#### **ORIGINAL PAPER**



# **Infuence of refning process and utilization of diferent slags on inclusions, titanium yield and total oxygen content of Ti‑stabilized 321 stainless steel**

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#### **Abstract**

Ti-stabilized 321 stainless steel was prepared using an electric arc furnace, argon oxygen decarburization (AOD) furnace, ladle furnace (LF), and continuous casting processes. In addition, the effect of refining process and utilization of different slags on the evolution of inclusions, titanium yield, and oxygen content was systematically investigated by experimental and thermodynamic analysis. The results reveal that the total oxygen content (TO) and inclusion density decreased during the refining process. The spherical CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO inclusions existed in the 321 stainless steel after the AOD process. Moreover, prior to the Ti addition, the spherical CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub> inclusions were observed during LF refining process. However, Ti addition resulted in multilayer CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions. Two different samples were prepared by conventional CaO–Al<sub>2</sub>O<sub>3</sub>-based slag (Heat-1) and TiO<sub>2</sub>-rich CaO–Al<sub>2</sub>O<sub>3</sub>-based slag (Heat-2). The statistical analysis revealed that the density of inclusions and the TiO<sub>x</sub> content in CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions found in Heat-2 sample are much lower than those in the Heat-1 sample. Furthermore, the TO content and Ti yield during the LF refning process were controlled by using TiO<sub>2</sub>-rich calcium aluminate synthetic slag. These results were consistent with the ion–molecule coexistence theory and FactSage™7.2 software calculations. When TiO<sub>2</sub>-rich CaO–Al<sub>2</sub>O<sub>3</sub>-based slag was used, the TiO<sub>2</sub> activity of the slag increased, and the equilibrium oxygen content signifcantly decreased from the AOD to LF processes. Therefore, the higher TiO<sub>2</sub> activity of slag and lower equilibrium oxygen content suppressed the undesirable reactions between Ti and O.

**Keywords** 321 Austenitic stainless steel · Oxygen content · Inclusion · TiO<sub>2</sub>-rich CaO–Al<sub>2</sub>O<sub>3</sub>-based slag · Ladle furnace (LF) refning process · Ion–molecule coexistence theory

## **1 Introduction**

As a Ti-stabilized austenitic stainless steel (SS), 321 SS renders a set of unique advantages, such as superior high-temperature strength, adequate creep resistance, and excellent oxidation and corrosion resistance, compared to 304 stainless steel. Hence, 321 SS is widely used in heat exchangers, high-pressure pipes, engine turbines, aerospace exhaust manifolds, and nuclear industry [[1–](#page-8-0)[5](#page-8-1)]. Nevertheless, as a Ti-stabilized steel, 321 steel has several casting

 $\boxtimes$  Guo-guang Cheng chengguoguang@metall.ustb.edu.cn and operational challenges such as low Ti yield, submerged entry nozzle (SEN) clogging during casting, deterioration of mold fux, defects on slab surface and line defects, which are quite similar to the issue with other Ti-stabilized stainless steels  $[6-11]$  $[6-11]$  $[6-11]$ .

Therefore, different research groups aimed to understand and use various strategies to resolve these issues. For instance, Yin et al. [[12\]](#page-8-4) reported the formation of inclusions in Ti-stabilized 17Cr austenitic SS. The results revealed that tapping and Ti wire feeding result in pure TiN particles and complex TiN-containing inclusions, with  $Al_2O_3-MgO-TiO<sub>x</sub>$ core, at a Ti content of 0.307 wt.%. Qian et al. [[13\]](#page-8-5) reported that the oxidation rate of Ti initially decreased with increasing  $TiO<sub>2</sub>$  content in slag and reached a minimum level at  $TiO<sub>2</sub>$  content of 8 wt.% in the slag, followed by a gradual increase. Kang et al.  $[14, 15]$  $[14, 15]$  $[14, 15]$  $[14, 15]$  $[14, 15]$  pointed out that  $Rb<sub>2</sub>O$  and  $Cs<sub>2</sub>O$  allow significant removal of TiN inclusions because of the ion compensation effect and supplementary free

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oxygen ions, whereas at the same time, the viscosity of the slag increased to retain the absorbed inclusions. Moreover, compared to the preexisting tundish flux compositions,  $K<sub>2</sub>O$  incorporation significantly improved the cleanliness of the as-quenched 321 stainless steel melts. Zheng and Chen [\[16](#page-8-8)] found the optimal composition for the formation of CaO–TiO<sub>2</sub>–MgO–Al<sub>2</sub>O<sub>3</sub> in 321 SS, exhibiting that the concentration of Ca, Ti, and Al should be higher than 0.001, 0.1, and 0.01 wt.%, respectively. Seo et al. [[17\]](#page-8-9) demonstrated that the Al deoxidation/Ca treatment/Ti alloying pattern of the ladle refning operation efectively reduces the spinel formation in Ti-stabilized steels and extends the life cycle of SEN nozzle. Lencina et al. [\[18](#page-8-10)] described the positive effect of TiO<sub>2</sub>-rich calcium aluminate flux in the formation of slags for 321 stainless steel. While previous reports have described the inclusions evolution of 321 stainless steel and some strategies to improve the cleanliness of the molten steel, the effect of different refining slags on the titanium yield, oxygen content, and inclusions during ladle furnace refning process has not yet been studied.

In this study, the titanium yield, the inclusions evolution, and oxygen content variation in 321 austenitic stainless steel under diferent refning slag conditions, produced by electric arc furnace (EAF), argon oxygen decarburization furnace (AOD), ladle furnace (LF), and continuous casting (CC) processes were systematically investigated. The role of  $TiO<sub>2</sub>$ -rich calcium aluminate synthetic slag on inclusions, titanium yield, and oxygen content was investigated by experimental analysis and thermodynamic calculations.

## **2 Experimental**

#### **2.1 Steel fabrication and sampling**

The 321 stainless steel was prepared by EAF-AOD-LF-CC process. First, the ferronickel, ferrochromium, and steel scrap were melted in an EAF, and subsequently the molten steel was poured into an AOD. After decarburization in the

AOD, the chromium oxide was reduced by adding ferrosilicon. Once the reduction was completed, the desulfurization process was conducted to obtain the target value of binary basicity ( $w_{\text{CaO}}/w_{\text{SiO}_2}$  = 2.50). Figure [1](#page-1-0) shows an illustration of the operation and sampling processes during the refning stage, where the time at which AOD was fnished was assumed as 0 min. The slag was tapped after the AOD process, and the ladle was hanged to the LF. Magnesia–calcium was used as the refractory material. The aluminum wires were fed into the molten steel to achieve the target value of 0.03 wt.%, followed by calcium treatment. Next, the refning slag was added for secondary refning, followed by titanium-alloying operation. Finally, the liquid steel was transported to the platform for continuous casting at the designated temperature and composition values. The industrial experiments involved diferent refning slags. For instance, Heat-1 used normal CaO– $\text{Al}_2\text{O}_3$  based slag, and Heat-2 utilized  $TiO<sub>2</sub>$ -rich calcium aluminate slag. The steel samples were taken after the AOD treatment, before titanium-alloying operation and after titanium-alloying operation during the LF refning process to analyze the steel composition and level of inclusions. Moreover, the slag samples were taken at the same time. Sample-A was collected after the AOD treatment, whereas LF1 and LF2 were collected before and after titanium-alloying operation during the LF refning process, respectively.

#### **2.2 Characterization**

The chemical composition of the steel samples  $(\phi 30$  mm × 10 mm) was determined by a direct reading spectrum. The C and S contents were analyzed using a C/S analyzer (CS-800, ELTRA, Haan, Germany). The cylindrical samples ( $\phi$ 5 mm × 5 mm) were machined to measure the total oxygen content using an O/N analyzer (EMGA-620 W, Horiba, Kyoto, Japan). The composition of the slags was analyzed by X-ray fuorescence spectrometry (ARL PERFORM'X, Thermo Fisher Scientifc, MA, USA).



<span id="page-1-0"></span>**Fig. 1** Illustration of operation and sampling processes during refning process

Heat	Stage	C	Si	Mn	P	S	Ni	Cr	Al	Ti	N
Heat-1	А	0.015	0.438	1.213	0.022	0.001	9.029	17.273	0.009	0.003	0.009
	LF1	0.020	0.568	1.234	0.022	0.001	9.136	17.334	0.028	0.004	0.012
	LF2	0.026	0.593	1.221	0.022	0.001	9.104	17.197	0.024	0.291	0.012
Heat-2	А	0.014	0.491	1.234	0.028	0.001	9.019	17.300	0.009	0.002	0.007
	LF1	0.021	0.584	1.234	0.028	0.001	9.182	17.299	0.027	0.009	0.010
	LF <sub>2</sub>	0.027	0.605	1.218	0.028	0.001	9.210	17.278	0.026	0.272	0.011

<span id="page-2-0"></span>**Table 1** Chemical composition of 321 stainless steel at diferent stages (wt.%)

<span id="page-2-1"></span>**Table 2** Chemical composition of slag at diferent stages (wt.%)

Heat	Stage	CaO	CaF <sub>2</sub>	MgO	$Al_2O_3$	SiO <sub>2</sub>	TiO <sub>2</sub>	TFe	MnO	$Cr_2O_3$	S
Heat-1	A	57.67	9.38	2.67	6.40	22.45	0.30	0.40	0.06	0.50	0.17
	LF1	55.81	7.41	3.35	15.94	16.73	0.35	0.12	0.05	0.15	0.09
	LF2	55.64	6.98	3.46	14.87	16.07	2.49	0.15	0.03	0.21	0.10
Heat-2	A	52.40	12.67	2.86	6.33	18.56	0.26	3.05	0.16	3.39	0.32
	LF1	60.87	6.86	3.45	17.45	7.95	3.05	0.15	0.05	0.10	0.07
	LF2	59.99	6.39	4.57	16.92	8.41	3.29	0.17	0.04	0.15	0.07

Moreover, steel samples (10 mm  $\times$  10 mm  $\times$  10 mm) were machined to analyze the morphology and composition of the inclusions. The surface was ground by using SiC paper (1200 grit), followed by polishing with diamond paste. The chemical composition of the inclusions was determined by energy-dispersive spectroscopy (EDS, X-Max 80, Oxford Instruments, High Wycombe, UK) coupled to scanning electron microscopy (SEM, Merlin Compact, Zeiss, Gottingen, Germany). For each sample, ~ 30 inclusions were selected for characterization. In addition, quantitative analysis of inclusions size was performed by using INCA software (Inca Energy 250, Oxford Instruments, High Wycombe, UK) of the scanning electron microscope. A sample size larger than1 µm was used to enhance the accuracy of EDS analysis of the inclusions. The scanning area was  $5.48 \times 10^7 \,\mathrm{\upmu m^2}$ .

#### **3 Results**

## **3.1 Composition of molten steel and slag**

The composition of diferent steels and slags is listed in Tables [1](#page-2-0) and [2](#page-2-1), respectively. Heat-1 utilized normal CaO- $Al_2O_3$ -based slag and both (CaO/SiO<sub>2</sub>) and  $Al_2O_3$  contents in the slag increased from A to LF1, whereas the  $SiO<sub>2</sub>$  content decreased. After feeding Ti wire in the LF process, the TiO<sub>2</sub> content increased from 0.35 to 2.49 wt.%, showing the oxidation of Ti in the slag. In contrast, Heat-2 utilized  $TiO<sub>2</sub>$ -rich calcium aluminate slag. Hence, both (CaO/SiO<sub>2</sub>) and  $Al_2O_3$  content in the slag increased from A to LF1,



<span id="page-2-2"></span>**Fig. 2** Total oxygen content in 321 stainless steel at diferent stages of steelmaking process

whereas compared to Heat-1, the total iron (TFe), MnO, and  $Cr_2O_3$  contents significantly decreased. The amount of  $TiO<sub>2</sub>$  in slag increased with the addition of Ti into molten steel; however, the variation is extremely negligible.

#### **3.2 Oxygen content in 321 stainless steel**

Figure [2](#page-2-2) shows the TO evolution for Heat-1 and Heat-2 samples at diferent stages, indicating that the total oxygen content in both samples decreased during the steelmaking process. The total oxygen content in Heat-1 and Heat-2 after the AOD process was  $53 \times 10^{-6}$  and  $76 \times 10^{-6}$ , respectively. However, the total oxygen content in the molten steel efectively reduced after secondary refning. The total oxygen content of Heat-2 decreased by  $35 \times 10^{-6}$ , which is three times as much as that of the Heat-1, prepared using normal  $CaO-Al<sub>2</sub>O<sub>3</sub>$ -based slag. During the refining process, the inclusions in molten steel constantly foated into the slag under argon stirring. Since these small inclusions grew, foated, and adsorbed by the slag after collision with each other, the total oxygen content of Heat-1 and Heat-2 samples decreased to  $38 \times 10^{-6}$  and  $35 \times 10^{-6}$ , respectively.

#### **3.3 Titanium yield during LF refning process**

Figure [3](#page-3-0) shows the Ti yield of Heat-1 and Heat-2 samples during the refning process, indicating that Heat-2 samples exhibited higher Ti yield than Heat-1 samples, and this can be ascribed to the utilization of  $TiO<sub>2</sub>-rich CaO–Al<sub>2</sub>O<sub>3</sub>$ -based slag instead of normal CaO– $\text{Al}_2\text{O}_3$ -based slag. In general, the recovery of Heat-2 was improved by 9.0%.

#### **3.4 Inclusion types at diferent stages**

The morphology and composition of the inclusions in molten steel during the refning process were characterized, as shown in Fig. [4](#page-4-0). The elemental mapping of the typical inclusions in molten steel is shown in Fig. [5,](#page-5-0) clearly indicating that the spherical CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO inclusions, ranging from several to tens of microns, exist in 321 stainless steel after the AOD process. Moreover, these inclusions contain a small amount of magnesium and aluminum. The composition of the inclusions after the AOD (size larger than  $10 \mu m$ ) was almost the same as the slag composition. The CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO inclusions which are smaller than 10 μm mainly originated from the oxidation reaction with Ca, Al, Mg, and Si. The Ca mainly derived from the metalslag reaction and the metal-refractory reaction. The Mg content in the steel originated from slag and refractory material.



<span id="page-3-0"></span>

Hence, the inclusion type was  $CaO-Al<sub>2</sub>O<sub>3</sub>–MgO-SiO<sub>2</sub>$ spherical inclusion before titanium-alloying operation during the LF process. In addition, the  $Al_2O_3$  content of these inclusions was higher than that of the AOD process, whereas some parts of inclusions exhibited Mg-rich regions. However, the inclusions changed to multilayer CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions after the titanium addition, as shown in Fig. [4](#page-4-0)c, f, where the black-colored areas correspond to higher  $\text{Al}_2\text{O}_3$  and MgO contents, whereas the gray-colored regions represent CaO–Al<sub>2</sub>O<sub>3</sub>–TiO<sub>x</sub>. Notably, MgO has been non-uniformly distributed, where a few inclusions exhibited lower content of MgO and others showed MgO enrichment in the local regions. In general, the TiO*<sup>x</sup>* content of inclusions in Heat-2 samples was lower than that of Heat-1 samples.

#### **3.5 Composition of inclusions at diferent stages**

To elucidate the evolution of inclusions at diferent stages, the inclusions were plotted on the ternary phase diagram, as shown in Fig. [6.](#page-6-0) After the AOD process, the inclusions were almost the same as for Heat-1 and Heat-2 samples. Before the Ti addition during the LF refning process, the total  $A1_2O_3$  and MgO content of inclusions significantly increased; however, the CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub> inclusions transformed into  $CaO-Al_2O_3-MgO-TiO_x$  inclusions after the Ti addition. Moreover, the TiO*x* content in Heat-2 sample was lower than that of Heat-1 sample.

## **3.6 Inclusion size and number density at diferent stages**

The size distribution of inclusions, at diferent stages of the steelmaking process, of both Heat-1 and Heat-2 samples is presented in Fig. [7](#page-6-1). Both samples exhibited a dominant proportion of small-size inclusions ( $\leq 10 \text{ }\mu\text{m}$ ); however, the concentration of large-size inclusions ( $\geq 10 \,\mu$ m) decreased from A to LF2. After the Ti addition, the number density of small-size inclusions ( $\leq$ 5  $\mu$ m) significantly increased in both samples, and this phenomenon can be ascribed to the formation of the new inclusions. Overall, the concentration of inclusions in Heat-1 sample is lower than the Heat-2 sample after the AOD process. Before the Ti addition during the LF refning process, the inclusion concentration in Heat-2 samples signifcantly decreased compared to that in the LF1 stage of Heat-1 sample.

## **4 Discussion**

The formation mechanism of inclusions during 321 stainless steel refning process is schematically illustrated in Fig. 3 Ti yield of Heat-1 and Heat-2 samples during refining process Fig. [8](#page-6-2). The spherical CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO inclusions



<span id="page-4-0"></span>**Fig. 4** Morphology and composition of typically encountered inclusions in Heat-1 and Heat-2 samples after various stages of steelmaking process. **a** Heat-1-A; **b** Heat-1-LF1; **c** Heat-1-LF2; **d** Heat-2-A; **e** Heat-2-LF1; **f** Heat-2-LF2



<span id="page-5-0"></span>**Fig. 5** Elemental maps of typically encountered inclusions in Heat-1 and Heat-2 samples. **a** Heat-1-A; **b** Heat-1-LF1; **c** Heat-1-LF2; **d** Heat-2-A; **e** Heat-2-LF1; **f** Heat-2-LF2

exist in 321 stainless steel after the AOD process. Then, Ca treatment was carried out after the Al addition for deoxidation, resulting in spherical CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub> inclusions. Once lime, fluorite, and  $CaO-Al<sub>2</sub>O<sub>3</sub>$ -based refining slag were added for secondary refning, large-size inclusions  $(>10 \mu m)$  were adsorbed by the slag, and both the total oxygen content and inclusion density decreased during the LF refning process. After the Ti addition, the spherical inclusions changed into multilayer CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions.

Ti is a highly active element and rapidly oxidizes at steelmaking temperatures. Therefore, to optimize the refning process, the addition of Ti should be reduced because of its high cost and undesirable oxidation. Herein, a large diference existed in the total oxygen content, Ti yield, and composition of the inclusions of Heat-1 and Heat-2 samples after the Ti addition during the LF refning. Therefore, the utilization of diferent refning slags signifcantly afected the oxygen content, Ti yield, and inclusions during the LF refning process, as discussed in the following sections.

#### **4.1 TiO<sub>2</sub> activity of different slags**

The activity of various structural units in diferent slags was calculated by using the ion–molecule coexistence theory. The thermodynamic model, used to calculate the active mass concentrations of structural units or ion couples in CaO–CaF<sub>2</sub>–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>2</sub>–MnO–Cr<sub>2</sub>O<sub>3</sub> slags



<span id="page-6-0"></span>**Fig. 6** Compositional distribution of inclusions at diferent stages of steelmaking process. **a** AOD; **b** LF1; **c** LF2



<span id="page-6-1"></span>**Fig. 7** Size distribution of inclusions at diferent stages of steelmaking process

equilibrated with the molten steel, is based on the assumptions referring to Refs. [[19](#page-8-11), [20](#page-8-12)].

In addition to the five simple ions, i.e.,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ , F<sup>-</sup>, and O<sup>2-</sup>, and four simple molecules, i.e., SiO<sub>2</sub>, TiO<sub>2</sub>,  $Al_2O_3$ , and  $Cr_2O_3$ , several complex molecules also exist in CaO–CaF<sub>2</sub>–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>2</sub>–MnO–Cr<sub>2</sub>O<sub>3</sub> slag. Approximately, 34 diferent complex molecules were formed in the studied slags. The details of the calculation process are described elsewhere [\[19](#page-8-11), [20](#page-8-12)].

The TiO<sub>2</sub> activity of different slags in Heat-1 and Heat-2 samples at diferent stages was calculated by using MAT-LAB 7.0 software, and the results are shown in Fig. [9](#page-6-3). After the AOD process, the  $TiO<sub>2</sub>$  activity of different slags in



<span id="page-6-2"></span>**Fig. 8** Schematic illustration of formation mechanism of inclusions during 321 stainless steel refning process



<span id="page-6-3"></span>**Fig. 9** TiO<sub>2</sub> activity of Heat-1 and Heat-2 samples at different stages of steelmaking process

Heat-1 and Heat-2 samples remained the same. In Heat-1 sample, which utilizing the conventional CaO-Al<sub>2</sub>O<sub>3</sub>-based slag, TiO<sub>2</sub> activity exhibited a small change from A to LF1. However,  $TiO<sub>2</sub>$  activity significantly increased after the Ti addition. In Heat-2 sample, using TiO<sub>2</sub>-rich CaO–Al<sub>2</sub>O<sub>3</sub>based slag,  $TiO<sub>2</sub>$  activity changed significantly. For instance, the TiO<sub>2</sub> activity of slag increased from  $0.00003$  to  $0.00010$ from A to LF1 stage, and then attained a stable value. Qian et al. [[13\]](#page-8-5) reported that the rate-determining step of Ti oxidation during steelmaking is the mass transfer on the slag side, and the oxidation of Ti exhibits an opposite trend to the activity of TiO<sub>2</sub>. In the case of Heat-2 sample, TiO<sub>2</sub> activity of slag increased before the Ti addition and can suppress reactions ([1\)](#page-7-0) and [\(2](#page-7-1)). Hence, the  $TiO<sub>2</sub>$  content changed from 3.05 to 3.29 wt.%. During the LF refining process, the  $TiO<sub>2</sub>$ activity of slag in Heat-1 sample is 0.00003, indicating that Ti was rapidly oxidized and entered into the slag after the Ti addition.

$$
2(\text{Al}_2\text{O}_3) + 3 [\text{Ti}] = 3(\text{TiO}_2) + 4 [ \text{Al}]
$$
 (1)

$$
(SiO2) + [Ti] = (TiO2) + [Si].
$$
 (2)

## **4.2 Efect of refning slags on equilibrium oxygen content based on IMCT**

Herein, 321 stainless steel is deoxidized with aluminum, and the chemical reaction in liquid steel is given as:

$$
Al_2O_3 = 2[Al] + 3[O]
$$
 (3)

$$
\lg K = \lg \frac{a_{\text{Al}}^2 \cdot a_{\text{O}}^3}{a_{\text{Al}_2\text{O}_3}} = -\frac{45,300}{T} + 11.62\tag{4}
$$

$$
\lg a_{\rm O} = \frac{-\frac{45,300}{T} + 11.62 + \lg a_{\rm Al_2O_3} - 2\lg a_{\rm Al}}{3} \tag{5}
$$

where  $K$  refers to the distribution coefficient of each element; *T* represents the temperature; and *ai* corresponds to the activity of each element *i*. The equilibrium oxygen content of Heat-1 and Heat-2 samples at diferent stages of the steelmaking process is calculated, and the results are shown in Fig. [10.](#page-7-2) The change in the equilibrium oxygen content in both the samples remained similar. The equilibrium oxygen content signifcantly decreased from A to LF1 and then slightly increased after the Ti addition during the LF refning



<span id="page-7-2"></span>**Fig. 10** Equilibrium oxygen content of Heat-1 and Heat-2 samples at diferent stages of steelmaking process

process. Moreover, Heat-2 exhibited lower equilibrium oxygen content than Heat-1 before the Ti addition.

<span id="page-7-0"></span>One should note that the lower oxygen content at equilibrium can suppress reaction [\(6](#page-7-3)) in the forward direction. Hence, the TiO<sub>x</sub> and TiO<sub>x</sub>-containing composite inclusions signifcantly reduced because of the reaction between Ti and O.

<span id="page-7-3"></span><span id="page-7-1"></span>
$$
[\text{Ti}] + x[\text{O}] = (\text{TiO}_x). \tag{6}
$$

## **4.3 Thermodynamic analysis of formation of CaO– Al2O3–MgO–TiO***x* **inclusions**

The CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions were formed after the addition of Ti feeding wire into 321 molten steel during the LF refning process, as shown in Figs. [4](#page-4-0) and [5.](#page-5-0) In order to study the formation mechanism of  $CaO-Al_2O_3-MgO-TiO<sub>x</sub>$ complex inclusions, oxide stability diagram of the Al–Ti–O system, with iso-oxygen contours, in 321 stainless steel system at 1873 K was calculated by using FactSage™7.2 software, as shown in Fig. [11.](#page-7-4) The oxide stability diagram, as shown in Fig. [11,](#page-7-4) mainly consists of four regions: slagliquid,  $Ti_2O_3$ ,  $Ti_3O_5$ , and  $Al_2O_3$ . Moreover, the contents of Al and Ti in both Heat-1 and Heat-2 samples are marked in Fig. [11](#page-7-4). In addition, Fig. [11](#page-7-4) shows that the point of both Heat-1 and Heat-2 samples is located near the  $Al_2O_3$ -TiO<sub>x</sub> zone. The collision of  $CaO-Al_2O_3-MgO$  liquid inclusions and TiO<sub>x</sub> inclusions modified the CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions. In addition, the lower equilibrium oxygen content can suppress the reaction between Ti and O. Notably, the Heat-1 sample is located in the  $Ti<sub>2</sub>O<sub>3</sub>$  zone, whereas Heat-2 sample is located in the  $Ti<sub>3</sub>O<sub>5</sub>$  zone, indicating that



<span id="page-7-4"></span>**Fig. 11** Calculated oxide stability diagram of Al–Ti–O system, with iso-oxygen contours, in 321 stainless steel system at 1873 K



<span id="page-8-13"></span>**Fig. 12** Schematic illustration of infuence of diferent refning slags on titanium yield during LF refning process in 321 stainless steel

a large quantity of Ti is oxidized during the formation of TiO*x* inclusions in Heat-1 sample. These results are consistent with the composition distribution of the inclusions, as shown in Fig. [6](#page-6-0).

Based on the experimental and thermodynamic analysis, the efect of diferent refning slags on the Ti yield during the LF refining is schematically illustrated in Fig. [12](#page-8-13). In general, reactions  $(1)$  $(1)$ ,  $(2)$  $(2)$  and  $(6)$  occurred after the addition of Ti feeding wire into the molten steel. Then, the oxidation of Ti in the CaO–Al<sub>2</sub>O<sub>3</sub> slag afforded 76% Ti yield. However, the Ti yield increased to  $85\%$  by using TiO<sub>2</sub>-rich CaO–Al<sub>2</sub>O<sub>3</sub> slag.

Furthermore, the thermodynamic calculations indicate that  $TiO<sub>2</sub>$  activity of the slag increased before the feeding of Ti wire into the molten steel. However, the oxidation of Ti in the slag exhibited an opposite trend to that of the  $TiO<sub>2</sub>$ activity, suppressing reactions  $(1)$  $(1)$  $(1)$ ,  $(2)$  $(2)$  $(2)$  and  $(6)$  $(6)$  in the forward direction. In contrast, the oxygen content decreased by using TiO<sub>2</sub>-rich CaO–Al<sub>2</sub>O<sub>3</sub> slag. Therefore, the content of TiO*x* and TiO*x*-containing composite inclusions, originating from the reactions between Ti and O, signifcantly reduced. Hence, Heat-2 sample exhibited a lower TiO<sub>x</sub> content in CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions than Heat-1 sample.

# **5 Conclusions**

- 1. The total oxygen content and inclusion density decreased during the 321 steelmaking processes. The TO content and the Ti yield during the LF refning process can be controlled by using  $TiO_2$ -rich CaO–Al<sub>2</sub>O<sub>3</sub>-based slag.
- 2. The spherical CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO inclusions existed in the 321 steel after the AOD process. Before the Ti addition in the LF process, the spherical CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–  $SiO<sub>2</sub>$  inclusions were observed. After the Ti addition in the LF process, the inclusions changed to multilayer CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions. Moreover, the inclu-

sion density and TiO<sub>x</sub> content of CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–TiO<sub>x</sub> inclusions of Heat-2 sample, utilizing  $TiO<sub>2</sub>-rich CaO Al_2O_3$ -based slag, were lower than those of Heat-1 sample, using traditional CaO–Al<sub>2</sub>O<sub>3</sub>-based slag.

3. When  $TiO<sub>2</sub>-rich CaO–A<sub>1</sub>,O<sub>3</sub>-based slag was used, the$  $TiO<sub>2</sub>$  activity of the slag increased, and the equilibrium oxygen content signifcantly decreased from the AOD to the LF processes. The oxidation of Ti exhibited an opposite trend to that of the  $TiO<sub>2</sub>$  activity in the slag. The lower equilibrium oxygen content suppressed the reactions between Ti and O.

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