Evolution Mechanism of Inclusions in Al-killed, Ti-bearing 11Cr Stainless Steel with Ca Treatment

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The evolution mechanism of non-metallic inclusions in Al-killed, Ti-bearing 11Cr stainless steel with Ca treatment was investigated by industrial trials and thermodynamic calculation. The morphology, composition, and size distribution of inclusions in steel specimens were analyzed by scanning electron microscopy and energy dispersive spectroscopy. The alloy addition and calcium contents in steel significantly influenced the characteristics of inclusions according to the present study. After the addition of Al, there were mainly alumina-rich inclusions in steel. With the titanium addition after calcium treatment, three types of inclusions were formed: irregular $\text{MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion, spherical $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion, and irregular dual phase Ti-containing inclusion. At the end of LF refining process, solid calcium titanates inclusions were formed due to the high calcium content in steel. The evolution of these inclusions was consistent with thermodynamic calculation, which indicated that the compositions of inclusions in steel specimens after the addition of titanium were mostly located in $\text{Al}_2\text{O}_3\text{-TiO}_x$ stable phase. Based on the characteristics of inclusions in steel and thermodynamic calculation, calcium could reduce the stability of spinel and strongly modify solid alumina and $\text{Al}_2\text{O}_3\text{-TiO}_x$ inclusions to form liquid oxides or solid calcium titanates. At the same time, the effects of calcium content in Al-killed, Ti-bearing 11Cr molten steel on the formation of inclusions were discussed through the coupling of thermodynamics calculation and experimental results.

KEY WORDS: stainless steel; titanium; calcium; aluminum; inclusion.

1. Introduction

Titanium-bearing stainless steel, due to their good formability, excellent corrosion resistance in high temperatures and cost-effectiveness, has been widely used in various applications including culinary, automobile and calorifier. Titanium suppresses chromium carbide precipitation at grain boundary through the formation of more stable titanium carbide, which substantially improves the resistance to intergranular corrosion.^{1,2)} What is more, the heterogeneous nucleation of delta ferrite on the TiN formed during primary solidification of stainless steel promotes the generation of the equiaxed fine-grain structure.^{3,4)} However, the generation of oxide inclusions is inevitable due to de-oxidation by Al before Ti alloy addition and the interactions between reactive elements in the steel melt and its environment (slag, refractory, or atmosphere). These inclusions generally cause the clogging of submerged entry nozzle (SEN) and deteriorate the quality of final steel products, such as skin laminations or line defects on the rolled strip.^{5–8)} Therefore, it is necessary to investigate the formation mechanism of oxide inclusion to control the inclusion population.

Aluminum is usually added to be the final deoxidizer

before the addition of Ti alloy for its stronger oxygen affinity than Ti,^{9–11)} which improves titanium yield and reduces inclusions containing Ti-oxides. However, the alumina inclusions were formed after the Al addition. In addition, spinel ($\text{MgO-Al}_2\text{O}_3$) inclusions can be generated due to soluble Mg supplied from the slag and MgO-based refractory.^{12–14)} These inclusions tended to adhere on the inner wall of the submerged entry nozzle.^{15–18)} Todoroki *et al.*¹⁶⁾ observed the immersion nozzles used after Al-killed SUS 430 stainless steel, and found that the boundary layer between the accretion and the nozzle consists of main alumina. In addition, the accretion of molten steel side was made of porous oxides identified to be spinel and metal droplets. It was pointed out that nozzle clogging took place when the inclusions were spinel while not in case of liquid calcium aluminate.

In order to solve the clogging problem of SEN in Al-killed molten steel, some studies have been carried out to modify the alumina and spinel ($\text{MgO-Al}_2\text{O}_3$) inclusions to liquid ones by calcium treatment.^{19–25)} Harkness *et al.*¹⁹⁾ reported that calcium treatment made little modification to the composition or morphology of spinel inclusions during ladle refining. It was concluded that the cubic crystal structure made the spinel phase more stable than alumina at high temperature. However, many researchers have pointed out that calcium treatment was an effective countermeasure

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to modify the alumina or spinel to harmless liquid calcium aluminate inclusions.^{21–25)} Ye *et al.*²¹⁾ have described calcium modification of aluminum oxide inclusions by using thermodynamic data. They suggested that it is much easier to modify alumina inclusions in a melt with moderate S-content at the early treatment stage when temperature is high and particle size is small. Park *et al.*²²⁾ have investigated the inclusion control of Al-killed ferritic stainless steel with calcium treatment and concluded that the transformation from alumina to calcium aluminates could be controlled by the diffusion of aluminate polyanions. Itoh *et al.*²⁰⁾ studied thermodynamics on the formation of spinel nonmetallic inclusion in liquid steel, and found that 1 ppm Ca in the steel at 1 873 K modified the alumina to the liquid phase and decreased the stability of spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) inclusions. Yang *et al.*²³⁾ have observed the $\text{MgO} \cdot \text{Al}_2\text{O}_3$ –CaO inclusions modified from $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusions after the calcium treatment. They found that many $\text{MgO} \cdot \text{Al}_2\text{O}_3$ –CaO inclusions have a two-layer structure: an outside CaO– Al_2O_3 layer and a $\text{MgO} \cdot \text{Al}_2\text{O}_3$ core. Their later study showed that the diffusion of Mg replaced by Ca in the inclusions was the rate-controlling step.²⁴⁾ It was also found that steel/slag reaction had a great effect on changing the morphology and composition of alumina and spinel inclusions.²⁵⁾ Jiang *et al.*²⁵⁾ have discussed the evolution mechanisms of non-metallic inclusions in molten steel refined by high basicity slag. They found that solid $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and MgO inclusions would be inevitably and gradually transferred into CaO– $\text{MgO} \cdot \text{Al}_2\text{O}_3$ system inclusions with lower melting temperature ($< 1\,773\text{ K}$) with the increase of Ca content in molten steel due to the reaction of steel and high basicity slag.

The presence of titanium in Al-killed molten steel generally causes more severe clogging of the submerged entry nozzle than Ti-free steel, and the titanium oxide inclusions have been suggested as a possible cause.^{26–28)} Thus, many studies of nonmetallic inclusions in Al-killed Ti-bearing steel have been carried out, such as nozzle clogging behavior,^{26,28)} thermodynamics and characteristics of inclusions,^{29–40)} modification of inclusions with Ca treatment^{41–47)} or Mg treatment^{48–52)} and evolution of inclusion during solidification and heating.^{41,48,53–55)} The two-layered inclusions of the Al–Ti–O phase with core Al_2O_3 were observed in Al-killed Ti-bearing molten steel, which was identical to the inclusions causing the nozzle clogging.^{26,28,29)} Wang *et al.*,^{30–33)} Matsuura *et al.*,³⁴⁾ Jung *et al.*³⁷⁾ and Van *et al.*³⁹⁾ pointed out that Al_2O_3 , Ti_2O_3 , Ti_3O_5 , and Al_2TiO_5 were equilibrium phases of the Al–Ti–O system in molten steel. Wang *et al.*^{30–33)} found when the Ti/Al ratio in the melt was increased to 15/1 within the Al_2TiO_5 stable phase region, the inclusion population evolved from spherical-dominant ones to irregular ones. Zhang *et al.*⁴⁹⁾ reported that irregular titanium aluminates inclusions were generated due to high titanium concentration (nearly 0.5 mass pct) in the melt. As mentioned above, calcium treatment in Al-killed steel has been widely investigated.^{19–25)} However, only a few available reports have discussed the inclusion formation of Al–Ti deoxidation with calcium treatment in stainless steel.^{44–47)} Zheng *et al.*⁵⁶⁾ investigated the clogging of SEN of Ti-bearing 321 stainless steel with Ca treatment, and found two types deposition, namely TiN and $\text{CaO} \cdot \text{TiO}_2$. Qian *et al.*⁷⁾ also reported that the $\text{CaO} \cdot \text{TiO}_2$ -rich ($\text{CaO} \cdot \text{TiO}_2$ –

$\text{MgO} \cdot \text{Al}_2\text{O}_3$) complex inclusions in Ti-bearing stainless steel were mainly inclusions in the clogging of SEN. Therefore, it is necessary to comprehensively study the effect of Ca treatment on the evolution mechanism of non-metallic inclusions in Al-killed, Ti-bearing 11Cr stainless steel.

In the present work, the samples taken at different stages in plant trial were investigated to reveal the evolution mechanism of oxide inclusions in Al-killed, Ti-bearing 11Cr stainless steel with Ca treatment. The morphology, composition and size distribution of inclusions in steel specimens were determined by scanning electron microscopy and energy dispersive spectroscopy. The formation mechanism and phase stability of inclusions observed in steel were discussed with the aid of thermodynamic calculation. At the same time, the effects of calcium content in molten steel on the controlling of inclusions during steelmaking process were analyzed through the coupling of thermodynamics calculation and experimental results.

2. Methodology

2.1. Experimental Procedures

3 heats industrial trials were carried out in a steel plant to investigate the formation and evolution of inclusions in molten steel. The titanium-bearing stainless steel was 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. Before tapping into the ladle, most of the slag was removed. The main material of ladle refractory was $\text{MgO} \cdot \text{CrO}_x$. After the additional decarburization and degassing in the VOD, ferrosilicon and aluminum were added to deoxidize. During LF refining process, aluminum was additionally added first according to the aluminum content in the molten steel at the end of VOD. Then, titanium wire was added after calcium treatment in LF. When the chemistry and temperature were on specification, the ladle with qualified molten steel was transported to the continuous casting platform for continuous casting.

In order to elucidate the evolution of nonmetallic inclusions in Al-killed, Ti-bearing stainless steel with Ca treatment, lollipop steel and slag samplings for determined analysis were carried out at the end of VOD process, 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.

Fig. 1. Schematic illustration of sampling locations.

2.2. Composition Analysis and Inclusion Characterization

The steel samples were cleaned by machining off the surface for chemical analysis. Cylinders ($\Phi 5 \text{ mm} \times 5 \text{ mm}$) were machined for the measurement of the total oxygen contents which were analyzed by the inert gas fusion-infrared absorptiometry method with an accuracy of $\pm 1 \text{ ppm}$. The acid-soluble Al, Ca and Mg contents in steel were determined by the inductively coupled plasma optical emission spectrometry method (ICP-OES) with $\pm 5 \text{ pct}$ relative standard deviation. The alloying element contents in steel were measured by the alkali fusion acid dissolution method. The composition of slag was determined by an X-ray fluorescence spectrometer. The chemical compositions of aluminum, titanium, magnesium, calcium, and oxygen in steel specimens of three heats were given in **Table 1**, while the compositions of CaO, MgO, Al_2O_3 , and SiO_2 in slags were listed in **Table 2**. The main purpose of this study was to determine the effect of alloy addition on the chemical and morphological evolution of nonmetallic oxide inclusions, while the main chemical compositions of slag were only included in this study for informative purpose.

The surfaces of steel specimens ($15 \text{ mm} \times 15 \text{ mm} \times 20 \text{ mm}$) were polished by SiC papers up to 2 000 grade and $2.5 \mu\text{m}$ pastes. The morphologies and compositions of non-metallic inclusions on the mirror-polished surfaces of the steel specimens were analyzed with the aid of an automatic scanning electron microscope (EVO18-INCAsteel, 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 $1 \mu\text{m}$, because the interaction volume may spread into the steel and excite electrons from the surrounding environment of the inclusions with diameters smaller than $1 \mu\text{m}$. The scanned area of each steel specimen was 41.5 mm^2 .

3. Results and Discussion

3.1. Characterization of Inclusions

For each of the samples taken at different stages, nearly 30 inclusions were selected for characterization. Three typical types of inclusions at each stage could be classified according to their distinctive appearance and composition, as exhibited in **Fig. 2** (the numbers beside the inclusion in the figures are atomic percentages determined by employing EDS analysis). Elemental mappings of typical complex inclusions at each stage were shown in **Fig. 3**. After the addition of Al, the inclusions containing alumina were formed. Due to the VOD converters lined by the MgO-based refractory the inclusions containing MgO were formed in molten steel. At the same time, the high basicity of slag might lead to the increase of the MgO content in inclusions, which has been investigated by Nishi *et al.*⁵⁷⁾ and Okuyama *et al.*⁵⁸⁾ Spherical homogeneous CaO–MgO– Al_2O_3 inclusions and dual phase CaO–MgO– Al_2O_3 inclusions were also observed in steel specimens at the end of VOD, which might be due to the indirect supply of calcium via high basic

Table 1. Chemical compositions of samples in three heats (mass percent).

Heat No.	Sample No.	Al	Ti	Mg	Ca	T.O
A	A1	0.0046	0.0013	0.0005	0.0009	0.0057
	A2	0.014	0.24	0.0007	0.0016	0.0058
	A3	0.015	0.25	0.0010	0.0012	0.0050
B	B1	0.054	0.0013	0.0005	0.0015	0.0061
	B2	0.034	0.29	0.0005	0.0025	0.0038
	B3	0.035	0.29	0.0006	0.0022	0.0038
C	C1	0.024	0.0016	0.0008	0.0023	0.0032
	C2	0.027	0.25	0.0008	0.0053	0.0029
	C3	0.023	0.26	0.0010	0.0026	0.0027

Table 2. The main slag compositions of samples in three heats (mass percent).

Heat No.	Sample No.	CaO	SiO_2	Al_2O_3	MgO
A	A1	51.39	11.65	18.70	5.48
	A2	50.32	10.22	18.37	7.41
	A3	50.08	9.32	18.39	7.16
B	B1	53.75	9.67	19.11	4.77
	B2	52.71	10.62	19.15	5.88
	B3	53.56	9.47	19.21	5.84
C	C1	54.91	9.58	13.86	6.58
	C2	54.8	9.65	13.34	6.62
	C3	54.47	9.35	13.04	6.63

Fig. 2. Morphology and composition of typical inclusions encountered in samples: (A1) irregular MgO– Al_2O_3 inclusion, (A2) irregular MgO– Al_2O_3 inclusion, (A3) spherical CaO–MgO– Al_2O_3 inclusion at VOD end, (B1) irregular MgO– Al_2O_3 – TiO_x inclusion, (B2) spherical CaO–MgO– Al_2O_3 – TiO_x inclusion, (B3) irregular dual phase Ti-containing inclusion 10 minutes after Ti addition in LF, (C1) irregular MgO– Al_2O_3 – TiO_x inclusion, (C2) irregular CaO–MgO– Al_2O_3 – TiO_x inclusion, (C3) spherical dual phase Ti-containing inclusion at LF end.

slag, as shown in Fig. 3(a). After Ti wire fed into molten steel after calcium treatment in LF refining process, three types of inclusions were found: irregular $\text{MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion, spherical $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion and irregular dual phase Ti-containing inclusion, as shown in Fig. 2(B). Although calcium was added before the addition of Ti, some $\text{MgO-Al}_2\text{O}_3$ inclusions still remained to react

with Ti to form $\text{MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusions. The elemental mapping of a multilayer $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion was shown in Fig. 3(b). As can be seen, the inclusion could be divided into two layers, the inner layer was an irregular shape $\text{MgO-Al}_2\text{O}_3$ core, and the main compositions of the outer layer were $\text{CaO-Al}_2\text{O}_3\text{-TiO}_x$. In addition, in the outer layer, the content of titanium in the white area of the inclusion was higher, and the aluminum content in other place was higher. The morphology of the complex inclusion was spherical. At the end of LF, the types of inclusions were essentially same as that of after titanium addition, as shown in Fig. 2(C). 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.⁵⁹ And a polymerized inclusion was observed in steel specimen taken at the end of LF, as shown in Fig. 3(c). It can be seen that the inclusion has several irregular shape $\text{MgO-Al}_2\text{O}_3$ core with an outer layer of $\text{CaO-Al}_2\text{O}_3\text{-TiO}_x$.

To elucidate the evolution of inclusions after aluminum addition, the compositions of inclusions analyzed in steel specimens were converted into mass percentage of CaO, MgO, and Al_2O_3 , which were plotted on the $\text{CaO-MgO-Al}_2\text{O}_3$ ternary system phase diagrams, as shown in Fig. 4. The phase diagram and liquid oxide phase (red line area) of the $\text{CaO-MgO-Al}_2\text{O}_3$ system at 1 873 K were marked with the aid of FactSageTM 7.0 software. It is shown that solid $\text{MgO-Al}_2\text{O}_3$ spinel phase was modified to all-liquid phase with the increase of CaO content. After the addition of aluminum, the inclusion compositions were mainly distributed close to the spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) region with small amounts of CaO (0 to 25 mass pct). The CaO contents of inclusions in sample A1 with lower aluminum content were higher than sample B1 and C1. After the addition of Ti, the Al_2O_3 contents of inclusions were rapidly decreasing, especially in

Fig. 3. Elemental mapping of typical complex inclusions at each stage: (a) dual phase $\text{CaO-MgO-Al}_2\text{O}_3$ inclusion at VOD end. (b) multilayer $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion 10 minutes after Ti addition in LF. (c) multilayer $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion at LF end.

Fig. 4. Composition distributions (mass fraction) of inclusions in $\text{CaO-MgO-Al}_2\text{O}_3$ phase diagrams. Solid lines represent the boundary line of different phases at 1 873 K.

sample B2 and C2. A major part of inclusions in sample B2 and C2 were far from the low-melting-point region (liquid oxide phase), which have higher MgO contents than that of sample A2. The compositions of inclusions in sample A3 and B3 taken at the end of LF were mainly located close to spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) region. Probably due to the high basic slag and calcium content in C3 sample the composition distribution of inclusion was close to the liquid area with high CaO content.

Titanium has different oxidation state in molten steel depending on the titanium content in steel and the oxygen partial pressure, such as TiO , TiO_2 , Ti_3O_5 , Ti_2O_3 , and Ti_4O_7 .^{11,60} According to the previous research, Ti_3O_5 was stable deoxidized product in the present study.^{11,60–62} The compositions of the inclusions analyzed in steel specimens after the addition of titanium from three heats are shown in Fig. 5. These compositions were projected into the $\text{CaO}-\text{Al}_2\text{O}_3-\text{Ti}_3\text{O}_5$ ternary compositional diagram. The phase diagram and liquid oxide phase (red line area) of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{Ti}_3\text{O}_5$ system under the oxygen partial pressure of $P_{\text{O}_2}=10^{-12}$ atm were calculated by FactSageTM 7.0 software. It is shown that all-liquid phase (called region 1) close to the $\text{CaO}-\text{Al}_2\text{O}_3$ binary region could expand with the increase of TiO_x content. Compared to the $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3$ ternary system shown in Fig. 4, a new liquid phase (called region 2) has formed with the Ti_3O_5 content ranged from 40 to 90 mass pct. The compositions of inclusions in sample B2 and C2 were mainly located in the liquid phase and perovskite region close to the low-melting-point region 1. However, the compositions of inclusions in sample A2 with low calcium content were mainly located close to the liquid phase of region 2. The calcium content and basicity of slag in sample A2 were lower than B2 and C2. It can be concluded that calcium treatment with different calcium

content would modify the inclusions to be different liquid phases (region 1 and region 2). At the end of LF, the inclusions in sample C3 with higher calcium content were mainly located in liquid oxide phase and perovskite region. The high basic slag and high calcium content in Ti-bearing molten steel might easily lead to the formation of calcium titanates. Moreover, the alumina distribution of inclusions in sample A3 and B3 increased at the end of LF, as shown in Figs. 4 and 5. The Al_2O_3 contents of slags in sample A3 and B3 were higher than that of sample C3, which might contribute to the increase of Al_2O_3 distribution of inclusions in steel.^{25,63}

The size distribution of inclusions in the samples was counted, as shown in Fig. 6. After the aluminum addition in VOD, the largest number density of inclusions bigger than $4 \mu\text{m}$ is 2.38 N/mm^2 in sample B1 which has

Fig. 6. Size distribution of inclusions in all samples.

Fig. 5. Composition distributions (mass fraction) of inclusions in $\text{CaO}-\text{Al}_2\text{O}_3-\text{Ti}_3\text{O}_5$ phase diagrams. Solid lines represent the boundary line of different phases at 1873 K under the oxygen partial pressure of $P_{\text{O}_2}=10^{-12}$ atm.

the highest aluminum content (540 ppm). And the largest number density of inclusions less than $4\ \mu\text{m}$ is $9.64\ \text{N/mm}^2$ in sample A1 which has the lowest aluminum content (37 ppm). After Ti–Fe wire addition, the number of inclusions in sample A2 with lowest aluminum and titanium content was the least ($5.92\ \text{N/mm}^2$). With the floatation and removal of oxide inclusions in LF, the number density of inclusions in sample A3 and B3 relatively decreased. However, due to the high calcium content and high basic slag in sample C3 calcium titanates might be formed to increase the number of inclusions.

3.2. Thermodynamic Calculation of Inclusion Formation

Spinel inclusions were formed in VOD after the addition

of aluminum, as shown in Fig. 2(A). Some works have been done to show that spinel inclusions tended to accumulate on the inner wall of submerged entry nozzle (SEN) during continuous casting, which could result in the clogging of SEN.^{7,15,28,52,64} Okuyama *et al.*⁵⁸ have experimentally proved that the metal-inclusion reaction is sufficiently faster than the slag-metal reaction. Thus, the local equilibrium between the molten steel and the inclusions in steel can be assumed to be valid. The phase stability diagrams of Al–Mg–O system in Fe-11Cr steel at 1 873 K were calculated with the aid of FactSage™ 7.0 software. As can be seen from the phase stability diagram in Fig. 7(a), there are three solid phases, viz. corundum (Al_2O_3), spinel ($\text{MgO}\cdot\text{Al}_2\text{O}_3$), and monoxide (MgO), with the content range of Mg from 0.1 ppm to 100 ppm and Al from 1 ppm to 1 wt%. And

Investigators	Ref.	Inclusion types		Steel compositions (mass%)
		MgO	MgO·Al ₂ O ₃	
Sakatal	15	●	○	Fe-17%Cr-12%Ni
Todoroki <i>et al.</i>	65	▲	△	Fe-23.5%Cr-22%Ni-6.23%Mo
Todoroki <i>et al.</i>	66		◇	Fe-18%Cr-8%Ni
Bi <i>et al.</i>	67	■	□	Fe-23%Cr-19%Ni
Okuyama <i>et al.</i>	58		▽	Fe-16%Cr
Park <i>et al.</i>	68		◁	Fe-16%Cr
Present work			⬡	Fe-11%Cr

Fig. 7. Calculated oxide stability diagrams of Al–Mg–O system with iso-oxygen contours in Fe-11Cr (a), Fe-17Cr-12Ni (b), Fe-23.5Cr-22Ni-6.23Mo (c), Fe-18Cr-8Ni (d), Fe-23Cr-19Ni (e), and Fe-16Cr (f) steels at 1 873 K.

the boundary lines of each solid phase were evaluated by using [O] ppm as a parameter. The present experimental results were marked in Fig. 7(a). These were positioned at the spinel phase, which agrees well with the observed inclusions in Fig. 2(A). The phase stability diagrams of Al–Mg–O system in Fe-17Cr-12Ni, Fe-23.5Cr-22Ni-6.23Mo, Fe-18Cr-8Ni, Fe-23Cr-19Ni, and Fe-16Cr steels at 1 873 K were also calculated, as shown in Fig. 7. The inclusions observed in the literature of stainless steel are also shown for comparison.^{15,58,65–68)} It can be seen that most of the data of different researchers were in accordance with the phase diagrams. However, some MgO inclusions observed by Todoroki *et al.*⁶⁵⁾ were located in spinel phase, as shown in Fig. 7(c). Most of the MgO inclusions shown in their research consisted of a MgO core embedded in a CaO–Al₂O₃ liquid matrix. It indicated that MgO was formed at the beginning and CaO–Al₂O₃ was formed later, which means that MgO in their research might be formed in a non-equilibrium state. In addition, majority of data of Park *et al.*⁶⁸⁾ were positioned at the MgO phase. They have pointed out that most of the spinel inclusions nearly saturated by MgO were observed in the steel melts equilibrated with the slags doubly saturated by MgO and MgAl₂O₄, which might significantly increase the content of Mg in steel and make the experimental data out of spinel phase. The composition of Mg (several ppm) in stainless steel was hard to decrease due to the refractory containing MgO, which made the spinel phase stable irrespective of Al content. However, several ppm Ca in molten steel can significantly decrease the stability of spinel. The stability diagrams of Mg–Al–O phase with 1 ppm and 5 ppm Ca contents in Fe-11Cr steel at 1 873 K were calculated, as shown in Fig. 8. There are three oxide phases, viz. monoxide (MgO), spinel (MgO·Al₂O₃), and liquid oxide. With 1 ppm Ca in molten steel, solid alumina phase in Fig. 8(a) was changed to liquid calcium aluminate phase, and the area of spinel phase was obviously reduced. When the calcium content increased to 5 ppm in molten steel, the area of spinel phase was further reduced. It can be seen that increasing the calcium content in molten steel could significantly expand the area of liquid oxide and decrease the area of spinel phase. At the same time, the area of MgO phase was almost unchanged with different calcium content. These indicated that Ca treatment can significantly modify the aluminate and spinel to form liquid oxide. However, MgO was hard to be modified by the addition of Ca. The similar results were also reported by Park *et al.*⁶⁹⁾ for stainless steel (Fe-18wt%Cr-8wt%Ni), Kang *et al.*⁷⁰⁾ for tool steel (Fe-5wt%Cr-1wt%Mo-1wt%V) and Itoh *et al.*²⁰⁾ for liquid iron. They concluded that several ppm Ca can strongly reduce the stability of spinel and modify the solid alumina to form liquid calcium aluminate. The experimental results were marked in Fig. 8(b). Most of the steel compositions were located in the liquid oxide phase. Since the diffusion in solid oxide was much slower than in liquid steel and liquid oxide, the formation rate of CaO–Al₂O₃ and CaO–Al₂O₃–MgO mainly depended on the diffusion in solid oxide, which was much slow.⁷¹⁾ Thus, solid inclusions with high Al₂O₃ contents were observed in the steel samples with more than 5 ppm Ca before calcium treatment. More calcium was added during calcium treatment to promote the modification. Yoshioka *et al.*⁷²⁾ have

investigated the evolution of inclusion compositions during the secondary refining process, and found newly generated inclusions during refining process. They pointed out that the inclusion compositions were determined by equilibrium state, removal and generation of inclusions. Some inclusions containing MgO–Al₂O₃ were still found in the steel samples at the end of LF refining process, which could be considered to be newly generated. Liquid oxide inclusions were the most stable state as shown in Fig. 8, which would promote to modify the solid inclusions to be liquid oxide. Based on the phase stability diagrams in Figs. 7 and 8, the following measures can be used to decrease the amount of spinel inclusions formed in 11wt%Cr steel. First, increasing the Mg content to more than 10 ppm and reducing the Al content in molten steel can reduce the formation of spinel. Second, Ca can be added to the molten stainless steel containing low Mg content to modify the solid spinel inclusions to be liquid oxide inclusions.

Before calcium addition in LF, CaO–MgO–Al₂O₃ inclusions were observed in steel samples at the end of VOD, as shown in Fig. 2(A). The highly basic slag might lead to change the morphology and composition of MgO–Al₂O₃ inclusions to be spherical inclusions containing CaO, which have been reported by Park *et al.*⁶⁸⁾ and Jiang *et al.*²⁵⁾ As shown in Table 2, basicity of slag was high, with CaO and SiO₂ in scope of 50.8–54.91 wt% and 9.32–11.65 wt% respectively. With high Al content in molten steel and high CaO content in slag, Ca could be reduced from slag to molten steel by reaction (1). When Ca content in molten steel increased, the formed MgO–Al₂O₃ inclusions were unstable and would be transferred into CaO–MgO–Al₂O₃ inclusions with low melting point, as shown in Fig. 4.

After the addition of titanium in LF, titanium oxide inclusions were formed, as shown in Fig. 2(B). In order to investigate the evolution mechanism of Al–Ti–O complex inclusions, the phase stability diagrams of Al–Ti–O system in 11wt%Cr steel at 1 873 K were calculated with the aid of FactSageTM 7.0 software. As can be seen from the phase stability diagram in Fig. 9, there are four oxide phases, viz. Al₂O₃, Ti₂O₃, Ti₃O₅, and Al₂O₃–TiO_x, 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 by using [O] ppm as a parameter. It can be seen from Fig. 9, the equilibrium titanium oxide stable phase was Ti₂O₃ with the titanium content ranging from 0.44 to 1 wt%, and Ti₃O₅ with the titanium content less than 0.44 wt% in 11wt%Cr steel at 1 873 K. The critical titanium content in 11wt%Cr molten steel at which both Ti₃O₅ and Ti₂O₃ coexist was 0.44 wt% at 1 873 K. It is also clear that it was important to appropriately control aluminum content in molten steel before the addition of titanium. When the aluminum content was too low, titanium would be oxidized to form too many titanium oxide inclusions; when the aluminum content was too high, the amounts of inclusions containing Al₂O₃ would be increased. The aluminum content and titanium content in steel specimens taken after titanium addition in LF were marked in Fig. 9. These points were almost located in Al₂O₃–TiO_x stable phase, which indicated that the aluminum content and titanium content were within

Fig. 8. Calculated oxide stability diagrams of Al-Mg-O system with iso-oxygen contours in 11wt%Cr-1 ppm Ca steel (a) and 11wt%Cr-5 ppm Ca steel (b) at 1 873 K.

Fig. 9. Calculated oxide stability diagrams of Al-Ti-O system with iso-oxygen contours in 11wt%Cr steel at 1 873 K. Solid circles are experimental points (AT: $\text{Al}_2\text{O}_3\text{-TiO}_x$).

a reasonable range. After the addition of titanium, there were also mainly inclusions containing $\text{Al}_2\text{O}_3\text{-TiO}_x$ in steel samples, as shown in Figs. 2(B) and 2(C). It was difficult to decrease the titanium content to make the points located in the liquid area, because it needs enough titanium to bind the soluble nitrogen or soluble carbon in the steel. In order to get a high titanium yield, aluminum should be added enough to deoxidize. Decreasing the formation of solid inclusions is limited by adjusting the titanium content or aluminum content in steel. Thus, the effect of calcium content in steel samples on the influence of $\text{Al}_2\text{O}_3\text{-TiO}_x$ inclusions would be discussed below.

As mentioned above in Fig. 5, solid phases in Al-Mg-O system were reduced with Ca addition. Therefore, in order to investigate the effect of calcium addition on the formation of inclusions in Al-killed Ti-bearing 11wt%Cr steel, the equilibrium formations of inclusions with different titanium contents in 11wt%Cr steel containing 200 ppm Al and 50 ppm O with calcium treatment were calculated by using FactSageTM 7.0 software, as shown in Fig. 10. When the titanium content in steel is 0%, the transformed sequence of oxide inclusions is Al_2O_3 , $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$ (CA6), $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ (CA2), and liquid oxide phase with the content range of Ca

from 0.5 ppm to 30 ppm. After the addition of 0.01% titanium content in steel, solid calcium titanates were formed with the increase of calcium content to 23 ppm, and the amount of liquid oxide phase was reduced. If the titanium content in steel increased to 0.04%, the liquid oxide phase and solid calcium titanates were formed earlier. Besides, the $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ (CA2) disappeared. As the content of titanium in steel increased from 0.04% to 0.25%, there were only the liquid oxide phase and the solid calcium titanates phase. With the increasing of calcium content, the amount of liquid oxide phase increased and then decreased, and the corresponding solid calcium titanates phase gradually increased after its formation. The calcium addition should be more than 22 ppm to modify all the alumina inclusions in molten steel containing 200 ppm aluminum to liquid oxide inclusions, as shown in Fig. 10(a). And a small amount of calcium in Al-killed Ti-bearing steel could modify the $\text{Al}_2\text{O}_3\text{-TiO}_x$ inclusion into liquid oxide inclusions, as shown in Fig. 10(d). However, more than 18 ppm of calcium content might lead to the formation of solid calcium titanates in molten steel with 0.25% titanium. As can be seen in Figs. 2 and 5, some high CaO-TiO_x content inclusions were formed with titanium addition after calcium treatment. Thus, the calcium content in molten steel should be controlled reasonably before the addition of titanium wire. What is more, with high Ti content in molten steel and high CaO content in slag, Ca could be reduced from slag to molten steel by reaction (2). The calcium reduced from high basic slag might also lead to the formation of CaO-TiO_x inclusion, as shown in Figs. 2(C) and 5. The calcium contents of sample A3, B3 and C3 were marked in Fig. 10(d). It can be seen that the high calcium contents in steel after titanium addition might lead to the formation of solid calcium titanates. Thus, in the present calcium content level, lower calcium content after titanium addition was beneficial to the formation of liquid oxide phase. For 11 Cr stainless steel with 0.25% titanium content, the compositions of inclusions modified by calcium treatment should be located in liquid phase close to Ti_3O_5 in $\text{CaO-Al}_2\text{O}_3\text{-Ti}_3\text{O}_5$ phase diagram, as shown in Fig. 5 of region 2. Otherwise, if a lot of calcium wire is added to form the liquid oxide located in liquid phase close to the $\text{CaO-Al}_2\text{O}_3$ binary region, too much solid calcium titanates will be formed. The formation of calcium titanates might lead to the decrease of titanium yield and the clogging of

Fig. 10. Equilibrium formations of inclusions during calcium treatment at 1 873 K for steel of composition: Fe-11Cr-Ti-0.02Al-0.005O-Ca in mass pct: Ti=0%, Ti=0.01%, Ti=0.04%, Ti=0.25% (CA2: $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, CA6: $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, CT: Calcium-titanites).

the submerged entry nozzle.^{7,56)}

$$x[\text{Ti}] + x(\text{CaO}) = x[\text{Ca}] + (\text{TiO}_x) \dots\dots\dots (2)$$

4. Conclusions

The objective of the study was to investigate the evolution mechanism of nonmetallic inclusions in Al-killed, Ti-bearing 11Cr stainless steel with Ca treatment. According to the analysis of inclusion characteristics and thermodynamic calculation, the following conclusions were drawn.

(1) After the addition of Al, there were mainly alumina-rich inclusions in steel. With the titanium addition after calcium treatment, three types of inclusions were formed: irregular $\text{MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion, spherical $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_x$ inclusion, and irregular dual phase Ti-containing inclusion. At the end of LF refining process, solid calcium titanates inclusions were formed due to the high calcium content in steel.

(2) Both the characteristics of inclusions and thermodynamic calculation indicated that the compositions of inclusions in steel specimens after the addition of titanium were mostly located in $\text{Al}_2\text{O}_3\text{-TiO}_x$ stable phase. Calcium could strongly reduce the stability of spinel and modify the solid alumina to form liquid calcium aluminate. And a small amount of calcium in Al-killed Ti-bearing 11Cr stainless steel could effectively modify the $\text{Al}_2\text{O}_3\text{-TiO}_x$ inclusions into liquid oxide inclusions.

(3) High calcium contents in steel after titanium addition would lead to the formation of solid calcium titanates. The formation of calcium titanates might lead to the decrease of titanium yield and the clogging of the submerged entry

nozzle. Therefore, it was necessary to accurately control the calcium content in molten steel before titanium addition.

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REFERENCES

- 1) M. B. Leban and R. Tisu: *Eng. Fail. Anal.*, **33** (2013), 430.
- 2) J. L. Cavazos, I. Gomez and M. P. Guerrero-Mata: *Mater. Sci. Technol.*, **27** (2011), 530.
- 3) H. Fujimura, S. Tsuge, Y. Komizo and T. Nishizawa: *Tetsu-to-Hagane*, **87** (2001), 707.
- 4) T. Koseki and H. Inoue: *J. Jpn. Inst. Met.*, **65** (2001), 644.
- 5) S. Basu, S. K. Choudhary and N. U. Girase: *ISIJ Int.*, **44** (2004), 1653.
- 6) C. W. Seo, S. H. Kim, S. K. Jo, M. O. Suk and S. M. Byun: *Metall. Mater. Trans. B*, **41** (2010), 790.
- 7) G. Qian and G. Cheng: Proc. Iron & Steel Technology Conf. and Exposition (AISTech 2014), Vol. 2, AIST, Warrendale, PA, (2014), 1823.
- 8) D. C. Park, I. H. Jung, P. C. H. Rhee and H. G. Lee: *ISIJ Int.*, **44** (2004), 1669.
- 9) S. B. Lee, J. H. Choi, H. G. Lee, P. C. H. Rhee and S. M. Jung: *Metall. Mater. Trans. B*, **36** (2005), 414.
- 10) M. A. Van Ende, M. Guo, J. Proost, B. Blanpain and P. Wollants: *ISIJ Int.*, **51** (2011), 27.
- 11) J. J. Pak, J. O. Jo, S. I. Kim, W. Y. Kim, T. I. Chung, S. M. Seo, J. H. Park and D. S. Kim: *ISIJ Int.*, **47** (2007), 16.
- 12) L. Zhang and B. G. Thomas: *ISIJ Int.*, **43** (2003), 271.
- 13) J. H. Park and D. S. Kim: *Metall. Mater. Trans. B*, **36** (2005), 495.
- 14) J. H. Park: *Mater. Sci. Eng. A*, **472** (2008), 43.
- 15) K. Sakata: *ISIJ Int.*, **46** (2006), 1795.
- 16) H. Todoroki and Y. Kobayashi: Proc. Asia Steel 2009 Int. Conf., KIMM, Busan, (2009), CD-ROM.

- 17) T. Ikemoto and K. Sawano: *Taikabutsu*, **46** (1994), 179.
- 18) S. Ogibayashi: *Taikabutsu*, **46** (1994), 166.
- 19) B. Harkness and D. Dyson: International Metallurgical Technology Trade Fair with Cong. (METEC Cong. 94) and 2nd European Continuous Casting Conf., VDEh, Düsseldorf, (1994), 70.
- 20) H. Itoh, M. Hino and S. Ban-ya: *Metall. Mater. Trans. B*, **28** (1997), 953.
- 21) G. Ye, P. Jönsson and T. Lund: *ISIJ Int.*, **36** (1996), S105.
- 22) J. H. Park, S. B. Lee and D. S. Kim: *Metall. Mater. Trans. B*, **36** (2005), 67.
- 23) S. Yang, Q. Wang, L. Zhang, J. Li and K. Peaslee: *Metall. Mater. Trans. B*, **43** (2012), 731.
- 24) S. F. Yang, J. S. Li, X. Z. Gao and Y. Ma: *Metall. Min. Ind.*, **6** (2014), 66.
- 25) M. Jiang, X. Wang, B. Chen and W. Wang: *ISIJ Int.*, **50** (2010), 95.
- 26) Y. Gao and K. Sorimachi: *ISIJ Int.*, **33** (1993), 291.
- 27) C. van der Eijk, Ø. Grong and J. Walmsley: *Mater. Sci. Technol.*, **16** (2000), 55.
- 28) S. Basu, S. K. Choudhary and N. U. Girase: *ISIJ Int.*, **44** (2004), 1653.
- 29) D. C. Park, I. H. Jung, P. C. H. Rhee and H. G. Lee: *ISIJ Int.*, **44** (2004), 1669.
- 30) C. Wang, N. T. Nuhfer and S. Sridhar: *Metall. Mater. Trans. B*, **40** (2009), 1005.
- 31) C. Wang, N. T. Nuhfer and S. Sridhar: *Metall. Mater. Trans. B*, **40** (2009), 1022.
- 32) C. Wang, N. T. Nuhfer and S. Sridhar: *Metall. Mater. Trans. B*, **41** (2010), 1084.
- 33) C. Wang, N. Verma, Y. Kwon, W. Tiekink, N. Kikuchi and S. Sridhar: *ISIJ Int.*, **51** (2011), 375.
- 34) H. Matsuura, C. Wang, G. Wen and S. Sridhar: *ISIJ Int.*, **47** (2007), 1265.
- 35) X. Yin, Y. Sun, Y. Yang, X. Bai, M. Barati and A. Mclean: *Metall. Mater. Trans. B*, **47** (2016), 3274.
- 36) W. Y. Kim, J. O. Jo, C. O. Lee, D. S. Kim and J. J. Pak: *ISIJ Int.*, **48** (2008), 17.
- 37) I. H. Jung, G. Eriksson, P. Wu and A. Pelton: *ISIJ Int.*, **49** (2009), 1290.
- 38) M. Wang, Y. Bao, H. Cui, H. Wu and W. Wu: *ISIJ Int.*, **50** (2010), 1606.
- 39) M. A. Van Ende, M. Guo, R. Dekkers, M. Burty, J. V. Dyck, P. T. Jones, B. Blanpain and P. Wollants: *ISIJ Int.*, **49** (2009), 1133.
- 40) D. Wang, M. Jiang, H. Matsuura and F. Tsukihashi: *Steel Res. Int.*, **85** (2014), 16.
- 41) W. Zheng, Z. Wu, G. Li, Z. Zhang and C. Zhu: *ISIJ Int.*, **54** (2014), 1755.
- 42) Y. Ren, Y. Zhang and L. Zhang: *Ironmaking Steelmaking*, **44** (2017), 497.
- 43) T. Zhang, C. Liu, J. Qiu, X. Li and M. Jiang: *ISIJ Int.*, **57** (2017), 314.
- 44) J. W. Kim, S. K. Kim, D. S. Kim, Y. D. Lee and P. K. Yang: *ISIJ Int.*, **36** (1996), S140.
- 45) D. Kruger and A. Garbers-Craig: *Metall. Mater. Trans. B*, **48** (2017), 1514.
- 46) C. W. Seo, S. H. Kim, S. K. Jo, M. O. Suk and S. M. Byun: *Metall. Mater. Trans. B*, **41** (2010), 790.
- 47) H. Zheng and W. Chen: *J. Univ. Sci. Technol. Beijing, Miner. Metall. Mater.*, **13** (2006), 16.
- 48) Z. Wu, W. Zheng, G. Li, H. Matsuura and F. Tsukihashi: *Metall. Mater. Trans. B*, **46** (2015), 1226.
- 49) T. Zhang, C. Liu and M. Jiang: *Metall. Mater. Trans. B*, **47** (2016), 2253.
- 50) Y. Ren, L. Zhang, W. Yang and H. Duan: *Metall. Mater. Trans. B*, **45** (2014), 2057.
- 51) Z. Hu, G. Yang, M. Jiang, W. Wang and X. Wang: *Int. J. Miner. Metall. Mater.*, **34** (2012), 1123.
- 52) H. Ono, K. Nakajima, S. Agawa, T. Ibata, R. Maruo and T. Usui: *Steel Res. Int.*, **86** (2015), 241.
- 53) H. Fujimura, S. Tsuge, Y. Komizo and T. Nishizawa: *Tetsu-to-Hagané*, **87** (2001), 707.
- 54) S. C. Park, I. H. Jung, K. S. Oh and H. G. Lee: *ISIJ Int.*, **44** (2004), 1016.
- 55) M. Li, H. Matsuura and F. Tsukihashi: *Metall. Mater. Trans. B*, **48** (2017), 1915.
- 56) H. Zheng, W. Chen and Y. Hu: Proc. Iron & Steel Technology Conf. (AISTech 2004), Vol. 2, AIST, Warrendale, PA, (2004), 397.
- 57) T. Nishi and K. Shimme: *Tetsu-to-Hagané*, **84** (1998), 837.
- 58) G. Okuyama, K. Yamaguchi, S. Takeuchi and K. Sorimachi: *ISIJ Int.*, **40** (2000), 121.
- 59) J. Z. Li, M. Jiang, X. F. He, W. Sun and X. H. Wang: *Metall. Mater. Trans. B*, **47** (2016), 2386.
- 60) W. Y. Cha, T. Nagasaka, T. Miki, Y. Sasaki and M. Hino: *ISIJ Int.*, **46** (2006), 996.
- 61) W. Y. Cha, T. Miki, Y. Sasaki and M. Hino: *ISIJ Int.*, **48** (2008), 729.
- 62) S. H. Seok, T. Miki and M. Hino: *ISIJ Int.*, **51** (2011), 566.
- 63) J. Guo, S. Cheng and Z. Cheng: *ISIJ Int.*, **53** (2013), 2142.
- 64) R. C. Nunnington and N. Sutcliffe: 59th Electric Furnace Conf. Proc., ISS, Warrendale, PA, (2001), 361.
- 65) H. Todoroki, F. Kiriara, Y. Kanbe and Y. Miyazaki: *Tetsu-to-Hagané*, **100** (2014), 539.
- 66) H. Todoroki and K. Mizuno: *ISIJ Int.*, **44** (2004), 1350.
- 67) Y. Bi, A. V. Karasev and P. G. Jönsson: *ISIJ Int.*, **53** (2013), 2099.
- 68) J. H. Park and D. S. Kim: *Metall. Mater. Trans. B*, **36** (2005), 495.
- 69) J. H. Park and H. Todoroki: *ISIJ Int.*, **50** (2010), 1333.
- 70) Y. J. Kang, F. Li, K. Morita and D. Sichen: *Steel Res. Int.*, **77** (2006), 785.
- 71) W. Yang, L. Zhang, X. Wang, Y. Ren, X. Liu and Q. Shan: *ISIJ Int.*, **53** (2013), 1401.
- 72) T. Yoshioka, K. Nakahata, T. Kawamura and Y. Ohba: *ISIJ Int.*, **56** (2016), 1973.