2 Composition and size distribution of inclusions

The compositions of inclusions have been plotted on the \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \)-\( \text{MgO} \) phase diagram in the molten steel at different sampling points. The evolution paths of inclusions in steel for both experiments are depicted in Figures 5 and 6, respectively. For the \( \text{Al}_2\text{O}_3 \)-lining ladle, it is observed that upon LF arrival, the inclusions in the molten steel are primarily composed of \( \text{Al}_2\text{O}_3 \). After LF heating, the inclusions mainly consist of \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions, indicating a transformation from \( \text{Al}_2\text{O}_3 \) inclusions to \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions during refining, as shown in Figure 5(a) and (b). Upon LF departure, the dominant inclusions in the molten steel are \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) and \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \). Notably, \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions tend to have larger sizes, while \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) inclusions generally have smaller sizes, as illustrated in Figure 5(c). During casting, \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions continue to be present in the molten steel, while the quantity of \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) inclusions significantly decreases, indicating that \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) series inclusions are more easily removed from the steel during tundish casting, as shown in Figure 5(d).

In the case of using an \( \text{Al}_2\text{O}_3 \)-\( \text{MgO} \)-\( \text{Al}_2\text{O}_3 \)-lining ladle, the molten steel contains three types of inclusions: \( \text{Al}_2\text{O}_3 \), \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \), and \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \), upon LF arrival. Large-sized inclusions are predominantly \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \), as seen in Figure 6(a). After electrode heating, the MgO content in \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions decreases, and \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) series inclusions increase. Some larger-sized \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) series inclusions appear in the low-melting zone, suggesting a trend of transformation from \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \) inclusions to \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) during refining with \( \text{Al}_2\text{O}_3 \)-\( \text{MgO} \)-\( \text{Al}_2\text{O}_3 \)-lining ladle. After LF refining, the low-melting \( \text{CaO} \cdot \text{Al}_2\text{O}_3 \) inclusions are no longer present, and
Figure 5: Composition and size distribution of non-metallic inclusions (Al$_2$O$_3$-lining ladle, (a) LF1, (b) LF2, (c) LF3, and (d) CC1).

Figure 6: Composition and size distribution of non-metallic inclusions (Al$_2$O$_3$–MgO·Al$_2$O$_3$-lining ladle, (a) LF1, (b) LF2, (c) LF3, and (d) CC1).
only MgO–Al₂O₃ inclusions and the high-melting CaO–Al₂O₃ inclusions remain in the molten steel, as shown in Figure 6(b) and (c). During casting, the inclusions tend to concentrate in the CaO–Al₂O₃ and MgO–Al₂O₃ regions with higher Al₂O₃ content. Figure 6(d) illustrates that there is only a small quantity of CaO–Al₂O₃ series inclusions present in the low-melting region. In comparison to using an Al₂O₃-lining ladle, the removal of CaO–Al₂O₃ inclusions is not as prominent during this step.

3.2.3 Number density and average size of non-metallic inclusions

Two steel samples were analyzed for non-metallic inclusions number density and average size. As shown in Figure 7(a), the number densities of inclusions in both experiments were quite similar at LF arrival, 13.5 and 15.5 mm⁻², respectively. During the refining process, the number density of inclusions in steel with Al₂O₃–MgO·Al₂O₃-lining ladle is much lower than in the case of Al₂O₃-lining ladle. Especially, the former has an inclusion number density of 14.8 mm⁻² during LF departure, while the latter is 43.1 mm⁻². This suggests that the use of Al₂O₃–MgO·Al₂O₃ lining-ladle is beneficial to the cleanliness of the molten steel. During casting, the steel refined with an Al₂O₃-lining ladle exhibited notably smaller average inclusion sizes compared to the Al₂O₃–MgO·Al₂O₃-lining ladle. At the end of electrode heating and LF departure, the average inclusion sizes were 1.35 and 1.56 μm for the Al₂O₃-lining ladle. This suggests that the use of an Al₂O₃-lining ladle effectively controlled the growth of inclusions. During the LF departure and casting process, CaO–Al₂O₃ inclusions are removed from the steel in the Al₂O₃-lining ladle. However, there are many large-sized MgO–Al₂O₃ inclusions in the steel, resulting in an increase in the average inclusion size to 2.2 μm. In contrast, the average size of inclusions in the steel refined with an Al₂O₃–MgO·Al₂O₃-lining ladle decreased from 1.9 to 1.6 μm during the LF departure and casting stages.

3.3 Number and number ratio of CaS inclusions in steel

The number of CaS inclusions in steel samples from two experiments was counted, as well as its ratio among all
inclusions. Only composite inclusions with a CaS greater than 5 wt% were considered. The results are presented in Figure 8. The number of CaS inclusions in the steel was relatively low when the Al$_2$O$_3$-lining ladle was used. The number of CaS inclusions peaked at LF departure at 3.9% of all inclusions.

Conversely, when using an Al$_2$O$_3$–MgO·Al$_2$O$_3$-lining ladle, the quantity of CaS inclusions at all sampling points is significantly higher. Upon LF arrival, the number of CaS inclusions in the steel sample is 54, accounting for 19.3% of the total. After the end of electrode heating, lime is added to the ladle for slag making, which leads to an increase in the number of CaS inclusions. At this point, the number of CaS is 138, accounting for 19.1% of all inclusions. During LF departure and Tundish casting, the number of CaS in the steel decreases but remains significantly higher than in steel refined with an Al$_2$O$_3$-lining ladle. This indicates that refining Al-killed steel using an Al$_2$O$_3$-lining ladle effectively prevents the formation of CaS inclusions in the steel.

4 Discussion

4.1 Effect of ladle-lining refractories on the formation of MgO–Al$_2$O$_3$ inclusions

In the refining process of Al-killed steel, the formation of MgO–Al$_2$O$_3$ inclusions is common. These inclusions are formed due to the interaction between [Al] in the steel and MgO in the refining slag or ladle-lining materials, as described in equation (6). When [Mg] is reduced and enters the steel, it further reacts with [Al] or Al$_2$O$_3$ in the steel to form MgO–Al$_2$O$_3$, as shown in equations (7) and (8) [25]. Therefore, it is widely accepted that the refining slag and MgO-containing refractory materials are the primary sources of MgO–Al$_2$O$_3$ inclusions in steel.

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

\[ [\text{Mg}] + 4[\text{O}] + 2[\text{Al}] = (\text{MgO} \cdot \text{Al}_2\text{O}_3), \quad (7) \]

\[ [\text{Mg}] + n/3(\text{Al}_2\text{O}_3)_{\text{inclusion}} = (\text{MgO} \cdot (n-1)/3\text{Al}_2\text{O}_3) + 2/3[\text{Al}], \quad (8) \]

The transformation and number ratios of MgO-Al$_2$O$_3$ inclusions in steel are shown in Figures 4 and 5. When an Al$_2$O$_3$-lining ladle was used, the refractory was not able to provide Mg into the steel. At LF arrival, the melting of the refining slag was incomplete and the steel–slag reaction had not yet occurred. However, as the slag–steel reaction progressed, the formation of MgO-Al$_2$O$_3$ inclusions became inevitable. The number ratio of MgO-Al$_2$O$_3$ inclusions in the steel did not show a significant advantage over the case where an Al$_2$O$_3$–MgO·Al$_2$O$_3$-lined ladle was used. Therefore, the Al$_2$O$_3$-lining ladle can prevent the formation of MgO-Al$_2$O$_3$ inclusions in the initial stages of refining, but it does not effectively control their formation during the refining process. In the case of using an Al$_2$O$_3$–MgO·Al$_2$O$_3$-lining ladle, the molten steel already contains a large number of MgO-Al$_2$O$_3$ inclusions at LF arrival due to the exfoliation of the ladle-lining. During the LF refining process, the MgO-Al$_2$O$_3$ inclusions were reduced by transformation to CaO–Al$_2$O$_3$ system inclusions or absorption by the refining slag. This is due to the fact that the heating before steel tapping intensifies the slag–steel reaction, and the blowing and stirring of molten steel intensifies the scouring of molten steel on the refractory material. Therefore, the effect of Al$_2$O$_3$–MgO·Al$_2$O$_3$-lining ladle on MgO-Al$_2$O$_3$ inclusions is mainly the spalling of the lining material. The use of Al$_2$O$_3$–MgO·Al$_2$O$_3$-lining ladle is detrimental to the reduction of MgO-Al$_2$O$_3$ inclusions in molten steel.

4.2 Effect of ladle-lining refractories on the formation of CaO–Al$_2$O$_3$ inclusions

In the process of LF refining of Al-killed steel, it is common to introduce calcium wire into the ladle for inclusions modification. This is aimed at transforming spinel inclusions into calcium-silicate inclusions or intermediate products such as CaO–Al$_2$O$_3$–MgO inclusions [26]. In reality, CaO–Al$_2$O$_3$ series inclusions can form in the steel even

Figure 8: Number and number ratio of CaS inclusions. (The column shape in the figure represents the total number of CaS inclusions detected on the steel sample when using two types of ladle liners. The red and black spherical markings indicate the proportion of CaS inclusions to all inclusions).
without calcium treatment during the refining process [2,3,6–10]. As the reaction between the slag and steel progresses to a certain extent, [Ca] will be introduced into the steel due to the reduction of CaO in the slag by [Al], as described in equation (9). The stability of MgO–Al2O3 inclusions is affected by the presence of a small amount of [Ca] in the steel. When [Ca] enters the steel, it replaces Mg in the MgO–Al2O3 inclusions, resulting in inclusions with a core of MgO–Al2O3 surrounded by CaO–Al2O3, as shown in equation (10). Furthermore, [Ca], in the steel can react directly with Al2O3 inclusions, leading to the formation of CaO–Al2O3 inclusions, as shown in equation (11) [3].

\[
2[\text{Al}] + 3[\text{CaO}]_{\text{slag}} = 3[\text{Ca}] + (\text{Al}_{2}\text{O}_{3}), \tag{9}
\]

\[
\chi[\text{Ca}] + (\gamma\text{MgO} \cdot \text{zAl}_{2}\text{O}_{3})_{\text{inclusion}} = (\chi\text{CaO} \cdot (\gamma-x)\text{MgO} \cdot \text{zAl}_{2}\text{O}_{3})_{\text{inclusion}} + \chi[\text{Mg}], \tag{10}
\]

\[
[\text{Ca}] + n/3(\text{Al}_{2}\text{O}_{3})_{\text{inclusion}} = (\text{CaO} - (n-1)/3\text{Al}_{2}\text{O}_{3})_{\text{inclusion}} + 2/3[\text{Al}]. \tag{11}
\]

The LF refining process for Al-killed steel in this study did not involve calcium treatment. The steel contained both CaO–Al2O3 inclusions and modified intermediate products, CaO–Al2O3–MgO inclusions, as mentioned before. When using an Al2O3-lining ladle for refining, the proportion of CaO–Al2O3 inclusions in the steel was initially low. This was due to the absence of MgO–Al2O3 inclusions in the steel upon LF arrival, which prevented equation (10). The CaO–Al2O3 inclusions in the steel are mainly formed through equations (9)–(11). As the refining process progresses, the reactions of between the slag and steel result in the emergence of MgO–Al2O3 inclusions. This leads to an increase in the quantity of CaO–Al2O3 inclusions in the steel, as described in equation (10). The transformation of MgO–Al2O3 inclusions into CaO–Al2O3 inclusions occurs gradually from the surface toward the center of the inclusions as reported in refs [3,27]. The Ca content in the steel is very low and is not sufficient to completely transform the MgO–Al2O3 inclusions. Therefore, the steel contains a significant amount of CaO–Al2O3–MgO intermediate products coexisting in the steel, which is in line with the reference findings [25]. The Al2O3-lining ladle can only reduce the formation of CaO–Al2O3 inclusions at the beginning of the refining process. On the other hand, in an Al2O3–MgO–Al2O3-lining ladle, the steel undergoes equations (9)–(11) simultaneously throughout the refining process. Figure 4(b) shows that the steel contains a higher quantity of CaO–Al2O3 inclusions. In addition, it was observed that CaO–Al2O3 inclusions with higher Ca content appeared in the low-melting region of the ternary phase diagram during the refining process. This observation suggests that the using of an Al2O3–MgO–Al2O3-lining ladle is more favorable for the formation of CaO–Al2O3 inclusions compared to an Al2O3-lining ladle.

### 4.3 Effect of ladle-lining refractories on formation of CaS inclusions

The desulfurization process in molten steel typically occurs at the steel–slag interface, and CaO is commonly used as the desulphurizing agent. Therefore, the refining slag used in the process of Al-killed steel refining often has higher basicity [28]. The desulfurization reaction in the Al-killed steel refining process is represented by equation (12). Liu's research [24] showed that the use of magnesium-containing ladle-linings in the refining process of Al-killed steel can add magnesium to molten steel. This suggests that in addition to Mg in the refining slag, Mg in the ladle can also participate in the desulfurization reaction, as shown in equations (12)–(16). The MgO–Al2O3 in the ladle lining is reduced by [Al], and [Mg] enters the molten steel. Subsequently, [Mg] directly reacts with [S] in the molten steel to form MgS. Due to the thermodynamic instability of MgS, it further reacts with CaO in the slag to generate CaS and MgO. While the desulfurization capability of Mg is weaker than that of Ca, the use of ladle materials containing Mg introduces more Mg into the molten steel due to the larger contact area between the steel and the refractory lining. Therefore, the desulfurization effect of Mg should not be underestimated [22,24,29,30].

\[
3[\text{CaO}] + 3[\text{S}] + 2[\text{Al}] = 3[\text{CaS}] + (\text{Al}_{2}\text{O}_{3}), \tag{12}
\]

\[
3[\text{MgO}] + 2[\text{Al}] = 3[\text{Mg}] + (\text{Al}_{2}\text{O}_{3}), \tag{13}
\]

\[
3[\text{MgO} \cdot \text{Al}_{2}\text{O}_{3}] + 2[\text{Al}] = 3[\text{Mg}] + 4(\text{Al}_{2}\text{O}_{3}), \tag{14}
\]

\[
[\text{Mg}] + [\text{S}] = [\text{MgS}], \tag{15}
\]

\[
(\text{MgS}) + (\text{CaO}) = (\text{CaS}) + (\text{MgO}). \tag{16}
\]

When refining Al-killed steel using an Al2O3-lining ladle, the introduction of Mg into the molten steel relies solely on the reaction with the steel and slag. Therefore, the desulfurization process at the slag–steel interface occurs only through the first method as shown in equation (12). However, when using an Al2O3–MgO–Al2O3-lining ladle for refining, the desulfurization reactions proceed through both methods simultaneously. Therefore, using an Al2O3–MgO–Al2O3-lining ladle during LF refining can improve the desulfurization reaction rate, resulting in increased CaS content in the steel. This finding is consistent with the present results.
5 Conclusion

The effect of two different types of ladle-lining refractories on non-metallic inclusions in steel was investigated by sampling Al-killed steel during refining and casting. However, there was a wide range of refractories used for ladle lining and only two of them were investigated in this study. In the future, it is necessary to investigate the effect of more types of ladle-lining refractories on inclusions in steel.

(1) The evolution of inclusions during the refining and casting of Al₂O₃-lining ladles follows the sequence Al₂O₃ → MgO·Al₂O₃ → CaO–Al₂O₃. For Al₂O₃–MgO·Al₂O₃-lining ladles, all three types of inclusions were observed in the steel throughout the experiments.

(2) In both industrial samples, the composition of inclusions was concentrated in the high Al₂O₃ region of the CaO–Al₂O₃–MgO phase diagram. Most of the CaO–Al₂O₃ inclusions did not transform to the low-melting point region. The size of inclusions were mainly concentrated in the range of less than 3 μm.

(3) When using an Al₂O₃ ladle, the Al₂O₃ inclusions in the steel gradually transformed into MgO·Al₂O₃ and CaO–Al₂O₃ inclusions. At the end of refining, the steel still contained predominantly Al₂O₃ inclusions. When using an Al₂O₃–MgO·Al₂O₃-lining ladle, the quantity ratio of CaO–Al₂O₃ inclusions in steel was higher, and these inclusions dominated during the refining process.

(4) The Al₂O₃–MgO·Al₂O₃-lining ladle was more conducive to improving steel cleanliness, while Al₂O₃ was more conducive to reducing the average size of inclusions.

(5) The effectiveness of molten steel desulfurization was enhanced when using an Al₂O₃–MgO·Al₂O₃-lining ladle. However, there was a significant increase in CaS inclusions in the steel compared to when using an Al₂O₃-lining ladle.

Acknowledgments: The authors gratefully acknowledge the fundamental support from the National Natural Science Foundation of China (52274341, 52074197) and State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology.

Funding information: This work was financially supported by the National Natural Science Foundation of China (52274341, 52074197) and State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology.

Author contributions: Fu-bin Gao: factory experiments and sampling; Xinbo Yan: data processing and analysis, manuscript writing; Fuming Wang, Jianli Li, Xinhua Wang: manuscript revision.

Conflict of interest: The authors state no conflict of interest.

Data availability statement: All authors can confirm that all data used in this article can be published by the Journal “High Temperature Materials and Processes.”

References


