Evolution of MgO·Al₂O₃ Based Inclusions in Alloy Steel During the Refining Process

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The transformation of MgO·Al₂O₃ based inclusions in alloy steel during refining has been studied by industrial trials. Besides Factsage software is applied to study the formation and modification of spinel inclusions in alloy steel using calcium treatment during refining process. The results show the transformation sequence of inclusions is: MgO·Al₂O₃ → CaO–Al₂O₃–MgO complex inclusions → MgO·Al₂O₃, and under present experimental condition, in order to avoid forming MgO·Al₂O₃ inclusions the content of dissolved Ca in the molten steel has to reach 1ppm. Also the results show that when more calcium was added into molten steel, the content of Al₂O₃ and MgO will be lower. Besides, increases the content of CaO in the inclusions will increase even if the content of SiO₂ changes little.

Keywords: ALLOY STEEL, NON-METALLIC INCLUSIONS, MGO·AL₂O₃ SPINEL, THERMODYNAMICS

Introduction

There are various factors affecting the quality of steel, and the presence of MgO·Al₂O₃ spinel inclusions is one of them. These inclusions are uneasy to deform when rolling due to their high melting point (2135 °C) and high hardness (HV : 2100~2400 kg/mm²), which will lead to surface defects on the casting product [1]. In addition, spinel inclusions tend to accumulate at the inner wall of the submerged entry nozzle, inducing clogging during continuous casting [1-3]. Nowadays the mechanisms of formation of MgO·Al₂O₃ based spinel inclusions are still not clear, though some investigations have been carried out on this topic. Stability diagrams of oxide inclusions have been created corresponding to Mg and Al contents using the thermodynamic data experimentally obtained [4-6]. It has been proven that very small amount of Mg and Al enables the formation of spinel. The effects of slag basicity and composition on spinel formation in Fe-16mass%Cr stainless steel deoxidized by Al were investigated by Okuyama et al [7] and Todoroki [8]. Young et al [9] studied the formation mechanism of liquid calcium aluminate inclusions from MgO·Al₂O₃ spinel, and found that spinel reacted with the dissolved Ca forming a liquid calcium aluminate phase. Pretorius et al [10] studied the modification of spinel inclusions by Ca- treatment in LCAK steel by industrial experiments and showed the feasibility for the modification of spinel inclusions by Ca-treatment. In the current study, evolution of MgO·Al₂O₃ based inclusions in alloy steel during refining was investigated. Factsage6.0 was applied to calculate formation and transformation of spinel inclusions in alloy steel, as well as the effect of calcium treatment on the composition of molten steel and inclusions. This study focuses on the effect of Ca-treatment on transformation of MgO·Al₂O₃ based inclusions.

Methodology

In the present work, the experimental steel is 30CrMo with a composition (in wt.%) of C 0.30; Si 0.22; Mn 0.52; P 0.015; S 0.007; Mo 0.10; Al 0.020; V 0.12; Cu 0.07; Cr 0.94. The process to produce 30CrMo is: Scrap+DRI+hot metal →100t EAF →100t LF – VD →CaSi treatment →CC. The time of LF refining is about 60 min and the time of VD treatment is 40 min. During tapping, aluminum (300 Kg), SiMn (800 Kg), and FeMn (400 Kg)
were added in order to deoxidize and alloy. After 30 min of LF refining, 60 kg of aluminum wire, 56 kg of ferromanganese, 113 Kg of ferromolybdenum and 180 kg alloy of standard ferrochromium were added to adjust the composition of the molten steel. The size of the billet is 210 mm. Steel samples under four heats were taken during refining (before (301) and during (302) LF treatment, before (401) and after (402) VD treatment). The temperatures of sampling are 1550 °C (301), 1620 °C (302), 1625 °C (401) and 1565 °C (402) respectively. During sampling, the samplers were immerged in the molten steel 300 mm below the surface of bath. The inclusions were observed and analyzed using SEM-EDS. In order to observe three-dimensional morphology of inclusions, the samples were treated by partial acid extraction [11].

Results and Discussion

Variation of Molten Steel Composition

The composition of each sample during the refining process is shown in Table 1. The average content of aluminum, calcium and magnesium during each step of the refining process is showed in Figure 1, indicating that the dissolved aluminum decreases from 0.0256 % to 0.019 % during the early period of the LF. At the beginning of VD, the aluminum content rises to 0.0217 %. And during the VD process, the aluminum content changes slightly. The calcium content increases from 0.0014 % to 0.0025 % during the early period of LF treatment while it decreases later. At the beginning of VD, the content of calcium is 0.0021 % and decreases sharply during degassing to finish at only 0.0005 %. The content of magnesium remains steady at 0.0005 %~0.0009 % during the entire refining process.

![Figure 1. Variations of Al, Ca and Mg in molten steel during refining](image)

Table 1. Compositions of molten steel during refining

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>Al</th>
<th>Ca</th>
<th>Mg</th>
<th>Compositions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>259301</td>
<td>0.232</td>
<td>0.27</td>
<td>0.91</td>
<td>0.019</td>
<td>0.035</td>
<td>0.0009</td>
<td>0.0005</td>
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</tr>
<tr>
<td>259302</td>
<td>0.252</td>
<td>0.27</td>
<td>0.011</td>
<td>0.011</td>
<td>0.027</td>
<td>0.0016</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>250401</td>
<td>0.249</td>
<td>0.25</td>
<td>0.004</td>
<td>0.004</td>
<td>0.023</td>
<td>0.001</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>250402</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>0.022</td>
<td>0.0005</td>
<td>0.0005</td>
<td></td>
</tr>
<tr>
<td>260301</td>
<td>0.205</td>
<td>0.21</td>
<td>0.90</td>
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<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>260302</td>
<td>0.233</td>
<td>0.20</td>
<td>0.95</td>
<td>0.002</td>
<td>0.018</td>
<td>0.003</td>
<td>0.001</td>
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<tr>
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<td>0.266</td>
<td>0.23</td>
<td>0.95</td>
<td>0.003</td>
<td>0.021</td>
<td>0.001</td>
<td>0.0006</td>
<td></td>
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<tr>
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<td>0.021</td>
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<tr>
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<td>0.89</td>
<td>0.013</td>
<td>0.017</td>
<td>0.002</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>261302</td>
<td>0.237</td>
<td>0.27</td>
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<tr>
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<td>0.247</td>
<td>0.26</td>
<td>0.95</td>
<td>0.002</td>
<td>0.021</td>
<td>0.0044</td>
<td>0.0008</td>
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<td>—</td>
<td>0.02</td>
<td>0.0005</td>
<td>0.0005</td>
<td></td>
</tr>
</tbody>
</table>

The low aluminum content during the early period of LF treatment may stem from the fact that most of inclusions of deoxidization are removed by floatation. In order to complete deoxidization and to control the content of aluminum, 60kg Al is added during the late period of LF. Thus the content of aluminum increases. Aluminum changes slightly during VD treatment due to the low oxygen. In the trials, Ca-treatment is completed just at the beginning of LF. Sample 301 is selected after Ca-treatment, so its calcium should be the highest. Due to the reaction between calcium and inclusions, the content of calcium decreases gradually. However, the result of the trial shows that the content of calcium increases. Maybe sampling 301 is selected at the time when calcium
hasn’t diffused uniformly. And the content of calcium still keeps the high level during the late period of LF refining, maybe because calcium which is produced by the reaction between the added Al and CaO in the slag balances the consumption of calcium in the molten steel. Then the content of calcium decreases sharply, because calcium reacts with inclusions and molten steel during VD, and inclusions are removed by flotation.

The Existence Forms of Inclusions in Alloy Steel

There are three kinds of forms of inclusions based MgO-Al2O3 in alloy steel. One is pure MgO-Al2O3, mainly containing Mg, Al and O elements, another is MgO-Al2O3-CaO complex inclusion, the third is MgO-Al2O3-CaO-SiO2 complex inclusion. The size of three kinds of forms of inclusions is 1–3 μm. Those inclusions are very small, so they can’t come from refining slag. The current study insist the MgO-Al2O3 based inclusions can be formed by following several steps: MgO in the slag or lings refractory was reduced by Al. The reaction equations are shown as equations (5) and (6).

\[
\text{Ca} + \text{MgO} - \text{Al}_2\text{O}_3 = \text{CaO} - \text{Al}_2\text{O}_3 + \text{Mg} + \text{O} \quad (\text{Eq. 5})
\]

Before LF refining, MgO-Al2O3 inclusions appeared, and during LF refining and VD refining MgO-Al2O3 inclusions disappeared, but at the end of VD refining MgO-Al2O3 inclusions reappeared again. So the transformation sequence of inclusion in alloy steel in current study is MgO-Al2O3 → CaO→ Al2O3− MgO complex inclusions→MgO-Al2O3. The reason why MgO-Al2O3 inclusions reappeared again may relate to the content of dissolved calcium. According to Table1, the average content of total calcium in the molten steel during LF and VD refining exceeds 0.001 %, however, the average content of total calcium in the molten steel at the end of VD refining is 0.0005 %. So in order to avoid forming MgO-Al2O3 inclusions, the content of dissolved calcium in the molten steel have to reach a certain value. But in current study the content of dissolved calcium wasn’t measured, so it is difficult to know this value. In the later section, thermodynamic calculations were used to get this value. In order to keep a certain content of dissolved calcium, the oxygen potential of molten steel should be low.
enough. Any increase of the oxygen potential from reoxidation may lead to the formation of the secondary spinel inclusions.

**Thermodynamic Calculations**

**Thermodynamics on Formation and Transformation of MgO·Al₂O₃ Inclusions**

**Figure 4** is the inclusions equilibrium diagram of Fe-O-Mg-Al-Ca, and the calcium aluminate inclusions are CaO, CaAl₂O₄ and CaAl₄O₇ in calculation. From **Figure 4**, when the dissolved aluminum content in molten steel is less than 10⁻², the content of dissolved magnesium is less than 10ppm and the content of dissolved calcium in molten steel is about 1ppm, the complex inclusions contained calcium aluminate is the stable form in molten steel. As 30CrMo alloy steel for example, the content of aluminum in molten steel is 0.034 %, the magnesium content is about 0.0005 %, when the dissolved calcium content in molten steel is about 1ppm, the MgO·Al₂O₃ spinel can be transformed into a liquid complex inclusions. From **Figure 4**, when the dissolved calcium content in molten steel is increased, liquid complex inclusion region expands rapidly; the lower content of dissolved aluminum in liquid steel, the lower dissolved calcium content required transforming into liquid inclusions from MgO·Al₂O₃ spinels.

**Effect of Ca-treatment on Transformation of MgO·Al₂O₃ Inclusions**

The effects of Ca-treatment on transformation of MgO·Al₂O₃ inclusions also were calculated by FactSage6.0 thermodynamic software. It should be noticed that the calcium yield was assumed to 100 % in the thermodynamic calculations.

**Figure 5** shows the effect of Ca-treatment on the compositions of liquid inclusions. According to **Figure 5**, when adding 1ppm calcium into molten steel, MgO·Al₂O₃ inclusions have transformed...
into liquid complex inclusions and both the content of Al$_2$O$_3$ and MgO in the liquid complex inclusions decrease rapidly, while the content of CaO increases sharply. The content of Al$_2$O$_3$ and MgO in the liquid complex inclusions go on decreasing with the increasing amount of calcium added into the molten steel. The content of CaO in the liquid complex inclusions go on increasing with the increasing amount of calcium added into the molten steel, while the content of SiO$_2$ in the liquid complex inclusions changes little. When the amount of calcium added into the molten steel reaches 10 ppm, the content of MgO in the liquid complex inclusions gets to 7.0 %, the content of Al$_2$O$_3$ 47.5 %, the content of CaO 44% and the content of SiO$_2$ 1.5 %.

The reason for the increase of both the content of CaO and MgO in the liquid complex inclusions is that MgO in the inclusions is reduced by calcium, producing CaO into inclusions. Figure 6 is the effect of Ca-treatment on the amount of MgO-Al$_2$O$_3$ in the molten steel. From Figure 6, when 2 ppm calcium is added into molten steel, the MgO-Al$_2$O$_3$ inclusions can transform liquid complex inclusions completely.
Conclusions

1. Mainly there are three types of inclusions containing MgO in alloy steel during LF refining: 1) Spinel inclusions; 2) CaO–Al₂O₃–MgO complex inclusions; 3) CaO–MgO–Al₂O₃–SiO₂ complex inclusions. The transformation sequence of inclusion during refining is: MgO·Al₂O₃ → CaO–Al₂O₃–MgO complex inclusions → MgO·Al₂O₃.

2. Under present experimental condition, in order to avoid forming MgO·Al₂O₃ inclusions the content of dissolved Ca in the molten steel has to reach 1ppm.

3. Spinel inclusions may form even with low magnesium in the steel. More calcium addition into molten steel lowers the content of the Al₂O₃ and MgO, increases CaO content in the inclusions, while changes SiO₂ content little.

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References


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