Effect of Calcium Content on Inclusions during LF Refining Process of AISI 321 Stainless Steel

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Abstract: During the ladle furnace (LF) refining process of AISI 321 stainless steel, the effects of three heats with different calcium contents on the evolution of inclusions were investigated. The size, morphology, and composition of inclusions were analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). After the addition of aluminum and titanium, the primary oxides in AISI 321 stainless steel were Al\textsubscript{2}O\textsubscript{3}-MgO-TiO\textsubscript{x} complex oxide, in which the mass ratio of Al\textsubscript{2}O\textsubscript{3}/MgO was highly consistent with spinel (MgO·Al\textsubscript{2}O\textsubscript{3}). After calcium treatment, the calcium content in the oxide increases significantly. The thermodynamic calculation result shows that when the Ti content was 0.2 wt %, the content of Al and Ca were below 0.1 wt % and 0.0005 wt %, respectively, which was beneficial to the formation of liquid inclusions in molten steel. The modification mechanism of calcium on TiN-wrapped oxides has been discussed in combination with temperature changes.

Keywords: inclusions; stainless steel; calcium treatment; thermodynamic calculation

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1. Introduction

Nonmetallic inclusions form during the deoxidation and alloying processes. The composition, morphology, size, and quantity of inclusions were changed with the addition of deoxidizer and alloying elements during the steel melting process. These inclusions with high melting point and hardness cause adverse effects on the mechanical properties, surface defects, pitting corrosion, stress corrosion cracks and nozzle clogging during continuous casting [1-3]. Therefore, it is necessary to remove or optimize harmful nonmetallic inclusions as much as possible [3].

Titanium, as an alloying element, is generally added to steel the addition to improve the mechanical properties by refining grains [4]. Particularly, the addition of titanium in stainless steel can improve the corrosion resistance of steel at a high temperature, which can inhibit the formation of chromium carbide [5,6]. However, titanium-containing inclusions are formed simultaneously during the reactions between titanium and oxygen, nitrogen or carbon [7,8]. It is reported that titanium-containing inclusions have deleterious effects on mechanical properties and corrosion resistance. For instance, the clogging of submerged entry nozzle and surface defect are caused by TiO\textsubscript{x} and TiN [9-11]. Zhou et al. [12] reported that TiN inclusions with larger size could cause the deleterious on the fatigue life of steel. Since titanium has a strong affinity with dissolved oxygen during the production of steel, aluminum is generally added to molten steel as a stronger deoxidizer for reducing the formation of Ti-containing oxides, which can improve the yield of Ti [4,13]. Besides, calcium treatment can effectively modify such inclusions due to the formation of inclusions such as Al\textsubscript{2}O\textsubscript{3} and spinel after the addition of aluminum to the steel [14-16].

Many researchers had studied the evolution of titanium-containing inclusions [17,18]. Wang et al. [19] discussed the effect of Ti/Al ratio on the transient behavior of inclusions, and then found that the
transformation of inclusions from spherical to irregular occurred when the Ti/Al ratio increased from 1/4 to 1/2. Yin et al. [20] observed three different forms of TiN inclusions, including single, twinned, and clusters. They believed that Turbulence and Stokes’ mechanisms play an significant role in the growth of TiN inclusions. Ren et al. [21] found that with the increasing of TiO content and the decreasing of MgAl2O4 content in the Mg-Al-Ti-O composite oxide inclusions, the inclusions changed from high melting point irregular inclusions to low melting spherical liquid inclusions. However, only a few available systematic reports to discuss the effect of Ca content on inclusions in stainless steel after addition of Al and Ti. Zhang et al. [22] investigated the effects of Ti content on inclusions in Al-Ca-Ti complex deoxidized steel, and found that the formation of liquid inclusions required simultaneous control of calcium and titanium content in molten steels. Seo et al. [14] studied the influence of the order of addition of Ca and Ti on inclusions after deoxidation of Al. The experiment results showed that Ca treatment before Ti addition can effectively inhibit the formation of spinel. Moreover, the mechanism of the effect of Ca treatment on TiN-wrapped oxides has received little attention.

The present work aims to compare the effects of different calcium contents on inclusions and to reveal the mechanisms of formation and evolution of inclusions. The results would be beneficial to guide for industrial application in Ti-bearing Al-killed stainless steel with Ca treatment.

2. Methodology

2.1. Experimental Procedures

The production process of AISI 321 stainless steel was “30 ton electric arc furnace (EAF) → 30 ton argon oxygen decarburization (AOD) → 30 ton ladle furnace (LF) → continuous casting (CC)”, as shown in Fig. 1. Al was added after AOD tapping, Ti was added at the beginning of the LF refining process, and Ca treatment was operated after LF refining for some time. Three heats with different Ca
content were investigated. Sample 1 was taken 10 minutes after the addition of titanium alloy, and sample 2 was obtained after 10 minutes of calcium treatment.

![Fig. 1. Schematic illustration of sampling locations.](image)

2.2. Compositions Analysis and Inclusions Characterizations

After the sampling was completed, the composition and inclusion characteristics in the samples were analyzed. The total oxygen and total nitrogen were analyzed by the inert gas fusion-infrared absorptiometry method. The acid-soluble alloying element content was analyzed by the inductively coupled plasma optical emission spectrometry method (ICP-OES). Table 1 presents the chemical compositions of the six samples. The part of the samples used for inclusions analysis were embedded in resin and polished. The inclusions were analyzed by SEM and EDS. The size of inclusions on the polished surfaces of the steel samples were analyzed with the aid of an automatic SEM-EDS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>Mg</th>
<th>Ca</th>
<th>T.O</th>
<th>T.N</th>
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<tr>
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<td>0.39</td>
<td>1.07</td>
<td>0.035</td>
<td>17.23</td>
<td>9.11</td>
<td>0.054</td>
<td>0.26</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0042</td>
<td>0.0140</td>
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<tr>
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<td>0.49</td>
<td>1.08</td>
<td>0.036</td>
<td>17.20</td>
<td>9.21</td>
<td>0.038</td>
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<td>0.0009</td>
<td>0.0012</td>
<td>0.0032</td>
<td>0.0157</td>
</tr>
<tr>
<td>B1</td>
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<td>0.34</td>
<td>1.13</td>
<td>0.038</td>
<td>17.21</td>
<td>9.02</td>
<td>0.065</td>
<td>0.23</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0024</td>
<td>0.0115</td>
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<tr>
<td>B2</td>
<td>0.024</td>
<td>0.43</td>
<td>1.14</td>
<td>0.038</td>
<td>17.17</td>
<td>9.10</td>
<td>0.052</td>
<td>0.23</td>
<td>0.0009</td>
<td>0.0018</td>
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<tr>
<td>C1</td>
<td>0.026</td>
<td>0.27</td>
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<td>17.4</td>
<td>9.10</td>
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<td>0.0016</td>
<td>0.0038</td>
<td>0.0154</td>
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3. Result and Discussion

3.1. Characterization and Composition of Inclusions

3.1.1. After the Addition of Aluminum and Ferrotitanium
After the addition of aluminum and titanium, three kinds of typical inclusions were observed: oxides, pure TiN, and TiN with oxide as the core. Fig. 2 shows the morphological and composition of these inclusions. MgO-Al₂O₃-TiOₓ was the main oxide inclusions after adding Ti, and others oxide included Al₂O₃, MgO-Al₂O₃, and Al₂O₃-TiOₓ. The oxide surface was usually wrapped by TiN. The morphology of the oxide inclusions was spherical or irregular, while the TiN inclusions was polygonal or cuboidal. The quantity and size distribution of the inclusions after addition of aluminum and titanium were shown in Fig. 3. It can be seen that the size of the inclusions was mainly concentrated below 5μm.

Fig. 2. Morphology and composition of typical inclusion after titanium added: (a1) pure TiN inclusion, (a2) irregular MgO-Al₂O₃ inclusion, (a3) irregular Al₂O₃ inclusion, (a4) TiN inclusion with spherical Al₂O₃-TiOₓ core, (a5) TiN inclusion with spherical MgO-Al₂O₃-TiOₓ core, (a6) TiN inclusion with irregular MgO-Al₂O₃-TiOₓ core.
According to the previous research [4,21,23,24], the oxygen partial pressure and titanium content in molten steel are the primary factors affecting the valence of titanium in oxides. In the present work, the stable deoxidized product was Ti$_3$O$_5$. Fig. 4 shows the Al$_2$O$_3$-MgO-Ti$_3$O$_5$ phase diagram under the oxygen partial pressure of $P_{O_2}=10^{-14}$ atm [3,21], which was calculated by the FactSage 7.2 software at 1873K. The inclusions of samples A1, B1 and C1 were plotted on the Al$_2$O$_3$-MgO-Ti$_3$O$_5$ phase diagram.

It can be seen that the compositions of the inclusions are mainly gathered in the (Liquid + Titania_Spinel) and (Liquid + Titania_Spinel + MgO·Al$_2$O$_3$) phase field, and the mass fraction of Al$_2$O$_3$/MgO in the composition of inclusions is highly consistent. The dotted line in Fig. 4 shows the mass ratio of Al$_2$O$_3$/MgO in the Al$_2$O$_3$-MgO-Ti$_3$O$_5$ oxides is between 2.13 to 2.70 (The mass ratio of Al$_2$O$_3$/MgO in MgO·Al$_2$O$_3$ is 2.55), indicating that the Mg-Al-O exists in the form of spinel (MgO·Al$_2$O$_3$) in the inclusions.
3.1.2. After the Calcium Treatment

The morphology and composition of TiN and TiN with oxide as the core were consistent with these before calcium treatment. However, the calcium content in the oxides increased significantly, and substantially all oxides contain calcium. Fig. 5 shows the morphology and composition of these three types of inclusions after calcium treatment. The main complex oxides include CaO-Al₂O₃, CaO-Al₂O₃-TiOₓ, and CaO-Al₂O₃-MgO-TiOₓ; calcium-containing complex oxide was wrapped by TiN the same as oxide before the calcium treatment. In terms of morphology, oxides show spherical or irregular shapes and these TiN inclusions show polygonal and cuboidal shapes. Fig. 6 shows the quantity and size distribution of inclusions after Ca added. It can be seen that the inclusions were still mainly concentrated below 5 μm, Ca treatment has no significant effect on the quantity and size of the...
Fig. 5. Morphology and compositing of typical inclusions after calcium treatment: (b1) pure TiN inclusion, (b2) TiN inclusion with spherical CaO-Al₂O₃-TiOₓ core, (b3) TiN inclusion with irregular CaO-Al₂O₃-TiOₓ core, (b4) TiN inclusion with spherical CaO-Al₂O₃-MgO-TiOₓ core, (b5) TiN inclusion with irregular CaO-Al₂O₃-MgO-TiOₓ core, (b6) spherical CaO-Al₂O₃ inclusion.

Fig. 6 Quantity and size distribution of inclusions after calcium treatment

In order to compare the effects of different calcium contents on oxide inclusions, the quaternary
isothermal phase of CaO-\text{Al}_2\text{O}_3-\text{Ti}_3\text{O}_5-5\%\text{MgO} at 1873K under the oxygen partial pressure at $P_{O_2}=10^{-14}$ atm was drawn by the FactSage 7.2 software, as shown in Fig. 7. The mass fraction of MgO was 5%, which is obtained through statistical analysis of a large number of inclusions. The compositions of steel samples taken after the calcium treatment were marked in Fig. 7. It can be seen that with the different calcium additions in heat A, B and C, the calcium content in the oxides of samples A2, B2 and C2 were different. In sample A2, there were a lot of inclusions located in all Liquid and (Liquid oxide + Al$_2$O$_3$) phase field. As the calcium content increases, the inclusions compositions of B2 and C2 were mainly located in the (Liquid + Perovskite) and (Liquid + Perovskite + CaO-2Al$_2$O$_3$) phase field. In addition, in the (Liquid + Perovskite + 3CaO-2TiO$_2$-3CaO-Ti$_2$O$_3$) and (Liquid + 3CaO-2TiO$_2$-3CaO-Ti$_2$O$_3$) phase field with higher calcium content, the number of inclusions of sample B2 was higher than C2. The result shows that the Ca content has an important influence on the morphology of inclusions.

Fig. 7. Compositions of inclusions from sample A2, B2 and C2, projected onto the 1873K isotherm of the CaO-Al$_2$O$_3$-Ti$_3$O$_5$-5%MgO quaternary diagram under the oxygen partial pressure of $P_{O_2}=10^{-14}$ atm. (Liquid (L): liquid oxide, Perovskite (Prv.): CaTiO$_3$, Spinel (Spl.): (MgO-Al$_2$O$_3$), CM$_2$A$_8$: CaO-2MgO-8Al$_2$O$_3$, C$_2$M$_2$A$_{14}$: 2CaO-2MgO-14Al$_2$O$_3$, C$_3$T$_2$-C$_3$T: 3CaO-2TiO$_2$-3CaO-Ti$_2$O$_3$. 9
3.2. Formation and Evolution Mechanism of Inclusions

3.2.1. Formation Mechanism of Al-Ti-O Composite Oxide

After adding aluminum and titanium, the oxide inclusions both containing aluminum and titanium can be found in six samples. Fig. 8 shows the phase stability diagram of the Al-Ti-O system in 321 steel at 1873K calculated by FactSage 7.2 software. As can be seen from Fig. 8, when the concentration of Al and Ti are ranges from 1 ppm to 1 wt % and 10 ppm to 1 wt %, respectively. Al₂O₃, Ti₂O₃, Ti₃O₅, and liquid phase are the four oxides phase equilibrium with molten steel. The 0.3 wt % Ti content is the boundary between Ti₂O₃ and Ti₃O₅. Ti₂O₃ is a stable phase present at a high Ti content, while the Ti₃O₅ is a stable phase present at a low Ti content. According to the titanium and aluminum content of six samples, six symbols were marked in the phase diagram. It can be seen that the composition of the six samples were close to or located in the liquid-oxide phase field. After analyzing the conclusions of previous researchers, the equilibrium phase of the Al-Ti-O system in molten steel still does not reach a consensus conclusion, Jung et al. [25] pointed out that the liquid phase exists between Al₂O₃ and Ti₃O₅ after thermodynamic calculations, Zhang et al. [17] found that Al₂O₃-TiOₓ type liquid oxide inclusions appeared after Al-Ti composite deoxidation. Matsuura et al. [26] and Van Ende et al. [18] though that the stable phases during the Al-Ti-O system only had Al₂O₃, Ti₂O₃, Ti₃O₅, and Al₂TiO₅. Fig. 9 shows spherical liquid Al₂O₃-TiOₓ oxide inclusions covered by TiN, which was founded in sample A1. The addition of titanium to the steel accelerates the dissolution of Mg from the MgO-based refractory or slag into the molten steel and promotes the formation of spinel [14]. Therefore, a large amount of Al-Ti-Mg-O composition oxides appeared in the steel after the addition of Al and Ti, and the ratio of Al/Mg was following the ratio of Al/Mg in spinel (MgO·Al₂O₃).
Fig. 8. Calculated oxide stability diagram of Al-Ti-O system with iso-oxygen contours (in ppm) in Fe-17Cr-9Ni steel at 1873K (liquid oxide: Al\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{x}).

3.2.2. Effect of Ca Content on the Evolution Mechanism of Oxides

The added calcium could modify solid phase alumina or spinel inclusions to harmless liquid inclusions effectively, which have been confirmed by many researchers [14-16]. In the current experiment, it is necessary to determine the optimum calcium content to facilitate the formation of liquid inclusions. Fig. 10 presents the evolution of inclusions with increasing calcium content under
different aluminum contents, which were calculated by the FactSage 7.2 software under the condition of AISI321 stainless steel. According to the composition analysis results of steel samples, the composition of the molten steel was set to Fe-17Cr-9Ni-0.2Ti-0.0025O, and the Al contents were taken to be 0.01%, 0.05%, 0.1%, and 0.15%, respectively. When the aluminum content is 0.01 and 0.05 wt %, respectively, three kinds of oxides were formed in the steel with the increase of Ca content. The first formed was liquid oxide phase, then the perovskite phase and 3CaO-2TiO2-3CaO·Ti2O3 phase. The liquid oxide phase was formed from the beginning of Ca treatment and increased to the maximum when the Ca content was 5 ppm, and disappeared when the Ca content was 10 ppm. The amount of perovskite phase increased to the maximum when the Ca content was 25 ppm. The 3CaO-2TiO2-3CaO·Ti2O3 phase occurs when the Ca content is 25 ppm, and increases as the Ca content increases. When the aluminum content is 0.1 and 0.15 wt %, respectively, there are four oxides formed in the steel due to an increase in the aluminum content. The Al2O3 phase coexists with the liquid phase when the Ca content was less than 2 ppm. Due to the consistent titanium content, with the increase of calcium content, the formation and evolution process of the perovskite phase and the 3CaO-2TiO2-3CaO·Ti2O3 phase are the same as the results of thermodynamic calculations when aluminum content is 0.01 and 0.05 wt %. Therefore, the thermodynamic calculation results show that when the Ti content was 0.2 wt %, the content of Al and Ca were below 0.1 wt % and 0.0005 wt %, respectively, which is favorable for the formation of liquid oxide inclusions.
Fig. 10. Equilibrium formation of inclusions during calcium treatment process at 1873 K for steel compositions: AISI321 stainless steel in mass pct: (a) Al=0.01 mass pct, (b) Al=0.05 mass pct, (c) Al=0.1 mass pct, (d) Al=0.15 mass pct (Liquid: Liquid oxide, Perovskite: CaTiO$_3$, C$_{3T2}$-C$_3$T: 3CaO·2TiO$_2$·3CaO·Ti$_2$O$_5$).

3.2.3. Thermodynamic Calculation of Formation Conditions of TiN

The thermodynamic calculation formula for the reaction of Ti and N in molten steel to form TiN is as follows [27]:

$$\text{[Ti]} + \text{[N]} = \text{TiN}$$

$$\Delta G^\circ = -314800 + 114.35T$$

To formation of TiN, the driving force of actual change in the Gibbs free energy is given by Eq.(3):
\[ \Delta G = \Delta G^0 + RT \ln \frac{a_{TiN}}{a_{[Ti]}a_{[N]}} = \Delta G^0 + RT \ln \frac{a_{TiN}}{f_{Ti}f_{N}[\text{pct Ti}][\text{pct N}]} \]  

\[ \lg f_{Ti} = \left( \frac{2557}{T} - 0.365 \right) \lg f_{Ti(1873K)} \]  

\[ \lg f_{N} = \left( \frac{3280}{T} - 0.75 \right) \lg f_{N(1873K)} \]  

\[ \lg f_i = \sum e'_i[\text{pct } j] + \sum \gamma'_i[\text{pct } j]^2 + \sum \sum \gamma'^{(i,k)}_i[\text{pct } j][\text{pct } k] \]  

where \( a_{TiN}, a_{[N]} \) and \( a_{[Ti]} \) are the activities of TiN, N and Ti, respectively. The activity of TiN is unity during the present experimental conditions. \( f_{Ti} \) and \( f_{N} \) are the activity coefficients of N and Ti, which is changed with temperature. The relationships between the activity coefficients of Ti and N and the temperature are given by Eqs. (4) and (5). [pct Ti] and [pct N] are the mass fractions of N and Ti in molten steel. At 1873K (1600°C), the activity coefficient \( f_i \) of the different solute element in molten steel can be calculated using the classical Wagner formalism, Eq. (6) with the first- and second-order interaction parameters [4, 28-31] that are listed in Table 2.

**Table 2. Interaction Coefficients of Fe-Cr-Ni-Ti-N System at 1873K (1600°C)**

<table>
<thead>
<tr>
<th>j</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Cr</th>
<th>Ni</th>
<th>Ti</th>
<th>N</th>
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</tr>
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<tr>
<td>e'_N</td>
<td>0.13</td>
<td>0.047</td>
<td>-0.02</td>
<td>0.45</td>
<td>-0.043</td>
<td>0.01</td>
<td>-0.6524</td>
<td>0</td>
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<tr>
<td>\gamma'_N</td>
<td>0.00749</td>
<td>-</td>
<td>0.00326</td>
<td>-</td>
<td>0.0003</td>
<td>0.000114</td>
<td>-0.0002</td>
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<td>-</td>
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<tr>
<td>e'_Ti</td>
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<td>0.0645</td>
<td>-0.043</td>
<td>-0.064</td>
<td>0.0158</td>
<td>0.0105</td>
<td>0.048</td>
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<tr>
<td>\gamma'_Ti</td>
<td>-</td>
<td>0.000184</td>
<td>-</td>
<td>-</td>
<td>0.000511</td>
<td>0.000372</td>
<td>-</td>
<td>-</td>
<td>-0.355</td>
</tr>
</tbody>
</table>

By utilizing the percentage concentration of the solute \( j \) in molten steel and the interaction coefficient of each element \( e'_i(\gamma'_i) \), the relationship between [pct Ti], [pct N] and temperature can be got. When the temperature is taken at 1723 K, 1773 K, 1823 K, 1873 K, and 1923 K, the equilibrium curve between [pct Ti] and [pct N] can be calculated with the aid of Matlab software, as shown in Fig. 11. It can be seen that the temperature and concentration of titanium and nitrogen all affect the precipitation of TiN inclusions in the steel. After marked the titanium and nitrogen content of six samples on the equilibrium diagram, it can be seen that the solubility products of titanium and nitrogen.
are higher than or equal to the equilibrium solubility products at 1600°C. Therefore, under the conditions of actual titanium and nitrogen contents in steel plant, the formation temperature of TiN should be above 1600°C.

3.2.4. Evolution Mechanism of TiN-wrapped Oxides after Ca Treatment

In this study, the analysis results of SEM-EDS show that TiN easily formed on the oxides surface and even completely wraps the oxide. Thermodynamic calculations show that TiN has formed in the molten steel below 1600 °C. Since the contents of titanium and nitrogen in the same process hardly changes, temperature is a major factor affecting the precipitation of TiN. The temperature of the molten steel at the time of sampling was about 1570°C, but the electrode can locally generate a high temperature of more than 1650°C during heated. Combine the results of this experimental analysis and thermodynamic calculations, Fig. 12 shows a schematic diagram of the process of calcium modification TiN-wrapped oxides. The specific reaction process is as follows: (1) after adding aluminum and titanium to the ladle, due to the lower temperature of the molten steel, TiN-wrapped oxides formed in
the molten steel. (2) The temperature of the molten steel rises due to the heating action of the graphite electrode, and the TiN on the surface of the oxide dissolves. After the calcium treatment, the dissolved calcium in the molten steel reacts with the oxides. The liquid oxides were easily formed at low calcium content, while the solid phase oxides were more easily formed under high calcium content. (3) After the graphite electrode heating process was finished, TiN re-formed on the oxide surface due to the temperature drop.

Fig. 12. Schematic diagram of the evolution of TiN-wrapped oxides after calcium treatment.

4. Conclusions

In current work, the effect of calcium content on inclusions during LF refining process of AISI 321 stainless steel was investigated. Based on the results of experimental and thermodynamic calculations, the following conclusions were obtained:

(1) After the addition of Al and Ti, oxide, pure titanium nitride and titanium nitride with oxide core were the three typical inclusions in molten steel. Al₂O₃-MgO-TiOₓ was the primary oxide inclusions, in which the Mg-Al-O exists in the form of spinel (MgO·Al₂O₃). The Ca content in the oxides of heat A is lower than that of heat B and C, resulting in the formation of more liquid oxides.

(2) Thermodynamic calculations by the number of inclusions indicated that when the titanium
content was 0.2 mass pct, the content of Al and Ca were below 0.1 wt % and 0.0005 wt % were more easily to obtained liquid oxide inclusions.

(3) When the contents of titanium and nitrogen in the molten steel does not change significantly, temperature is a key factor leading to the formation of TiN. High temperature conditions during electrode heating play an important role in Ca modified TiN-wrapped oxides.

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References


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