Research Article

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Kinetic study on the reaction between Incoloy 825 alloy and low-fluoride slag for electroslag remelting

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Abstract: A kinetic model for the reactions between the low-fluoride slag CaF₂–CaO–Al₂O₃–MgO–Li₂O–TiO₂ and Incoloy 825 alloy was proposed based on the two-film theory. The applicability of the model was verified to predict the variation of components in the slag–metal reaction process. The results show that the controlling step of the reaction 4[Al] + 3[TiO₂] = 3[Ti] + 2(Al₂O₃) is the mass transfer of Al and Ti in the liquid alloy and the controlling step of the reactions 4[Al] + 3(SiO₂) = 3[Si] + 2(Al₂O₃) and [Si] + (TiO₂) = [Ti] + (SiO₂) is the mass transfer of SiO₂ in the molten slag. With increasing TiO₂ content in the slag from 3.57% to 11.27%, the Al content in the alloy decreased whereas the Ti content increased gradually. The Si content continued to decrease during the slag–metal reaction. Soluble oxygen in the alloy reacts with Al, Ti, and Si, resulting in a decrease of the oxygen content in the alloy. The variations of TiO₂ content were in good agreement with the calculated results by the kinetic model whereas the measured results of Al₂O₃ and SiO₂ in the slag were lower than the calculated results, which is mainly due to the volatilization of fluoride.

Keywords: low-fluoride slag, kinetics, Incoloy 825 alloy, mass transfer, two film theory

1 Introduction

Incoloy 825 alloy is extensively used in the aerospace and petrochemical industries for its excellent corrosion resistance and mechanical properties [1,2]. Electroslag remelting (ESR) is used to refine Incoloy 825 alloy because it improves the solidification structure of the remelted ingot [3,4] and has the superior ability to remove non-metallic inclusions in liquid steel during ESR [5–7]. However, in the process of producing Incoloy 825 alloy by electroslag remelting, the elements Al and Ti are always lost due to the reaction between the slag components and the alloying elements, which cause the concentrations of the elements to vary from the bottom to the top of the remelted ingot [8,9]. To improve the homogeneity of alloy composition, thermodynamic models [10,11] and kinetic models [12,13] were proposed by researchers to predict the change of alloying element content during ESR.

Many efforts have been carried out to develop the kinetic model to predict the components of ESR. Fraser and Mitchell [14,15] proposed a kinetic model to describe the reaction between FeO in slag and Mn in steel during ESR. Duan et al. [16,17] developed a mass transfer model to expound the desulfurization mechanism. Wei and Mitchell [18,19] elucidated the reaction principle of Al and Si in steel with Al₂O₃ and SiO₂ in the slag to explain the effect of different atmosphere conditions on the loss of elements in steel by proposing a kinetic model of multiphase reaction of the electroslag process. Hou et al. [20,21] optimized the mass transfer kinetic model of multiphase reactions during the electroslag remelting process (the reactions are mainly [Ti] + (SiO₂) = [Si] + (TiO₂), 3[Ti] + 2(Al₂O₃) = 4[Al] + 3(TiO₂), and 4[Al] + 3(SiO₂)), which could predict the variation of the elements Al, Ti, and Si in the steel and slag components. However, the slag used in the aforementioned models is high-fluorine slag. Li et al. [13] established a kinetic model for the investigation of aluminum and oxidation variations and proposed that the oxygen potential of the slag pool has a better effect.
of improving cleanliness than improving the Al content in the electrode. Fluoride volatilization from the high-fluorine slag not only causes environmental pollution but also changes the composition of the slag and also breaks the equilibrium between the slag and metal. To reduce the volatilization of fluoride in the ESR process, many investigators pay more attention to low-fluorine slag based on its stable composition compared with high-fluorine slag [22–25]. However, the kinetic study of electroslag remelting between low-fluorine slag and Incoloy 825 alloy in the process of electroslag remelting has not been reported.

In the present study, the kinetic model of the reaction process between CaF$_2$–CaO–Al$_2$O$_3$–MgO–Li$_2$O–TiO$_2$ and Incoloy 825 alloy was proposed based on the two-film theory. The variation of the elements Al, Ti, Si, and O in the alloy and the content of each component in the slag were investigated. The mechanism of content change in both slag components and alloying elements and the rate-determining step of the reaction were determined. A slag–metal experiment was proceeded under Ar atmosphere at 1,773 K with different TiO$_2$ content (3.57%, 7.27%, and 11.28%) of slag to verify the application of the model.

### 2 Kinetic model

The mass transfer process of each component in the slag–metal reaction is shown in Figure 1. There are three systems of mass transfer in the slag–metal reaction: Al + Al$_2$O$_3$, Ti + TiO$_2$, and Si + SiO$_2$. In this experiment, about 0.1% SiO$_2$ is present in the slag, which may be attributed to the introduction of impurities. Considering the inevitable existence of a little SiO$_2$ in the industrial slag, therefore, it is of practical significance to consider the Si + SiO$_2$ system for industrial production. In order to establish the model, the following assumptions are considered in this model: (1) Only two phases of slag and metal are considered in the slag–metal reaction. (2) Before the reaction, the components in the slag and metal phase are evenly distributed. (3) The interface reacts rapidly and reaches a chemical equilibrium state at the setting temperature. The rate of reactions is controlled by the diffusion of reactants and products through boundary layer at the reacting interface. (4) The slag–metal reaction is not considered from slag addition to melting. (5) The influence of the crucible on the slag–metal reaction is not considered.

The main reactions in the slag–metal reaction can be expressed by Eqs. 1–3:

\[
\begin{align*}
4[\text{Al}] + 3(\text{TiO}_2) &= 3[\text{Ti}] + 2(\text{Al}_2\text{O}_3) \\
[\text{Si}] + (\text{TiO}_2) &= [\text{Ti}] + (\text{SiO}_2) \\
4[\text{Al}] + 3(\text{SiO}_2) &= 3[\text{Si}] + 2(\text{Al}_2\text{O}_3)
\end{align*}
\]

Considering the thermodynamic equilibrium and the convenience of calculation, Eqs. 1–3 were simplified to Eqs. 4–6:

\[
\begin{align*}
[\text{Al}] + 1.5[\text{O}] &= (\text{AlO}_{1.5}) \\
[\text{Ti}] + 2[\text{O}] &= (\text{TiO}_2) \\
[\text{Si}] + 2[\text{O}] &= (\text{SiO}_2)
\end{align*}
\]

The expression of equilibrium constants of Eqs. 4–6 is given as Eqs. 7–9 [26–28]:

\[
\begin{align*}
\lg K_{\text{Al}} &= \lg \frac{a^{*}_{\text{Al}} a_{0,5}^{1.5}}{a_{\text{Al}} a_{\text{O}}^{1.5}} = \frac{32,000}{T} - 10.29 \\
\lg K_{\text{Ti}} &= \lg \frac{a^{*}_{\text{Ti}} a_{2,0}^{1.2}}{a_{\text{Ti}} a_{\text{O}}^{1.2}} = \frac{34,458}{T} - 11.96 \\
\lg K_{\text{Si}} &= \lg \frac{a^{*}_{\text{Si}} a_{2,0}^{1.2}}{a_{\text{Si}} a_{\text{O}}^{1.2}} = \frac{30,410}{T} - 11.59
\end{align*}
\]

According to the film theory, the diffusion flux of element $i$ at the slag–metal interface is

\[
J_i = \frac{k_{i,m} \rho_{i} \left([\% i] - [\% i]^* \right)}{100M_i} = \frac{k_{i,s} \rho_{i} \left([\% iO_2]^* - (\% iO_2) \right)}{100M_{o,s}}
\]

where $J_i$ is the molar flow, mol·m$^{-2}$·s$^{-1}$; $k_{i,m}$ and $k_{i,s}$ are the mass transfer coefficients for components in molten alloy and slag; and $k_{Al} = k_{Ti} = k_{Si} = 2 \times 10^{-4}$ m·s$^{-1}$,

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**Figure 1:** Mass transfer diagram of the slag–metal interface ($a_0^*$ is the oxygen activity at the interface).
According to Eq. 11, the interface concentration of element i in the alloy can be expressed as

\[
\text{[\% i]*} = \frac{k_\text{cat}*M_{\text{AI}}}{k_{\text{cat}*M_{\text{AI}}} + B_i a_{O*}^i}
\]

where \(B_i\) is the apparent equilibrium constant, which is expressed as Eq. 12:

\[
B_i = \frac{(\% O*)}{[\% i]*a_{O*}^i}
\]

where \(K_{ii}\) is the equilibrium constant, \(f_i\) is the activity coefficient of component i in alloy, and \(Y_{O*}\) is the activity coefficient of component i in the slag. \(f_i\) and \(Y_{O*}\) are calculated by Eqs. 13 and 14:

\[
\log f_i = \sum (e_i[\% j] + r_i[\% j]^2)
\]

\[
Y_{O*} = \frac{a_{O*}}{(\% O*)}
\]

where \(e_i\) and \(r_i\) are the first-order interaction parameter and second-order interaction parameter. The first-order interaction parameters used in the present study are listed in Table 1. The available second-order interaction parameters are summarized as \(r_{\text{AI}}^\text{Si} = -0.004, r_{\text{AL}}^\text{Ni} = (-0.0011 + 0.17/T), r_{\text{AL}}^\text{Cr} = -0.0006, r_{\text{AL}}^\text{Cu} = 0.00164, r_{\text{AL}}^\text{Mo} = (-0.0055 + 6.5/T), r_{\text{AL}}^\text{Si} = 0.00043, r_{\text{AL}}^\text{Ti} = -0.001, \) and \(r_{\text{AL}}^\text{Ni} = 0.0005\) [30]. \(a_{O*}\) is the activity of components in the slag, calculated by the FactSage7.3 software, and the standard state activity of components in the slag is the pure substance standard.

The reaction rate of Al, Ti, Si, and O are given as Eqs. 15–18:

\[
-d[\% \text{Al}] = \frac{A_{\text{Wm}}}{\text{Wm}} \left( [\% \text{Al}] - \left( \frac{M_{\text{Al}}}{{\text{B}_i a_{O*}^i}} \right) \right)
\]

\[
-d[\% \text{Ti}] = \frac{A_{\text{Wm}}}{\text{Wm}} \left( [\% \text{Ti}] - \left( \frac{M_{\text{Ti}}}{{B}_i a_{O*}^i} \right) \right)
\]

\[
-d[\% \text{Si}] = \frac{A_{\text{Wm}}}{\text{Wm}} \left( [\% \text{Si}] - \left( \frac{M_{\text{Si}}}{{B}_i a_{O*}^i} \right) \right)
\]

\[
-d[\% \text{O}] = \frac{A_{\text{Wm}}}{\text{Wm}} \left( [\% \text{O}] - \left( \frac{M_{\text{O}}}{{B}_i a_{O*}^i} \right) \right)
\]

where \(W_m\) is the mass of molten steel and \(k_i\) is the comprehensive mass transfer coefficient of i. The oxygen activity at the slag–metal interface can be obtained from the above equations and the mass balance equation for oxygen at the interface. Therefore, the following equation can be obtained:

\[
\frac{1.5}{M_{\text{Al}}} \frac{d[\% \text{Al}]}{dt} + \frac{2}{M_{\text{Ti}}} \frac{d[\% \text{Ti}]}{dt} + \frac{2}{M_{\text{Si}}} \frac{d[\% \text{Si}]}{dt} - \frac{1}{M_{\text{O}}} \frac{d[\% \text{O}]}{dt} = 0
\]

The variation of Al2O3, TiO2, and SiO2 in the slag without considering volatilization can be determined on the basis of Eqs. 15–18 and mass conservation.

### 3 Experimental

Incoloy 825 alloy was smelted in a vacuum induction furnace, and its composition is shown in Table 2. The experimental slag samples were prepared by analytical-grade pure chemical reagents (CaF2 ≥ 99%, CaO ≥ 98%, Al2O3 ≥ 99%, MgO ≥ 99%, Li2O ≥ 99%, TiO2 ≥ 99%). The CaF2 and Li2O reagent powders were heated at 973 K for 4 h, and CaO, Al2O3, MgO, and TiO2 reagent powders were heated at 1,273 K for 4 h to remove the moisture. The thoroughly mixed powders were melted at 1,773 K for 15 min in a graphite crucible to ensure complete melting and homogenization. When the experiments

### Table 1: A first-order interaction parameter \(e_i\) used in the current study [31–34]

| \(e_i\) | Mn | Cr | Ni | Al | Ti | Cu | Mo | Si | O |
|--------|----|----|----|----|----|----|----|----|----|
| Al     | 0.034 | 0.045 | -0.0376 | 0.040 | - | - | - | - | -34.740/T + 11.95 |
| Ti     | -0.12 | 0.025 | -0.0166 | - | 0.048 | 0.014 | 0.016 | - | -1.6 |
| Si     | - | -0.021 | -0.009 | 0.058 | - | - | - | 0.132 | -0.23 |
| O      | -0.021 | -0.032 | 0.006 | 7.15–20,600/T | -0.6 | - | - | -0.331 | 0.734–1,750/T |
were finished, the liquid sample was taken out and quenched quickly on a water-cooled copper plate. Then, the quenched slag samples were pulverized to 200 mesh for chemical analysis. The chemical composition of the slag before and after melting is shown in Table 3.

The equipment for the experiment is shown in Figure 2, where the sample was heated to the target temperature by six MoSi₂ heating elements. The temperature of liquid metal is measured by a B-type reference thermocouple. An Ar flow of 2 L·min⁻¹ is used to prevent the alloy elements from being oxidized by air during the experiment. About 350 g of alloy and 50 g of slag were used in each experiment. The certain reaction time intervals were 5, 10, 15, 20, 25, and 30 min respectively. Firstly, the alloy was placed in the MgO crucible (Φ 50 mm × 60 mm). Then, the crucible was placed in a graphite crucible (Φ 70 mm × 80 mm) to prevent the liquid metal from leaking. The resistance furnace was heated to 1,773 K at a rate of 8 K·min⁻¹ under an Ar atmosphere, holding it at 1,773 K for 10 min to ensure the complete melting of the alloy. Then, 50 g of the slag sample was quickly added into the MgO crucible by a quartz tube having an inner diameter of 10 mm. After reaching the set time, the whole crucible was rapidly removed from the furnace and quenched. The Al, Ti, and Si content in the alloy were determined by inductively coupled plasma-atomic emission spectroscopy. The oxygen content in the alloy was determined by the G8GALILEO oxygen nitrogen hydrogen analyzer, and the chemical composition of the slag was analyzed by X-ray fluorescence.

### 4 Results and discussion

#### 4.1 Changes of Al, Ti, and Si content in the alloy

Figure 3 shows the variation of the calculated and measured contents of Al, Ti, Si in the alloy. The content of Al, Ti, and Si in the alloy changing within 15 min indicates that the slag–metal reaction reached the equilibrium at 15 min. As shown in Figure 3a and b, when TiO₂ content in slag increases from 3.57% to 7.27%, the content of Ti in the alloy decreased from 1% to 0.61% and 0.87%, respectively. The Al content in the alloy respectively increased from 0.12% to 0.21% and 0.14%, and the change of Si content in the alloy showed a decreasing trend and was independent of the change in TiO₂ content in the slag.

### Table 2: Chemical composition of the Incoloy 825 alloy (%)  

| C  | Mn | Si | P | S  | Cr | Mo | Ni | Cu | Al | Ti | T[O] | Fe |
|----|----|----|---|----|----|----|----|----|----|----|------|----|
| 0.101 | 0.107 | 0.131 | 0.009 | 0.009 | 20.62 | 3.18 | 38.88 | 1.66 | 0.12 | 1.00 | 0.0026 | Bal. |

### Table 3: Chemical composition of the slag before and after premelting (%)  

| Slag Before premelting | After premelting |
|------------------------|------------------|
| CaF₂ | CaO | Al₂O₃ | MgO | Li₂O | TiO₂ | CaF₂ | CaO | Al₂O₃ | MgO | Li₂O | TiO₂ | SiO₂ |
| N1 | 23.00 | 31.70 | 35.30 | 2.00 | 4.00 | 4.00 | 20.48 | 36.13 | 34.68 | 1.63 | 3.21 | 3.57 | 0.08 |
| N2 | 23.00 | 29.80 | 33.20 | 2.00 | 4.00 | 8.00 | 20.62 | 34.21 | 32.54 | 1.49 | 3.24 | 7.27 | 0.11 |
| N3 | 23.00 | 27.90 | 31.10 | 2.00 | 4.00 | 12.00 | 20.39 | 32.94 | 30.25 | 1.50 | 3.41 | 11.28 | 0.09 |

Figure 2: Schematic diagram of the equipment of the experiment.
The equilibrium Al and Ti content and their linear fitting after the slag–metal reaction are shown in Figure 4. It can be seen that the equilibrium Al and Ti content in the alloy show a completely opposite linear relationship. It indicates that elements Ti and Al in the alloy were oxidized by Al₂O₃ and TiO₂ in the slag when the content of TiO₂ was less than 7.27% during the process of slag–metal loss of Ti to increase Al. Moreover, with the increase of TiO₂ content in the slag, the TiO₂ activity increased and enhanced the reactivity with Al in the alloy. The reaction $4[\text{Al}] + 3(\text{TiO}_2) = 3[\text{Ti}] + 2(\text{Al}_2\text{O}_3)$ is going in the positive direction with increasing TiO₂ content. When TiO₂ content in slag was 11.27%, the Ti content in the alloy increased from 1% to 1.18% and Al content decreased from 0.12% to 0.10% during the experiment. It indicates that the element Al in the alloy was oxidized by TiO₂ in the slag, the Gibbs

![Figure 3](image)

**Figure 3:** Experimental and calculated results of the content of Al, Ti, and Si in the alloy: (a) 3.57% TiO₂, (b) 7.27% TiO₂, (c) 11.27% TiO₂.

![Figure 4](image)

**Figure 4:** (a) and (b) Fitting lines of experimental results.
free energy for the reaction \(4\text{[Al]} + 3\text{(TiO}_2\text{)} = 3\text{[Ti]} + 2\text{(Al}_2\text{O}_3\text{)}\) was more negative (the authors have performed the calculation process listed in the literature [35]), leading to the loss of Al and increase of Ti in alloy.

The equilibrium constant expression of Eq. 1 is shown in Eq. 21:

\[
\lg \frac{X^3_{\text{Al}}}{X^3_{\text{Al}}} = \frac{35,300}{T} - 9.94 - \frac{\Delta G_1^0}{R} \frac{2}{a_{\text{Al}_2\text{O}_3}^2} - \frac{\Delta G_1^0}{R} \frac{3}{a_{\text{Ti}_2\text{O}_3}^3} \tag{21}
\]

According to Eq. 21, the appropriate value of \(\lg \frac{a_{\text{Al}_2\text{O}_3}^2}{a_{\text{Ti}_2\text{O}_3}^3}\) in the slag was 4.24. The activities of \(\text{Al}_2\text{O}_3\), \(\text{Ti}_2\text{O}_3\), and \(\lg (a_{\text{Al}_2\text{O}_3}^2/a_{\text{Ti}_2\text{O}_3}^3)\) values of three slags were calculated by Fact-Sage as shown in Table 4. It can be seen from Table 4 that the values of \(\lg (a_{\text{Al}_2\text{O}_3}^2/a_{\text{Ti}_2\text{O}_3}^3)\) decreased gradually with the increase of \(\text{Ti}_2\text{O}_3\) content, and it indicates that the equilibrium Ti content increased and equilibrium Al content decreased. But the values of \(\lg (a_{\text{Al}_2\text{O}_3}^2/a_{\text{Ti}_2\text{O}_3}^3)\) in N1 and N2 slags greater than 4.24. It can be concluded that the Ti content decreased and Al content increased whereas the values of \(\lg (a_{\text{Al}_2\text{O}_3}^2/a_{\text{Ti}_2\text{O}_3}^3)\) in N3 slag was smaller than 4.24. Therefore, the content of Ti and Al in the alloy increased and decreased, respectively. The calculated result was in good agreement with experimental result.

\[
\Delta G = -RT \ln K^\theta \tag{22}
\]

\[
\Delta G = \Delta G^0 + RT \ln \frac{a_{\text{Al}_2\text{O}_3}^2}{a_{\text{Ti}_2\text{O}_3}^3} \tag{23}
\]

The Gibbs free energy of the reactions according to Eqs. 7–9, 22, and 23 between Si in the alloy, \(\text{Al}_2\text{O}_3\), and \(\text{Ti}_2\text{O}_3\) in the slag were 49.6 and 487.2 kJ mol\(^{-1}\) respectively, which were both positive. The reaction between oxygen and Si in the liquid alloy was \(-188\) kJ mol\(^{-1}\), which was negative. It can be concluded that Si in the alloy reacts with oxygen, which is also reason for the changes of the element Si in Figure 3a–c, and it decreased from 0.13% to about 0.04%. The results showed that changes of Al and Ti in the alloy were determined by the reaction \(4\text{[Al]} + 3\text{(TiO}_2\text{)} = 3\text{[Ti]} + 2\text{(Al}_2\text{O}_3\text{)}\).

The calculated results are in good agreement with the experimental results, indicating that the kinetic model proposed by the two-film theory can predict the changes of Al, Ti, and Si content of the alloy with the progress of the slag–metal reaction.

### 4.2 Changes of oxygen content in the alloy and mass transfer resistance of the slag–metal reaction

Figure 5 shows the changes of oxygen content in the alloy. Figure 5a–c shows the variation of oxygen in the alloy with N1, N2, and N3 slags during the slag–metal reaction. As shown in Figure 5, the content of oxygen in the alloy continues to decrease, which is caused by the reaction of Al, Ti, and Si in the alloy with oxygen in the melt. Moreover, the contents of measured oxygen were higher than the calculated results; this is because that the oxygen content is taken as soluble oxygen in the above theoretical calculation. However, the total oxygen consists of soluble oxygen and oxygen in the form of oxide inclusions. This is consistent with the calculation results of Duan et al. [36].

Table 5 shows the mass transfer resistance components in the alloy and slag during the progress of the slag–metal reaction. As shown in Table 4, with the increase of \(\text{TiO}_2\) content, the mass transfer resistance of \(\text{TiO}_2\) in the slag decreased from 0.031 to 0.012 m\(^2\)-kg\(^{-1}\), resulting in an increasing trend of Al oxidation. The mass transfer resistance of \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\) changed little. The controlling step of the reaction \(4\text{[Al]} + 3\text{(TiO}_2\text{)} = 3\text{[Ti]} + 2\text{(Al}_2\text{O}_3\text{)}\) was the mass transfer of Al and Ti in the liquid alloy. The controlling step of reactions \([\text{Si]} + \text{[TiO}_2\text{]} = \text{[Ti]} + \text{[SiO}_2\text{]}\) and \([\text{Al]} + \text{[SiO}_2]) = \text{[Si]} + \text{[Al}_2\text{O}_3\text{]}\) was the mass transfer of \(\text{SiO}_2\) in the molten slag, which caused the low content of \(\text{SiO}_2\) in slag.

### 4.3 Variation of components in the slag

Figure 6 shows the variation of \(\text{Al}_2\text{O}_3\), \(\text{TiO}_2\), and \(\text{SiO}_2\) in the slag. As shown in Figure 6a, the calculated results of \(\text{Al}_2\text{O}_3\) are different from the measured results. This is because the initial \(\text{Al}_2\text{O}_3\) content in the slag is relatively high whereas the Al content in the alloy is low, so the change in Al content has a small effect on the \(\text{Al}_2\text{O}_3\) content in the slag. Meanwhile, it also can be seen that when

| Slag | \(a_{\text{TiO}_2}\) | \(a_{\text{Al}_2\text{O}_3}\) | \(\lg (a_{\text{Al}_2\text{O}_3}^2/a_{\text{TiO}_2}^3)\) |
|------|-----------------|-----------------|-----------------|
| N1   | \(1.55 \times 10^{-3}\) | \(1.32 \times 10^{-2}\) | 4.67            |
| N2   | \(4.51 \times 10^{-3}\) | \(4.78 \times 10^{-2}\) | 4.39            |
| N3   | \(8.17 \times 10^{-3}\) | \(8.11 \times 10^{-2}\) | 4.08            |
the TiO₂ content increases, the activity of Al₂O₃ also increases. This is due to the combination of TiO₂ and CaO in the slag to form CaTiO₃. The content of CaO combined with Al₂O₃ decreases, which increases the activity of Al₂O₃ and strengthens the reactivity of CaF₂. Some researchers have confirmed that AlF₃ volatilization is large in the electroslag system [37,38]. Li et al. [39] also found that the content of Al₂O₃ in the slag decreased after the completion of the industrial electroslag experiment. Therefore, the change in the content of Al₂O₃ in the slag is dominated by the reaction $3\text{CaF}_2 + \text{Al}_2\text{O}_3 = 3\text{CaO} + 2\text{AlF}_3(g)$.

Figure 6b shows that the measured results of TiO₂ content in the slag were in good agreement with the calculated results. The TiO₂ content increased in the N1 and N2 slags and decreased slightly in the N3 slag. The reaction between Ti in the alloy and Al₂O₃ in the slag caused the increase of TiO₂ content in the N1 and N2 slags, and the decrease of TiO₂ content in the N3 slag was due to the reaction between TiO₂ in the slags and Al in the alloy.

The variation of SiO₂ is shown in Figure 6c. There is a deviation between the measured and calculated results, which is also caused by volatilization. The Si element in the alloy reacts with soluble oxygen to form SiO₂ entering into the slag, and the SiO₂ content in the slag increases at the initial stage of the slag–metal reaction. When the SiO₂ content accumulates to a certain extent, the reaction CaF₂ + 2SiO₂ = CaO + 2SiF₄(g) [40] occurred. Although the SiO₂ content is small, the vapor pressure of SiF₄ is larger than that of AlF₃ under standard conditions [41], so a

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**Table 5:** Mass transfer resistance of components in the alloy and slag

| Slag | Mass transfer resistance of Al, Ti, and Si | Mass transfer resistance of Al₂O₃ | Mass transfer resistance of TiO₂ | Mass transfer resistance of SiO₂ |
|------|------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
|      | $1/\rho_{w} K_i i_m$                      | $M_{\text{AlO}_1.5}$            | $M_{\text{TiO}_2}$             | $M_{\text{SiO}_2}$             |
| N1   | 0.625                                    | $9.6 \times 10^{-4}$            | 0.031                          | 11.07                          |
| N2   | 0.625                                    | $8.9 \times 10^{-4}$            | 0.019                          | 12.7                           |
| N3   | 0.625                                    | $8.9 \times 10^{-4}$            | 0.012                          | 13.1                           |

---

*Figure 5:* Changes of oxygen content in alloys: (a) N1, (b) N2, and (c) N3.
small amount of SiF$_4$ is volatilized and reduces the SiO$_2$ content in the slag. Compared with the measured result, the Al$_2$O$_3$ and SiO$_2$ content in the slag decreased about 3% and 0.5% respectively, which had no influence on the slag–metal equilibrium. This is supported by the measured and calculated results of Al and Ti content in the alloy as shown in Section 4.1.

The content variation of CaF$_2$ in the slag is shown in Figure 7. During the process reaction of the slag–metal, the CaF$_2$ content decreased significantly within 15 min, and then tended to stabilize. The content of Al$_2$O$_3$ and SiO$_2$ in the slag also changed within 15 min. This proves that the content of CaF$_2$, Al$_2$O$_3$, and SiO$_2$ decreased in the slag because they reacted with each other within 15 min, and the change in the CaF$_2$ content was not affected by the content of TiO$_2$ in the slag. The content of all was reduced by about 5% each.

5 Conclusion

1. The experimental results of Al and Ti content in the alloy are in good agreement with the calculated results. The Al content in the alloy decreases with the increase of TiO$_2$ content in the slag whereas the change of Ti content is the opposite.
2. The content of Si and O in the alloy decreased continuously during the experiment, and the change of Si content was not affected by the change of TiO$_2$ content in the slag.
3. The controlling step of the reaction 4[Al] + 3(TiO$_2$) = 3[Ti] + 2(Al$_2$O$_3$) was the mass transfer of Al and Ti in the liquid alloy. The controlling step of reactions [Si] + (TiO$_2$) = [Ti] + (SiO$_2$) and [Al] + (SiO$_2$) = [Si] + (Al$_2$O$_3$) was the mass transfer of SiO$_2$ in the molten slag.
4. The measured results of $Al_2O_3$ and $SiO_2$ in the slag were lower than the calculated results, which were reduced by about 3% and 0.5%, respectively. The measured results of TiO$_2$ content were in accordance with the calculated results and change of Ti content in the alloy.

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