Original Article

Investigation of desulfurization of Inconel 718 superalloys by ESR type slags with different TiO$_2$ content

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**ABSTRACT**

In the present study, effect of CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slag with various TiO$_2$ contents on the desulfurization of Inconel 718 alloy was investigated at 1773 K to provide the fundamental information for the establishment of desulfurization procedure during electroslag remelting (ESR) process. The melt-quenching method did not accurately determine the change in content of sulfur and oxygen in the nickel-based alloy with time for the present study, which uses a novel experimental apparatus. The results indicated that the final sulfur content in the nickel-based alloy increased from 7 to 9 ppm when the TiO$_2$ content in slag of CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ system increased from 2.17 to 10% without addition of deoxidizer. In order to further expound the desulfurization mechanism, meanwhile, the relationship between the oxygen activity at slag–metal interface and reaction time under conditions of various TiO$_2$ in the slag was studied by coupling with the developed mass transfer model. The calculated oxygen content in bulk metal has a good corresponding relationship with the measured oxygen content in the nickel-based alloy. The oxygen activity at slag–metal interface increased up to 9.6 ppm when TiO$_2$ content was 10% in the slag, giving rise to the decrease in desulfurization ratio in high TiO$_2$ content. The optimal condition for simultaneously ensuring low sulfur content and maintaining oxidative elements, such as Al and Ti, uniformly from bottom to top of the ESR ingot is also discussed.

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1. Introduction

Inconel 718, a precipitation strengthened nickel-based super-alloy, currently containing approximately 5.3% niobium exhibits adequate strength, ductility, and fatigue resistance up to 923 K [1–3]. However, the presence of impurities, such as sulfur, phosphorous, oxygen, and nitrogen, in nickel-based alloy can combine with the host metal or other alloying elements to form precipitates that have detrimental effects on mechanical properties of the final product [4–7]. For instance, sulfur, origins from the raw materials or scraps, most seriously aggrivate dendritic segregation by decreasing solidus temperature and lowering the solubility of Nb in matrix [8,9]. It is these Nb segregation and Laves phase formation during solidification process that has been regarded as the most serious problem in Inconel 718 production [10–12]. Stronger grain boundary segregation has also been observed for sulfur and is known to cause hot shortness and decrease stress-rupture life dramatically, since it forms low melting NiS$_2$ phase with a melting point of 908 K even at low sulfur concentration 10 ppm and higher [13–16].

In order to meet the increasing demand on the quality and performance of nickel-based alloy, therefore, many efforts have been made to reduce the sulfur content below the critical values during the production of superalloy since 1970s [17–19]. The mature desulfurization practices during vacuum induction melting (VIM) refining Ni-based alloy are the addition of NiCa and NiMg in a vacuum induction furnace and/or using a CaO crucible [16,20–23]. In consideration of the limits of desulfurization in VIM [24], however, lots of attention has been given to electroslag remelting (ESR) in recent years [25–32]. To the best of the authors’ knowledge, up to now, effect of CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slag with different TiO$_2$ content on the desulfurization of Inconel 718 alloy has not been reported. In the current study, therefore, the desulfurization behavior of the nickel-based alloy was investigated at 1773 K. In order to further elaborate the desulfurization mechanism, meanwhile, the relationship between the oxygen activity at the slag-metal interface and reaction time was studied by coupling with the developed mass transfer model.

The melt-quenching method is widely used to investigate slag-metal kinetics [33], viz., slag and metal are periodically sampled by using quartz tubes and quenched in ice water, which is based on the assumption that the ratio of the interfacial reaction area to the effective liquid melt volume $\phi$ (we introduce the concept of “specific reaction interface” (SRI)) is a constant [34]. Actually, the quality of the SRI can be increased by means of the above-mentioned experimental method, either as result of the turbulence of the reaction interface or as a result of a decrease in the absolute amount of melts during sampling [35]. To lower the impact, the desulfurization reaction of Inconel 718 alloy via CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slag was investigated by means of the novel experimental apparatus under the same experimental conditions, such as slag and metal concentration, temperature, as well as protective atmosphere. The aim of this study is in order to investigate the desulfurization limitation of Inconel 718 alloy by different slag composition without deoxidizer addition, which provides fundamental information for the establishment of desulfurization procedure in the course of ESR.

2. Experimental

2.1. Metal and slag preparation

To begin the experiment, Inconel 718 alloy samples were produced in a MgO crucible in a vacuum-induction melting (VIM) furnace under a high-purity argon atmosphere, and the chemical composition is listed in Table 1. Reagent-grade powders of CaF$_2$, CaO, MgO, Al$_2$O$_3$, and TiO$_2$ were used as raw materials. The thoroughly mixed powders were melted at 1773 K in a graphite crucible under a high-purity Ar atmosphere to ensure complete melting and homogenization, and the liquid sample was then quenched on the cooled copper plate and ground. The chemical composition of the experimental slag is listed in Table 2.

2.2. Experimental apparatus and process

The slag-metal equilibrium reaction between CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slags and Inconel 718 alloy was conducted in a vertical resistance-heated alumina tube furnace equipped with MoSi$_2$ heating elements. Fig. 1 shows a schematic of the resistance furnace used in the present study. The temperature of the furnace was controlled by a proportional-integral-derivative (PID) controller connected to a B-type reference thermocouple. The temperature was calibrated to 1773 K using another B-type thermocouple before the experiment. The kinetic experiments were carried out using the double-layer (DL) graphite crucible shown in Fig. 2. The experimental procedure is detailedly summarized in steps as follows:

(1) Pre-melted slag (12 g) was held in the upper graphite crucible with a small hole in its bottom after a carbon stopper was used to plug the hole. The inner wall of the upper crucible makes an angle of 110 degrees with the bottom to ensure that the melted slag drops fully into the lower separate crucible. Face-cleaned Inconel 718 alloy (50 g) was accommodated in a MgO crucible (ID: 25 mm; OD: 30 mm; H: 35 mm). The MgO crucible was then placed in the lower graphite crucible (ID: 31 mm; OD: 36 mm; H: 40 mm) to prevent the reactant from leaking.

(2) The DL crucible with reactants was placed in a graphite tray, which was then positioned in the constant-temperature zone of a resistance furnace after the furnace temperature reached the pre-set temperature of 1773 K. High-purity Ar was flushed into the reaction chamber at a constant flow rate to avoid the oxidation of the Ni-based alloy.

(3) Prior to the experiment, the time required for the slag and metal to melt completely was estimated; these estimates indicated that the samples had fully melted after the graphite crucible was placed into the resistance furnace for 10 min.

(4) The moment the carbon stopper was removed (viz., the moment contact occurred between the molten slag and...
Table 1 – Composition of the Inconel 718 alloy used in the present study (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>Cr</th>
<th>Nb</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>T.O.</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>%</td>
<td>0.02</td>
<td>0.2</td>
<td>0.09</td>
<td>3.13</td>
<td>52.72</td>
<td>18.26</td>
<td>4.92</td>
<td>0.43</td>
<td>1.13</td>
<td>Bal.</td>
<td>0.00196</td>
<td>0.00276</td>
</tr>
</tbody>
</table>

Table 2 – Composition of slag used in this study (wt%).

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaF₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>Optical basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>40.22</td>
<td>27.17</td>
<td>27.17</td>
<td>3.26</td>
<td>2.17</td>
<td>0.731</td>
</tr>
<tr>
<td>S2</td>
<td>39.36</td>
<td>26.6</td>
<td>26.6</td>
<td>3.16</td>
<td>4.26</td>
<td>0.728</td>
</tr>
<tr>
<td>S3</td>
<td>37</td>
<td>25</td>
<td>25</td>
<td>3</td>
<td>10</td>
<td>0.719</td>
</tr>
</tbody>
</table>

Fig. 1 – Schematic of the experimental apparatus used in the present study.

Fig. 2 – Schematic of double-layer crucible: (a) melting process, (b) experiment starts, (c) slag-metal reaction and (d) equipment image.

Metal) was taken as the starting time of the reaction. After certain reaction time intervals (1, 3, 5 and 10 min), the whole crucible containing liquid samples was rapidly removed from the furnace and quenched in ice water. The flow sheet for the experimental procedure is shown in Fig. 3. In each experiment, no deoxidizer was added into the slag mixtures before the experiment. After completion of the experiments, the content of the sulfur and total oxygen content in the nickel-based alloy samples was analyzed by Carbon-Sulfur Analyzer (EMIA-820V) at the National Analysis Center for Iron and Steel (NACIS) and Leco Analyzer (TCH 600) at the National Experimental Teaching Demonstration Center for Metallurgical Engineering at University of Science and Technology Beijing (USTB), respectively.

3. Development of mass transfer model for Al + Al₂O₃ and Ti + TiO₂ system

According to the classic metallurgical physicochemistry [36], [Al]–[O] and [Ti]–[O] equilibrium are considered to coexist at
slag–metal interface when CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ ESR-type slag contacts Inconel 718 alloy. Therefore, the following reactions (1) and (2) are simultaneously used to investigate the changes in oxygen activity at the slag–metal interface, which is in order to illuminate the influence mechanism of ESR slag with different TiO$_2$ contents on desulfurization of Inconel 718 alloy.

$$\text{[Al]} + 1.5\text{[O]} = (\text{AlO})_5 \quad (1)$$
$$\text{[Ti]} + 2\text{[O]} = (\text{TiO})_2 \quad (2)$$

Given that the reactions (1) and (2) occur rapidly at metallurgical temperature, and local equilibrium can hence be assumed at the slag–metal interface [36]. The corresponding equilibrium constants $K_i$ for above-mentioned reactions can be expressed as follows [32,37]:

$$\ln K_{\text{Al}} = \frac{a^*_{\text{AlO}} a_{\text{TiO}}}{a^*_{\text{Al}} a_{\text{O}}^5} = \ln \frac{\gamma_{\text{AlO}} \gamma_{\text{TiO}} \gamma_{\text{O}}^5}{f_{\text{Al}} f_{\text{O}}^5} = \frac{32000}{T} - 10.29 \quad (3)$$
$$\ln K_{\text{Ti}} = \frac{a^*_{\text{TiO}} a_{\text{AlO}}}{a^*_{\text{Ti}} a_{\text{O}}^5} = \ln \frac{\gamma_{\text{TiO}} \gamma_{\text{AlO}} \gamma_{\text{O}}^5}{f_{\text{Ti}} f_{\text{O}}^5} = \frac{34458}{T} - 11.96 \quad (4)$$

Apparent equilibrium constant $E_i$ can be expressed by Eq. (5).

$$E_i = \left(\frac{[\text{O}]_s}{[\text{O}]_s^*}\right) = \frac{M_{\text{O}} f_{\text{O}} K_i \sum \left(\frac{[\text{O}]_s}{M_{\text{O}}} \right)}{\gamma_{\text{O}} a_{\text{O}}^5} \quad (5)$$

where $a_{\text{O}}$ and $f_{\text{O}}$ are the activity and activity coefficient of composition i in a metal referred to the 1% standard state, with mass percentage [% i] as the concentration unit (γ), $x_{\text{O}}$, and $\gamma_{\text{O}}$ are the activity and activity coefficient of composition i in the slag relative to pure matter as a standard state, with mole fraction $x_{\text{O}}$ as the concentration unit (γ). $M_{\text{O}}$, $K_i$, and $T$ are the molar mass of composition i in the slag (g·mol$^{-1}$) and absolute temperature (K), respectively.

According to the fundamental equation of heterogeneous reaction kinetics based on the concept of the effective boundary layer proposed by Wagner [38], the flux of component i across unit area $J_i$ is defined as

$$J_i = k_i \left( C_{i,s}^* - C_{i,m}^b \right) = k_i m \left( C_{i,m}^b - C_{i,m}^* \right) \quad (6)$$

where $J_i$, $k_i$, and $C_i$ stand for the molar flow (mol·m$^{-2}$·s$^{-1}$), mass transfer coefficient (m·s$^{-1}$), and molar concentration of element i in liquid alloy or slag (mol·m$^{-3}$), respectively. Superscript ‘s’ and ‘b’ represent the interface and bulk phase, respectively, while subscript ‘s’ and ‘m’ indicate the slag and metal phase. Eqs. (7)–(10) can be derived by combining Eqs. (3)–(6).

$$J_{\text{Al}} = F_{\text{Al}} \left( [\text{Al}]^b - F_{\text{Al}} a_{\text{Al}} [\text{Al}]^k \gamma_{\text{AlO}} \gamma_{\text{O}} \right) \quad (7)$$
$$J_{\text{Ti}} = F_{\text{Ti}} \left( [\text{Ti}]^b - F_{\text{Ti}} a_{\text{Ti}} [\text{Ti}]^k \gamma_{\text{TiO}} \gamma_{\text{O}} \right) \quad (8)$$
$$J_{\text{O}} = F_{\text{O}} \left( [\text{O}]^b - [\text{O}]^* \right) = F_{\text{O}} \left( a_{\text{O}}^b - a_{\text{O}}^* \right) \quad (9)$$

The modified mass transfer coefficients as shown in Eqs. (7)–(10) can be illustrated by Eqs. (10) and (11).

$$F_{\text{O}} = \frac{k_{\text{m,O}}}{100M_{\text{O}}} \quad (10)$$
$$F_{\text{O}} = \frac{k_{\text{O}}}{100M_{\text{O}}} \quad (11)$$

The oxygen activity $a_{\text{O}}^*$ at the slag–metal interface can be determined by Equation (12).

$$1.5J_{\text{Al}} + 2J_{\text{Ti}} - J_{\text{O}} = 0 \quad (12)$$

$$\frac{d[\text{O}]}{dt} = k_m \frac{A}{V_m} \left( [\text{O}]^* - [\text{O}]^b \right) \quad (13)$$

$$\frac{d[\text{O}_i]}{dt} = k_{\text{O}_i} A \left( [\text{O}_i]^* - [\text{O}_i]^b \right) \quad (14)$$

Then, the concentrations of each element in the metal and slag phase as the function of reaction time can be calculated from Eqs. (13) and (14) after the relevant parameters be obtained: (i) The activity coefficient $\gamma_{\text{O}} = N_i / x_{\text{O}}$ of each component i in CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slag can be calculated using the reported activity model (for details of the modeling and solution procedure, see Ref. [39]) based on the
Table 3 - Interaction coefficients used in the present study [41–45].

<table>
<thead>
<tr>
<th>i</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.034</td>
<td>0.045</td>
<td>−0.0376</td>
<td>0.08</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Ti</td>
<td>−0.12</td>
<td>0.025</td>
<td>−0.0166</td>
<td>−0.0561</td>
<td>0.016</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4 - Changes of sulfur content in Ni-based alloy with reaction time at different slag compositions at 1773 K.

ion and molecule coexistence theory (IMCT). (II) The activity coefficient $f_i$ can be calculated by Eq. (15) and the first-order interaction coefficients used in the present study are listed in Table 3. (III) The mass transfer coefficient $k_{i,\text{slag}}$ and $k_{i,\text{metal}}$ of the component $i$ in the metal and slag obtained by Richardson [40]. The density $\rho_i$ and $\rho_m$ of the slag and nickel-based alloy is estimated about 2646 kg m$^{-3}$ and 8240 kg m$^{-3}$, respectively.

$$\ln f_{i} = \sum \varepsilon_i \%$$

(15)

4. Results and discussion

4.1. Effect of slag composition with different TiO$_2$ contents on desulfurization ability of Inconel 718 alloy at 1773 K

Shown in Fig. 4 is the composition change of sulfur in Inconel 718 alloy under different slag compositions at 1773 K. It can be seen that the desulfurization rate of S3 slag was faster than that of S1 and S2 slag during first 1 min, which is likely due to the decrease in viscosity of CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slag, resulting in the decrease in the diffusion resistance of sulfur in the slag. The similar results also reported by Shi et al. [46] who concluded that the decrease in viscosity in high TiO$_2$ content CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slag was because of the activation energy and the Al–O–Al structural units decreased with increasing TiO$_2$ content. It can be noted from Fig. 4 that the sulfur content in the nickel-based alloy continuously decreases within the first 5 minutes of the desulfurization reaction, after which it remains nearly constant. The final content of sulfur in the nickel-based alloy decreases from 27.6 ppm to about 7 ppm, 6 ppm, and 9 ppm as 2.17% (S1), 4.26% (S2) and 10% (S3) TiO$_2$ content within the slag, respectively. The rationale behind such results is that the slag basicity decreases with an increase in TiO$_2$ content in the slag. The optical basicity is regarded as a useful basis for the self-slag slag containing halide [47], and the optical basicity values of S1, S2, and S3 slag are calculated by coupling with Pauling electronegativity are listed in Table 2. These results imply that the desulfurization ratio decreases with increasing added TiO$_2$ in the slag. This is consistent with the results reported by Shankar et al. [48], Tong et al. [49], Tang et al. [50], and Zhang et al. [51], who investigated the sulfur distribution partition between blast furnace slag and hot metal. TiO$_2$ is present in high basicity slag in the form of [TiO$_6$]$^{8-}$ octahedron [51,52], resulting in the amount of free O$_2^-$ is consumed, which leads to the decrease in desulfurization ability of slag. It can also be seen that the influence of TiO$_2$ content (S1 and S2 slag) on sulfur content in the nickel-based alloy is not pronounced, which is likely to be due to the narrow range of TiO$_2$ content and measuring error. Except for the slag basicity, the oxygen activity at slag–metal interface also plays an important role in desulfurization reaction. Therefore, the difference in desulfurization ability between S1, S2 and S3 will be expound in detail later from point of view of deoxidation kinetics.

4.2. Effect of slag composition with different TiO$_2$ contents on oxygen content in Inconel 718 alloy at 1773 K

With initial alloy content, such as [Al], [Ti] and [O] in Inconel 718 alloy, and slag content listed in Table 2, the calculated oxygen content in the nickel-based alloy under conditions of various TiO$_2$ contents in CaF$_2$–CaO–Al$_2$O$_3$–MgO–TiO$_2$ slag can be shown in Fig. 5. The solid and dashed lines calculated by the developed mass transfer model represent bulk and interfacial concentrations, respectively. While the measured experimental data in the present study are shown as symbols in Fig. 5(a)–(c). Fig. 5(a) represents the oxygen content evolution during the reaction between S1 slag and Inconel 718 alloy at 1773 K as time passes. As expected, both oxygen content in bulk phase and oxygen activity at slag–metal interface decreased. Meanwhile, the oxygen content in bulk metal almost equals to the oxygen activity at slag–metal interface observed at 5 minutes, indicating that the deoxidation reactions are very nearly an equilibrium state. The similar results can be found in all runs in the present study. In order to further testify the feasibility of the developed kinetic model, the comparisons between calculated and measured oxygen content in nickel-based alloy at various TiO$_2$ contents are as illustrated in Fig. 5(a)–(c). It can be found from Fig. 5(a)–(c) that the measured oxygen content is slightly higher than the calculated ones due to all of the oxygen content (19.6 ppm) is treated as soluble oxygen and introduced into the mass transfer model. Actually, the total oxygen consists of soluble oxygen and the oxygen as a form of oxide inclusions at the elevated temperature. Fig. 6 shows the SEM image and EDS analysis results of typical inclusions in the nickel-based alloy in different heats. It appears from Fig. 6 that all the oxide inclusions observed by SEM-EDS in the nickel-based alloy are mainly the inclusions of MgO-Al$_2$O$_3$ spinel core surrounded by (Nb,Ti)CN layer. It is evident from Fig. 5(c) and (d), (g) and (h), and (k) and (l) that there are some inclusions still
Fig. 5 – Model predictions (lines) and experimental data (points) of change of oxygen content with time for slag composition with different TiO$_2$ contents (a) 2.17%, (b) 4.26%, and (c) 10% at 1773 K.

<table>
<thead>
<tr>
<th></th>
<th>1 min</th>
<th>5 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
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<td></td>
<td><img src="image3.png" alt="Image" /></td>
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<td>S3</td>
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<td></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
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</tbody>
</table>

Fig. 6 – SEM images and EDS analysis results of typical inclusions observed in Inconel 718 alloy in different heats: (a)–(d) S1 slag, (e)–(h) S2 slag, and (i)–(l) S3 slag.
retain in the nickel-based alloy after 5 min reaction, giving rise to the fact that the measured oxygen content is a little higher than the calculated ones. It is interesting that the oxygen activity at the slag–metal interface increases with the increase of TiO$_2$ content in CaF$_2$–CaO–AI$_2$O$_3$–Mgo–TiO$_2$ slag as shown in Fig. 5(d), giving rise to the fact that the equilibrium content of sulfur in the nickel based alloy increases with increasing TiO$_2$ content in the slag. As mentioned above, the optical basicity shows negative correlation with TiO$_2$ content in the range of 2.17–10% in the slag. In other words, increasing basicity in the slag, CaF$_2$–CaO–AI$_2$O$_3$–Mgo–TiO$_2$, decreases the oxygen activity at the slag–metal interface, which is due to the activity of AI$_2$O$_3$ and TiO$_2$ decrease with the increase in slag basicity, rendering the reactions (1) and (2) proceed in the positive direction at slag–metal interface. Consequently, an increase in the desulfurization ratio can be found when reduction of TiO$_2$ content in CaF$_2$–CaO–AI$_2$O$_3$–Mgo–TiO$_2$ slag. A similar behavior has been proved by the wok of Kang et al. [37] in the study of desulfurization in secondary refining process. Hou et al. [53] also found that the interfacial oxygen activity decreased with the increase in CaO content in CaF$_2$–CaO–AI$_2$O$_3$–Mgo–TiO$_2$ slag during electroslag remelting of 1Cr21Ni5Ti stainless steel.

4.3. Optimal TiO$_2$ content for refining of Inconel 718 alloy during ESR process

In order to acquire the optimal TiO$_2$ content in CaF$_2$–CaO–AI$_2$O$_3$–Mgo–TiO$_2$ slag to refine Inconel 718 alloy in the courses of ESR, the accessional experiments with the three kinds of slags (S1, S2, and S3) were carried out. The metal samples were rapidly pulled out of the tube furnace when the predetermined time lapsed (1, 2, 3, 4, 5, 7 and 10 min). The details of the experimental process can be found in the author’s previous study [54]. Fig. 7 shows the change of Al and Ti concentrations in the nickel-based alloy at 1773 K. It can be observed from Fig. 7(a) and (c) that the initial Ti and Al content is 1.13 and 0.43% in nickel-based master alloy and decreases sharply during the first 5 min, and remained nearly constant thereafter. At the same time, Al and Ti markedly increased during the first 5 min, after which it remained nearly constant, respectively. It is very interesting that Al and Ti content did not vary with time, as shown in Fig. 5(b). These changes are primarily a result of the reaction (16) at the slag–metal interface [55].

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

$$\Delta_r G_m = -675894 + 190.32T \text{(J/mol)}$$  \hspace{1cm} (16)

It can be deduced from combining Figs. 5 and 7 that TiO$_2$ in the slag not only affects the oxidation behavior of Al or Ti but the oxygen content in bulk metal. To ensure the critical elements, such as Al and Ti, within specification of Inconel 718 alloy, the 4.26% TiO$_2$ should be added in CaF$_2$–CaO–AI$_2$O$_3$–Mgo–TiO$_2$ slag to diminish loss of Al or Ti caused by reaction (16) at 1773 K. From early discussion, however, the decrease in desulfurization ratio in high TiO$_2$ content slag is because of the reduction of basicity of the slag. Chen et al. [31] investigated the effect of different experimental conditions (under
atmosphere, Ar gas atmosphere and Ar gas atmosphere with Ca additions) on desulfurization of Inconel 718 alloy with (60%) CaF₂–(20%) CaO–(20%) Al₂O₃ slag in a laboratory 50-kg scale P-ESR furnace. They found that the sulfur content of 18 ppm in electrode is reduced to 6 ppm in ingot under atmosphere, lowered to 9 ppm under Ar gas atmosphere and diminished to 3 ppm by addition of calcium as deoxidizer under the insert atmosphere. Hou et al. [32] studied desulfurization reaction kinetics between CaF₂–CaO–Al₂O₃–MgO–TiO₂ slags and 1Cr21Ni5Ti stainless steel in a 50 kg ESR furnace. They concluded that the addition of calcium can improve the mass transfer of sulfur in liquid steel by the reaction \[ \text{S} + [\text{Ca}] = (\text{CaS} \] and thus promote desulfurization during the ESR process.

The fluctuation of temperature is usually occurred in ESR process, particularly in the first temperature-rising period. Yang et al. [56] reported that oxidation of Ti is more prone to occur compared to that of Al as the temperature increases. Hou et al. [57] also pointed out that the slag combined with extra TiO₂ constantly added into slag bath in the first temperature-rising period is suitable for electroslag remelting of high Ti-low Al type stainless steel. The influence of temperature on the desulfurization and oxidation behavior of Al and Ti in Inconel 718 alloy will be investigated in future.

5. Conclusions

In the current study, effect of slag composition with different TiO₂ contents on the desulfurization of Inconel 718 alloy was investigated at 1773 K. Moreover, in order to explain the desulfurization mechanism, the effect of TiO₂ content on oxygen content in the nickel based alloy was also studied. The following is a summary of the major findings in the present study. The desulfurization ratio decreased with an increase in TiO₂ content in CaF₂–CaO–Al₂O₃–MgO–TiO₂ slag not only due to a decrease in slag basicity, but also due to an increase in oxygen activity at slag–metal interface. The final sulfur content in the nickel-based alloy decreased from 27.6 ppm to 7.6, and 9 ppm, which is due to the oxygen activity at the slag–metal interface increased from 7.6 to 9.6 ppm under conditions of TiO₂ content increased from 2.17% to 10% TiO₂ in the slag. The TiO₂ in the slag not only affects desulfurization but oxidation behavior of Al and Ti in Inconel 718 alloy. On the prerequisite of satisfying the stringent composition of the alloy by controlling TiO₂ content in the slag, to properly increase deoxidizer in molten metal can increase desulfurization ratio.

Conflicts of interest

The authors declare no conflicts of interest.

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