Formation and Evolution of Oxide Inclusions in Titanium-Stabilized 18Cr Stainless Steel

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During Ti-stabilized stainless steelmaking process, oxide inclusions in steel generally cause the clogging of submerged entry nozzle and surface defects of cold-rolled products. Therefore, the evolution mechanism of oxide inclusions in Ti-stabilized 18Cr stainless steel was investigated by industrial experiments. The characteristics of inclusions in specimens were analyzed by scanning electron microscopy and energy dispersive spectroscopy. After Al deoxidation, the main inclusions were irregular MgO–Al2O3 spinel. After calcium treatment, MgO–Al2O3 inclusions were modified to be spherical multilayer CaO–MgO–Al2O3 inclusions consisting of spinel crystal embedded in CaO–Al2O3 liquid matrix. Thermodynamic calculation indicated that several ppm Ca could significantly expand the liquid oxides phase in Mg–Al–O phase diagram. After Ti addition, multilayer CaO–MgO–Al2O3–TiOx inclusions were formed. The compositions of steel were located close to Al2O3–TiO2 liquid oxide phase, which would help to reduce oxide inclusions and increase titanium yield. Titanium addition has modified spinel inclusions to multilayer MgO–Al2O3–TiOx inclusions containing solid spinel inner layer and MgO–Al2O3–TiOx liquid oxide outer layer. As for improving the cleanliness of molten steel, the contents of magnesium, aluminum, and titanium could be considered simultaneously to liquefy oxide inclusions during Ti-stabilized stainless steelmaking process.

KEY WORDS: stainless steel; inclusion control; titanium; aluminum; secondary steelmaking.

1. Introduction

The LF refining process of Ti-stabilized stainless steel melts involves deoxidation by Al followed by Ti alloy addition for binding the interstitial elements C and N.1–2) However, the deoxidation products can potentially cause the clogging of submerged entry nozzle (SEN) and the surface defects of steel products.3–5) Thus, it is necessary to control the formation of oxide inclusions in Ti-bearing stainless steel.

Aluminum is usually added before titanium addition to reduce the formation of Ti-containing inclusions and improve Ti yield.6,7) Al2O3 and spinel (MgO–Al2O3) inclusions were generally formed after Al deoxidation. Spinel inclusions were formed due to soluble Mg supplied from the slag and MgO-based refractory.7–9) These inclusions could lead to the nozzle clogging.10–13) In order to prevent the clogging of SEN, some studies have been carried out to modify these inclusions to liquid oxide by calcium treatment. Harkness et al.14) reported that calcium treatment made little difference to the composition or morphology of spinel inclusions. Kor15) also have pointed out that the modification of MgO–Al2O3 spinel with calcium was expected to be less effective than the modification of pure alumina. However, more researchers have found that calcium treatment could modify Al2O3 or MgO–Al2O3 (MA) inclusions to harmless liquid calcium aluminate inclusions, which could promote the removal of these oxide inclusions during Al-killed steelmaking process.16–20)

Al-killed molten steel containing Ti generally causes more severe nozzle clogging than Ti-free steel, and titanium oxide inclusions have been suggested as a possible cause.21,22) Therefore, the formation mechanism of oxide inclusions in Al-killed Ti-bearing steel has been investigated by many researchers.23–32) Matsura et al.23) and Van Ende et al.26) pointed out that Al2O3, Ti2O3, TiO2, and Al2TiO5 were equilibrium phases of the Al–Ti–O system in molten steel. Wang et al.27–31) found when the Ti/Al ratio in the melt was increased to 15/1 within the Al2TiO5 stable phase region, the inclusion population evolved from spherical-dominant ones to irregular ones. In addition, Mg–Al–Ti–O complex inclusions are almost unavoidable during Al-killed Ti-bearing steelmaking process due to the MgO-based refractory.4) Park et al.33) investigate the effect of Al on the evolution of non-metallic inclusions in the Mn–Si–Ti–Mg deoxidized steels. They found that the composition of major oxide inclusion was continuously changed from the Mg–Ti–O to MgAl2O4 with the concentration AI in steels. Ren et al.34) observed liquid Mg–Al–Ti–O complex inclusion with high TiO2 content at 1 873 K and pointed out that MgAl2O4 spinel inclusions can be modified to low melting temperature ones by combining TiO2 component. Ono et al.35–37) have studied the equilibrium relationship between

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the oxide compounds in MgO–Al2O3–Ti2O3 and molten iron to avoid Al2O3 or MgO–Al2O3 formation and for inclusion control. According to their experimental results, it is necessary to lower the Al content and to adjust the Ti content to an appropriate concentration range to form Mg2TiO4 instead of MgAl2O4. Recently, they reported that the transformation of the stable compound from Mg–Ti spinel to Mg–Al spinel occurred at Mg contents ranging from 1 to 10 ppm by mass. It was also found, on the Mg–Ti spinel, the stable compound is transformed from inverse-spinel Mg3TiO5 to normal-spinel Mg2TiO4 at Ti = about 60 ppm. Zhang et al. investigate the effect of magnesium addition on the evolution of inclusions in Al–Ti deoxidized melts. Liquid Al–Ti–O inclusions could be quickly modified to be liquid Mg–Al–Ti–O inclusions. What is more, the beneficial effect of Ti-containing inclusions and Mg-containing particles on phase transformation behavior has been recognized and termed “oxide metallurgy”, which can refine grain size by acting as intragranular nucleation sites for acicular ferrite. Recently, Wu et al. have investigated the effect of inclusions’ behavior on the microstructure in Al–Ti deoxidized and Mg-treated steel. They found that a large amount of finely dispersed Al2O3–TiO2–MgO inclusions in low aluminum steel can pin austenite grain boundaries and induce interlocking acicular ferrite effectively. This result indicated that Mg–Al–Ti–O inclusions can be used as agents of “oxide metallurgy”. Therefore, it is necessary to investigate the characteristics and evolution mechanism of Mg–Al–Ti–O inclusions during Al-killed Ti-stabilized stainless steelmaking process.

In the present work, steel samples were taken at different stages in industrial trials to investigate the characteristics and evolution mechanism of oxide inclusions in Ti-stabilized stainless steel. The characteristics of inclusions in steel samples were determined by scanning electron microscopy and energy dispersive spectroscopy. The formation mechanism and phase stability of oxide inclusions observed in steel were investigated with the aid of thermodynamic calculation. The effect of titanium addition in 18Cr stainless steel containing different initial aluminum content on the evolution of Mg–Al–Ti–O inclusions was discussed through the coupling of thermodynamics calculation and experimental results.

2. Methodology

2.1. Experimental Procedures

Industrial trials were carried out in a steel plant to investigate the evolution of inclusions in molten steel. The titanium-bearing stainless steels were produced through the steelmaking route of “100 ton electric arc furnace (EAF) → 100 ton argon oxygen decarburization furnace (AOD) → 100 ton vacuum oxygen decarburization (VOD) → 100 ton ladle furnace (LF) → continuous casting (CC)”, as shown in Fig. 1. In EAF steelmaking, steel scrap and alloys were initially melted. Subsequently, molten steel was decarburized, deoxidized, and desulfurized in AOD. During the reduction of AOD, ferrosilicon alloys were used for deoxidation. Before tapping into the ladle, most of the slag was removed. After the additional decarburization and degassing in the VOD, ferrosilicon was added to deoxidize. During LF refining process, aluminum was added first. Then, titanium wire was added after calcium treatment in LF. The main material of ladle refractory was MgO-graphite bricks. When the chemistry and temperature were on the specification, the ladle with qualified molten steel was transported to the continuous casting platform for continuous casting.

Lollipop steel samples for determined analysis were carried out 10 min after the addition of Al, 10 min after the addition of Ca, 10 min after feeding titanium alloy wire, and at the end of LF refining, respectively. The lollipop steel samples taken in the steelmaking process were immediately quenched in water. Schematic illustration of sampling locations was shown in Fig. 1.

2.2. Composition Analysis and Inclusion Characterization

The steel samples were cleaned by machining off the surface for chemical analysis. Cylinders (Φ5 mm × 5 mm) were machined for the measurement of the total oxygen contents which were analyzed by the inert gas fusion-infrared absorption spectrometry method with an accuracy of ±1 ppm. The Al, Si, Ti, Ca and Mg contents in steel were determined by the inductively coupled plasma optical emission spectrometry method (ICP-OES) with ±5 pct relative standard deviation. The Cr contents in steel were measured by the alkali fusion acid dissolution method: steel samples were dissolving using aqua regia; then, Cr3+ was converted to Cr6+ by adding perchloric acid and heating the solution; finally, Cr contents in samples were titrated using ammonium ferrous sulfate standard solution. The chemical compositions of chromium, silicon, titanium, aluminum, calcium, magnesium, and oxygen in steel specimens were given in Table 1.

The surfaces of steel specimens (15 mm × 15 mm × 20 mm) were polished by SiC papers up to 2 000 grade and 2.5 μm pastes. The morphologies and compositions of nonmetallic inclusions on the mirror-polished surfaces of the steel specimens were analyzed with the aid of an automatic scanning electron microscope (EVO18-ICASTeel, ZEISS Co. Ltd.) combined scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). The compositions of the multilayer inclusions were determined on average by the automatic scanning electron microscope.
The maximum diameter of the inclusion was defined as the size of the inclusion. For the accuracy of automated EDS analysis of inclusions, the size was taken larger than 1 μm, because the interaction volume may spread into the steel and excite electrons from the surrounding environment of the inclusions with diameters smaller than 1 μm.

3. Results and Discussion

3.1. Characterization of Inclusions

After the addition of Al, the main inclusions in sample 1 were alumina-rich inclusions, including MgO–Al₂O₃ spinel and CaO–MgO–Al₂O₃, as shown in Fig. 2(a). The MgO-based refractory supplied soluble Mg in molten steel to form MgO–Al₂O₃ inclusions. Elemental mapping of a typical MgO–Al₂O₃ inclusion is shown in Fig. 3(a). The compositions of Al, Mg, and O in the square inclusion were homogeneous. According to the irregular shape of the inclusion, it was clear that it was solid at steelmaking temperatures. After the calcium treatment, the main inclusions in sample 2 were spherical complex CaO–MgO–Al₂O₃. At the same time, few amounts of MgO–Al₂O₃ inclusions were also observed, as shown in Fig. 2(b). Elemental mapping of a typical CaO–MgO–Al₂O₃ inclusion is shown in Fig. 3(b). This inclusion consisted of a spinel crystal embedded in a CaO–Al₂O₃ liquid matrix. The non-uniform distribution of the inclusions was related to the difference of modification ability of MgO–Al₂O₃ spinel and alumina with calcium treatment. It has been reported that the modification of spinel with calcium was less effective than the modification of pure alumina. After the addition of Ti-cored wire, the main inclusions in sample 3 were CaO–MgO–Al₂O₃–TiOₓ, as shown in Fig. 2(c). Figure 3(c) shows an elemental mapping of a multilayer CaO–MgO–Al₂O₃–TiOₓ inclusion. As can be seen, the inclusion could be divided into two layers, the inner layer was an irregular shape MgO–Al₂O₃ core, and the main compositions of the outer layer were CaO–Al₂O₃–TiOₓ. At the end of LF, there were mainly MgO–Al₂O₃–TiOₓ and CaO–MgO–Al₂O₃–TiOₓ inclusions in sample 4, as shown in Fig. 2(d). Most of CaO–MgO–Al₂O₃–TiOₓ inclusions were multilayer inclusions with large size (>5 μm). The size of most MgO–Al₂O₃–TiOₓ inclusions was smaller than 5 μm. Elemental mapping of a typical MgO–Al₂O₃–TiOₓ inclusion is shown in Fig. 3(d). It can be found that the titanium content of the outer layer was higher. According to the shape and the composition distribu-

![Fig. 2. Morphology and composition of typical inclusions encountered in samples: (a) typical inclusions after Al deoxidation. (b) typical inclusions after calcium treatment. (c) typical inclusions after Ti addition. (d) typical inclusions at LF end.](image)

![Fig. 3. Elemental mapping of typical inclusions at each stage: (a) MgO–Al₂O₃ inclusion after Al addition. (b) CaO–MgO–Al₂O₃ inclusion after calcium treatment. (c) CaO–MgO–Al₂O₃–TiOₓ inclusion after Ti addition. (d) MgO–Al₂O₃–TiOₓ inclusion at LF end. (Online version in color.)](image)
tion of the MgO–Al2O3–TiOx inclusion, the outer layer with high titanium was liquid oxide at steelmaking temperature. What is more, with the agitation of argon gas in liquid steel the inclusions, gradually polymerized and floated up, which led to the decrease of total oxygen content during LF refining process. An agglomerated CaO–MgO–Al2O3–TiOx inclusion was observed in steel specimen taken at the end of LF, as shown in Fig. 2(d3).

To investigate the evolution of inclusions, compositions of inclusions in steel samples, projected onto the 1 873 K isotherm of CaO–MgO–Al2O3 ternary system phase diagrams are shown in Fig. 4. The phase diagram and liquid oxide phase (red line area) of the CaO–MgO–Al2O3 system at 1 873 K were marked with the aid of FactSage™ 7.0 software. It can be seen that solid MgO–Al2O3 spinel phase was modified to all-liquid phase with the increase of CaO content. After the addition of aluminum, the compositions of inclusion were mainly distributed close to the spinel (MgO–Al2O3) region. After calcium treatment, many inclusions with high CaO content were formed and located in the liquid oxide phase, which would be helpful for the flotation and removal of inclusions during LF refining. After the addition of titanium, the CaO contents of some inclusions decreased. At the end of LF refining, the contents of Al2O3 in some inclusions were decreased.

The oxidation state of titanium in molten steel was determined by the titanium content in steel and the oxygen partial pressure, such as TiO, TiO2, Ti3O5, Ti2O3, and Ti4O7. According to the previous research, Ti3O5 was a stable deoxidized product in the present study. The mass percentages of MgO, Al2O3, and TiO2 of inclusions were plotted on the MgO–Al2O3–Ti3O5 ternary compositional diagram, as shown in Fig. 5. The phase diagram and liquid oxides phase (red line area) of the MgO–Al2O3–Ti3O5 system under the oxygen partial pressure of P02=10−12 atm were calculated by FactSage™ 7.0 software. It can be found that the MgO/Al2O3 mass ratio of most inclusions in steel samples taken after titanium addition was close to 3:7, which belongs to the MgO–Al2O3 spinel. Only a small amount of inclusions had an average composition close to the liquid phase. The compositions of the outer layer and inner layer of some multilayer inclusions were also shown in Fig. 5. The compositions of the inner layer of most inclusions were also located out of liquid phase. However, the compositions of most inclusions in outer layer were close to the liquid phase. This indicated that the outer layer of solid MgO–Al2O3 inclusions has been changed to be MgO–Al2O3–Ti3O5 liquid oxide after titanium addition during LF.

![Fig. 4. Compositions of inclusions in steel samples, projected onto the 1 873 K isotherm of the CaO–MgO–Al2O3 ternary diagram (axes in mass percentage). (Online version in color.)](image)

![Fig. 5. Composition distributions of inclusions in MgO–Al2O3–Ti3O5 phase diagrams. Solid lines represent the boundary line of different phases at 1 873 K under the oxygen partial pressure of P02=10−12 atm. (Online version in color.)](image)

![Fig. 6. Evolution of the main composition of inclusions in samples with various sizes: (a) is sample 3 taken after Ti addition. (b) is sample 4 taken at the end of LF. (Online version in color.)](image)
refining process.

The mass fraction of CaO, MgO, Al\(_2\)O\(_3\), and TiO\(_2\) of inclusions with various sizes was calculated by the atomic percentages determined by EDS, as shown in Fig. 6. It has been found that the size of most inclusions was smaller than 10 \(\mu\)m. Thus, the size of the inclusions taken into consideration in Fig. 6 ranged from 1 \(\mu\)m to 10 \(\mu\)m. After the addition of titanium, the main inclusions in steel were CaO–MgO–Al\(_2\)O\(_3–\)TiO\(_2\). It can be found that the main composition of the inclusions with size smaller than 2 \(\mu\)m was MgO–Al\(_2\)O\(_3–\)TiO\(_2\). The titanium oxide contents of these inclusions were higher than 20%. In addition, the alumina contents and magnesia contents of most inclusions were around 60% and 20%, respectively. The CaO contents of inclusions were usually lower than 15%. After 40 min of titanium addition, the size of the inclusions has changed in sample 4 taken at the end of LF refining, as shown in Fig. 6(b). The alumina contents of most inclusions have decreased to lower than 60%. The titanium contents have increased in some inclusions, especially in the inclusions with the size within 2 to 3 \(\mu\)m. MgO and CaO contents of most inclusions were basically stable.

3.2. Thermodynamic Calculation of Inclusion Formation

The phase stability diagram of Mg–Al–O system in Fe-18Cr steel at 1 873 K was calculated with the aid of FactSage\textsuperscript{TM} 7.0 software to investigate the formation of spinel observed in samples. The FactPS and FToxid databases were used to calculate. The associate model stored in the Factsage software is used together with other FactSage databases for oxides, slags, gases, etc., to calculate complex multiphase, multicomponent equilibria during steelmaking process.\textsuperscript{56–58} The calculation result is shown in Fig. 7. It can be seen from the phase diagram that alumina, spinel (MgO–Al\(_2\)O\(_3\)), and MgO are mainly phases in molten steel with magnesium and aluminum contents ranging from 0.1 ppm to 100 ppm and 1 ppm to 1 wt%, respectively. The boundary lines of each phase were evaluated using [O] ppm as a parameter. The compositions of present work were marked in Fig. 7. The present experimental results were located in the spinel phase, which agrees well with the observed inclusions in Fig. 2(a). Spinel inclusions were easily attached to the inner wall of submerged entry nozzle (SEN) during continuous casting, which could lead to the clogging of SEN.\textsuperscript{3,10,38,59,60} Thus, many works have been done to avoid the formation of spinel inclusions or modify the solid spinel inclusions to be liquid inclusions at steelmaking temperature. Todoroki et al.\textsuperscript{59} have prevented nozzle clogging in an industrial experiment by controlling the inclusion composition in MgO phase instead of spinel or alumina phase. At the same time, more researchers have found that calcium treatment was an effective way to modify the solid Al\(_2\)O\(_3\) or spinel to liquid oxide. Therefore, the phase stability diagrams of Mg–Al–O phase with 1 ppm and 5 ppm Ca contents in Fe-18Cr steel at 1 873 K were also calculated, as shown in Fig. 8. As can be seen in Fig. 8, there are three oxide phases, viz. liquid oxides, spinel (MgO–Al\(_2\)O\(_3\)), and MgO. After the addition of 1 ppm Ca, all of the alumina phase was changed to the liquid oxide phase. At the same time, partial spinel area was modified to the liquid oxide phase. The experimental results were marked in Fig. 8. It can be found that the steel composition was still located in spinel phase of Fe-18Cr steel with 1 ppm Ca. However, the spinel phase was further decreased after the addition of 5 ppm Ca. All of the experimental results were located in liquid oxide phase. After the calcium treatment during LF refining, most of the inclusions in sample 2 were spherical complex CaO–MgO–Al\(_2\)O\(_3\) inclusions. The outer layer of most inclusions was modified

Fig. 7. Calculated oxide stability diagram of Mg–Al–O system with iso-oxygen contours in Fe-18Cr steel at 1 873 K. (Online version in color.)

Fig. 8. Calculated oxide stability diagrams of Mg–Al–O system with iso-oxygen contours in Fe-18Cr-1 ppm Ca steel (a) and Fe-18Cr-5 ppm Ca steel (b) at 1 873 K. (Online version in color.)
to be liquid CaO–MgO–Al2O3. However, some MgO–Al2O3 spinel and the MgO–Al2O3 inner layer of most complex inclusions still existed.

During Ti-bearing stainless steelmaking process, it is important to control the aluminum content before titanium addition, which influences the formation of Ti-containing oxide inclusions and titanium yield. Therefore, the phase diagram of Al–Ti–O system in Fe-18Cr steel at 1 873 K was calculated with the aid of FactSage™ 7.0 software, as shown in Fig. 9. There are four oxide phases, viz. Al2O3, Ti2O3, Ti3O5, and Al2O3–TiOx, with the content range of Ti from 0.001 wt% to 1 wt% and Al from 1 ppm to 1 wt%. The boundary lines of each oxide phase were evaluated using [O] ppm as a parameter. The experimental results were marked in Fig. 9. When the Ti2O3 phase was stable with the titanium content ranging from 0.34 wt% to 1 wt%, Ti3O5 phase was stable with the titanium content less than 0.34 wt%. Both Ti2O3 and Ti3O5 coexisted with 0.34 wt% titanium content in Fe-18Cr molten steel at 1 873 K. What is more, too many alumina inclusions would be formed with the steel composition containing high Al content which was located in Al2O3 phase. Similarly, titanium would be oxidized with the steel composition containing low Al content which was located in titanium oxide phase (Ti2O3 phase or Ti3O5 phase). Thus, appropriate Al content and Ti content in molten steel should be located in Al2O3–TiOx phase, which would help to reduce oxide inclusions and increase the titanium yield. It also can be found that the compositions of most steel samples were located close to Al2O3–TiOx phase. According to Fig. 9, the reasonable range of Al content and Ti content in Fe-18Cr steel were obtained, as shown in formula (1).

\[
0.0639Ti + 0.0014 \leq Al \leq 0.1362Ti + 0.0057 \quad (0.1 \leq Ti \leq 0.34)
\]

\[
0.1118Ti + 0.0155 \leq Al \leq 0.1362Ti + 0.0057 \quad (0.34 < Ti \leq 1)
\]

After titanium addition, the main inclusions changed to be MgO–Al2O3–Ti3O5 inclusions in sample 4 taken at the end of LF refining. Thus, the evolution of inclusions with different aluminum contents in Fe-18Cr steel containing 4 ppm Mg and 50 ppm O with the increase of titanium content was calculated with the aid of FactSage™ 7.0 software, as shown in Fig. 10. When the aluminum content in steel was 0.01 wt%, the transformed sequence of oxide inclusions was spinel (MgO–Al2O3), liquid oxide, TiOx (Ti2O3 phase or Ti3O5 phase). With the increase of titanium content,
spinel phase gradually reduced. When the titanium content increased to 0.05 wt%, liquid oxide began to form. Spinel phase disappeared in the molten steel with more than 0.055 wt% titanium. When the titanium content increased to 0.245 wt%, TiO phase was formed and liquid oxide phase began to decrease. Thus, it can be found that pure liquid oxide phase existed with the content range of titanium from 0.055 wt% to 0.245 wt%. As can be seen in Figs. 10(a) and 10(b), inclusion transition trend in molten steel containing 0.015 wt% Al was basically similar to that in molten steel containing 0.01 wt% Al. When the initial aluminum content in steel was 0.02 wt%, Al$_2$O$_3$ phase was formed, as shown in Fig. 10(c). In addition, the Al$_2$O$_3$ phase decreased with the increase of titanium content. As the titanium content increased to more than 0.075 wt%, the amount of liquid oxide phase increased and then decreased. The pure liquid oxide phase in molten steel containing 0.02 wt% Al existed with the content range of titanium from 0.095 wt% to 0.365 wt%. When the initial aluminum content increased to 0.025 wt%, the range of titanium content containing pure liquid oxide phase was changed to be 0.115 wt% to 0.425 wt%. During LF refining process, the magnesium content was relatively stable due to the MgO-based refractory. The titanium content and aluminum content in molten steel should be controlled within a reasonable range, so that the compositions of molten steel were located in pure liquid oxide phase, which could promote the removal of oxide inclusions to avoid the clogging of SEN. The titanium contents of this work were marked in Fig. 10. All the experimental results were located in pure liquid oxide phase. The mass percentages of MgO, Al$_2$O$_3$, and TiO$_x$ calculated in Figs. 10(a) and 10(d) were further plotted in the MgO–Al$_2$O$_3$–Ti$_3$O$_5$ ternary phase diagram, as shown in Fig. 11. The empty marks represent the calculated results and the curve with an arrow represents the compositional changing direction with the increase of titanium content in molten steel. It can be found that the composition of inclusions would be located in liquid oxide phase field with the increase of titanium content. Comparing to the composition distribution of inclusions in samples shown in Fig. 5, the calculated curve passes through the composition distribution of inclusions observed in samples. The titanium contents of samples were also marked in Fig. 11. These compositions were located in liquid oxide phase field. The average compositions of most MgO–Al$_2$O$_3$–Ti$_3$O$_5$ inclusions in Fig. 5 were out of liquid oxide phase. However, the outer layer compositions of most spherical complex inclusions were close to liquid oxide phase, as shown in Figs. 3 and 5. This indicated that titanium in molten steel reacted with spinel (MgO–Al$_2$O$_3$) inclusions to form MgO–Al$_2$O$_3$–Ti$_3$O$_5$ liquid oxide during LF refining process. The inclusions with a liquid oxide outer layer were also easy to polymerize and float up. Thus, the magnesium content, aluminum content, and titanium content could be controlled within a reasonable range to promote the formation of MgO–Al$_2$O$_3$–Ti$_3$O$_5$ liquid oxide inclusions during Ti-stabilized stainless steelmaking process, which would help to improve the cleanliness of molten steel.

4. Conclusions

In order to investigate the evolution mechanism of oxide inclusions in Ti-stabilized 18Cr stainless steel, molten steel specimens were taken at different stages in industrial trials. According to the results of the chemical analysis, inclusion characteristics, and thermodynamic calculation, the following conclusions were obtained:

(1) The main inclusions were changed from MgO–Al$_2$O$_3$ after Al deoxidation to spherical complex CaO–MgO–Al$_2$O$_3$ after calcium treatment. After the addition of Ti-cored wire, multilayer CaO–MgO–Al$_2$O$_3$–TiO$_x$ inclusions were formed. At the end of LF, there were mainly multilayer MgO–Al$_2$O$_3$–TiO$_x$ and CaO–MgO–Al$_2$O$_3$–TiO$_x$ inclusions.

(2) Thermodynamic calculation indicated that several ppm Ca could significantly expand the liquid oxide field in Mg–Al–O phase stability diagram. Most of MgO–Al$_2$O$_3$ inclusions formed after Al addition were modified to be spherical multilayer CaO–MgO–Al$_2$O$_3$ inclusions consisting of a spinel crystal embedded in a CaO–Al$_2$O$_3$ liquid matrix after Ca treatment. After titanium addition, the compositions of most steel samples were located close to Al$_2$O$_3$–TiO$_x$ liquid oxide phase, which would help to reduce oxide inclusions and increase the titanium yield. According to the thermodynamic calculation, the reasonable range of Al content and Ti content in Fe–18Cr steel were obtained:

$$0.0639 \text{Ti} + 0.0014 \leq \text{Al} \leq 0.1362 \text{Ti} + 0.0057 (0.1 \leq \text{Ti} \leq 0.34)$$

$$0.1118 \text{Ti} + 0.0155 \leq \text{Al} \leq 0.1362 \text{Ti} + 0.0057 (0.34 < \text{Ti} \leq 1)$$

(3) Titanium addition has changed the main inclusions to be MgO–Al$_2$O$_3$–Ti$_3$O$_5$ inclusions containing solid spinel (MgO–Al$_2$O$_3$) inner layer and MgO–Al$_2$O$_3$–Ti$_3$O$_5$ liquid oxide outer layer in the steel specimen taken at the end of LF. Thermodynamic calculation also indicated that pure liquid oxide phase in molten steel containing 0.01 wt% Al and 4 ppm Mg existed with the content range of titanium from 0.055 wt% to 0.24 wt%. As for improving the cleanliness of molten steel, the contents of magnesium, aluminum, and titanium should be considered simultaneously to liquefy oxide inclusions during Ti-stabilized stainless steelmaking process.
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