Article

Study on the Melting Temperature of CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ Slag under the Condition of a Fixed Ratio of Titanium and Aluminum in the Steel during the Electroslag Remelting Process

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Abstract: During the process of electroslag remelting (ESR) of steel containing titanium and aluminum, the activity ratio between titania and alumina in CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ slag must be fixed in order to guarantee the titanium and aluminum contents in the ESR ingots. Under the condition of fixed activity ratio between titania and alumina in the slag, the melting temperature of slag should be investigated to improve the surface quality of ESR ingots. Therefore, this paper focuses on finding a kind of slag with low melting temperature that can be used for producing steel containing titanium. In the current study, the thermodynamic equilibrium of $3[\text{Ti}]+2(\text{Al}_2\text{O}_3)=4[\text{Al}]+3(\text{TiO}_2)$ between SUS321 steel and the two slag systems (CaF$_2$:MgO:CaO:Al$_2$O$_3$:TiO$_2$=46:4:25:(25–x):x) and CaF$_2$:MgO:CaO:Al$_2$O$_3$:TiO$_2$=46:4:25:0.5:x) are studied in an electrical resistance furnace based on Factsage software. After obtaining the equilibrium slag with fixed activity ratio between titania and alumina, the melting temperatures of the two slag systems are studied using slag melting experimental measurements and phase diagrams. The results show that the slag systems CaF$_2$:MgO:CaO:Al$_2$O$_3$:TiO$_2$=46:4:25:(25–x):x, which consists of pre-melted slag (CaF$_2$:MgO:CaO:Al$_2$O$_3$=46:4:25:25) and pre-melted slag F1 (CaF$_2$:MgO:CaO:TiO$_2$=46:4:25:25), can not only control the aluminum and titanium contents in steel, but also have the desired low melting temperature property.

Keywords: electroslag remelting; melting temperature of slag; steel containing titanium; thermodynamics; phase diagram

1. Introduction

Electroslag remelting (ESR) [1,2] is one of the processes used to produce high quality special steels. During ESR process, the slag plays important roles in chemical composition and surface quality of ingot. On the one hand, the slag CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ should have the fixed activity ratio of $\lg(a^3_{\text{TiO}_2}/a^2_{\text{Al}_2\text{O}_3})$ to guarantee the thermodynamic equilibrium of $3[\text{Ti}]+2(\text{Al}_2\text{O}_3)=4[\text{Al}]+3(\text{TiO}_2)$ and the ratio of $\lg(w^3_{\text{Ti}}/w^4_{\text{Al}})$ in steel. On the other hand, the slag should also have a low melting temperature to improve the surface quality of the ESR ingots. Especially for superalloy or stainless steel with a melting temperature lower than 1370 °C (1643 K), the melting point of the slag used for ESR of superalloy and stainless steel should be lower than 1270 °C (1543 K). Therefore, it is essential to investigate the melting temperature of CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ slag under the condition of fixing activity ratio of titania and alumina in the slag during the ESR process.

The studies on CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ slag used for steel containing titanium are mainly divided into two categories: one is about the effect of TiO$_2$ on the physical
property of slag, and the other is about the effect of each slag component on the activities of TiO$_2$ and Al$_2$O$_3$. Shi [3–5] studied the effect of TiO$_2$ on the crystallization behavior of CaF$_2$-CaO-Al$_2$O$_3$-MgO-TiO$_2$ slag and pointed out that TiO$_2$ has large effect on the physical property of the slag. Duan [6,7] studied the effect of each slag component on the activities of Al$_2$O$_3$ and TiO$_2$, and determined an appropriate slag to be used for ESR of superalloys based on experiments and thermodynamics. Jiang [8–16] investigated the thermodynamic equilibrium of 3[Ti] + 2(Al$_2$O$_3$) = 4[Al] + 3(TiO$_2$) and the effect of slag components on activities of Al$_2$O$_3$ and TiO$_2$ in CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ slag system, and then TiO$_2$ in slag was calculated to control the titanium and aluminum contents in ESR ingot. However, the above researches [17–21] did not comprehensively consider the physical properties and thermodynamic equilibrium of 3[Ti] + 2(Al$_2$O$_3$) = 4[Al] + 3(TiO$_2$). Under the condition of controlling the titanium and aluminum contents in steel, the optimized slag with low melting temperature cannot be acquired according to the studies above.

To the best of the authors’ knowledge, under the condition of fixing activity ratio between titania and alumina in slag, investigation on the melting temperature of slag has not been reported so far. In the present work, the thermodynamic equilibrium of 3[Ti] + 2(Al$_2$O$_3$) = 4[Al] + 3(TiO$_2$) was studied by the slag-metal reaction in a resistance furnace and the Factsage software. After obtaining the equilibrium slag with fixed activity ratio between titania and alumina, the melting temperature of CaF$_2$-CaO-Al$_2$O$_3$-MgO-TiO$_2$ slag was studied by slag melting experimental measurements and phase diagram. At last, the slag design diagram consisting of $\log(a_{\text{TiO}_2}/a_{\text{Al}_2\text{O}_3})$ isoactivity lines and slag phase diagram (CaF$_2$:MgO:CaO:Al$_2$O$_3$:TiO$_2$ = 46:4:x:y:z, x + y + z = 50) was made for acquiring the optimized CaF$_2$-CaO-Al$_2$O$_3$-MgO-TiO$_2$ slag with low melting temperature.

2. Experimental

2.1. Slag-Metal Reaction Experiments in Resistance Furnace

SUS321 stainless steel produced by Dongbei special steel group Co. Ltd, Dalian, China was used in current study. Its chemical composition is listed in Table 1. Its chemical composition is listed in Table 1. The chemical compositions of Slag S0F1-82, S0F1-64, S0F2-82 and S0F2-64 are listed in Table 2, and the chemical compositions of pre-melted slag S0, F1 and F2 are listed in Table 3. Each slag-metal reaction experiment is carried out with 80 g slag and 50 g steel by using a resistance furnace, as shown in Figure 1. The heating unit is made of molybdenum disilicide. The temperature of the liquid metal is continuously measured by means of a B-type reference thermocouple produced by Kejing material technology Co. Ltd, Hefei, China. Argon is used to protect the slag-metal reaction system from top and bottom of the furnace at the rate of 2 Nl/min.

| Exp. | Slag | CaF$_2$ | CaO | MgO | Al$_2$O$_3$ | TiO$_2$ |
|------|------|---------|------|------|-------------|--------|
| S0F1-82 | S0:F1 = 8:2 | 46 | 25 | 4 | 20 | 5 |
| S0F2-82 | S0:F2 = 8:2 | 46 | 22.5 | 4 | 22.5 | 5 |
| S0F1-64 | S0:F1 = 6:4 | 46 | 25 | 4 | 15 | 10 |
| S0F2-64 | S0:F2 = 6:4 | 46 | 20 | 4 | 20 | 10 |
Table 1. Chemical composition of the SUS321 (Mass pct).

| Slag     | Slag Ratio | CaF<sub>2</sub> | CaO | Al<sub>2</sub>O<sub>3</sub> | MgO | TiO<sub>2</sub> | Halfsphere Temperature, K | Flowing Temperature, K |
|----------|------------|-----------------|-----|----------------|-----|--------------|--------------------------|------------------------|
| S0       | –          | 46              | 25  | 25              | 4   | 0            | 1560                     | 1570                   |
| F1       | –          | 46              | 25  | 22              | 4   | 3            | 1605                     | 1614                   |
| F2       | –          | 46              | 12.5| 12.5            | 4   | 25           | 1618                     | 1629                   |
| S0F1-1   | S0:F1 = 88:12 | 46         | 25  | 22              | 4   | 6            | 1543                     | 1554                   |
| S0F1-2   | S0:F1 = 76:24 | 46         | 25  | 19              | 4   | 6            | 1534                     | 1546                   |
| S0F1-3   | S0:F1 = 64:36 | 46         | 25  | 16              | 4   | 9            | 1533                     | 1539                   |
| S0F1-4   | S0:F1 = 60:40 | 46         | 25  | 15              | 4   | 10           | 1535                     | 1542                   |
| S0F2-1   | S0:F2 = 88:12 | 46         | 23.5| 23.5            | 4   | 3            | 1548                     | 1559                   |
| S0F2-2   | S0:F2 = 79:21 | 46         | 22.375| 22.375        | 4   | 5.25         | 1550                     | 1559                   |
| S0F2-3   | S0:F2 = 76:24 | 46         | 22  | 22              | 4   | 6            | 1549                     | 1560                   |
| S0F2-4   | S0:F2 = 67:33 | 46         | 20.875| 20.875         | 4   | 8.25         | 1566                     | 1576                   |
| S0F2-5   | S0:F2 = 64:36 | 46         | 20.5| 20.5            | 4   | 9            | 1572                     | 1581                   |

Figure 1. Schematic diagram of resistance furnace with function of dropping crucible from bottom.

The experimental procedures can be described as follows. Firstly, 50 g of steel and 80 g of slag are placed into a MgO crucible with 30 mm inner diameter and 70 mm in depth. Then the crucible is placed in a graphite crucible with molybdenum wire for suspension. After the whole crucible is placed in the chamber, the power is switched on and the furnace is heated to the experimental temperature (1823 K (1550 °C)) at a rate of 8 K/min.

After the furnace temperature was held for 60 min at 1823 K (1550 °C) [8,9], the crucible was dropped into liquid water quickly. The contents of Si, Al and Ti in each steel sample are analyzed by the inductively coupled plasma-mass spectroscopy (ICP-MS) technique and the concentrations of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and MgO in slag samples are analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The results are listed in Table 4.

Table 4. The chemical composition of steel and slag after slag-metal reaction experiments (Mass pct).

| Exp.     | Si  | Ti  | Al  | Al<sub>2</sub>O<sub>3</sub> | TiO<sub>2</sub> | MgO  | lg(Al<sup>3+<sub>TiO<sub>2</sub></sub>) / lg(Al<sup>3+<sub>MgO</sub></sub>) |
|----------|-----|-----|-----|----------------|-------------|------|----------------------------------|
| S0F1-82  | 0.68| 0.33| 0.058| 18.91            | 4.75        | 9.84 | −3.57                            |
| S0F2-82  | 0.69| 0.35| 0.053| 21.28            | 4.64        | 10.69| −3.21                            |
| S0F1-64  | 0.66| 0.40| 0.032| 14.39            | 9.51        | 9.61 | −3.42                            |
| S0F2-64  | 0.68| 0.42| 0.028| 18.91            | 9.37        | 10.93| −2.89                            |
2.2. Slag Melting Temperature Tests

During industrial ESR of steel containing different titanium and aluminum contents process, the TiO\textsubscript{2} powder combined with pre-melted slag CaF\textsubscript{2}-CaO-Al\textsubscript{2}O\textsubscript{3}-MgO are added into the water cooling molds of the ESR furnace. In order to prevent the TiO\textsubscript{2} powder from volatilizing with the air flow during the slag addition process, a new pre-melted slag S0 without TiO\textsubscript{2} and a pre-melted slag F1(F2) with high TiO\textsubscript{2} are designed. Their compositions are listed in Table 3. By mixing S0 and F1 in the ratio of 88:12, the slag S0F1-1 in Table 3 was acquired. Slag S0F1-2 and S0F1-3 can be acquired when the ratios of S0:F1 are 76:24 and 64:36, respectively. Slag S0F2-1, S0F2-2 and S0F2-3 can be acquired when the ratios of S0:F2 are 88:12, 76:24 and 64:36, respectively.

Slag melting experiments were carried out by using a high temperature specimen deformation method. A diagram of the test system is shown in Figure 2. In order to evaluate the melting behavior, the pre-melted slag powders were compressed into cylindrical samples of 3 mm diameter and 3 mm high. For each test, the slag sample was placed at the centre of a corundum substrate which was then located within the hot zone of a molybdenum wire furnace. The furnace was heated at 10 °C/min up to the slag melting temperature, which is defined as the temperature at which the cylindrical specimen attained a hemispherical shape. The melting temperature of slag was measured using a high temperature microscope, and the results are listed in Table 3.

![Figure 2. Test facility for determination of slag melting behavior.](image)

3. Results and Discussion

3.1. Slag-Metal Reaction Experiments Results

The results of slag-metal reaction experiments in resistance furnace are shown in Table 4. Due to the existence of unstable oxides SiO\textsubscript{2} and FeO, both aluminum and titanium are lower than them in the steel before experiments. If assuming that the slag-metal reaction of $3[\text{Ti}] + 2(\text{Al}_2\text{O}_3) = 4[\text{Al}] + 3(\text{TiO}_2)$ in Table 4 reaches thermodynamic equilibrium \cite{8,9}, the activity coefficients of alloy element in steel and oxide component in slag can be experimental measured based on thermodynamics. At the slag-metal interface under 1550 °C, the following Reaction (1) will take place \cite{22,23}. After substituting Ti, Al, Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} of Table 4 into Equation (2), the activity coefficient value of Equation (2) in Exp.S0F1-82, Exp.S0F2-82, Exp.S0F1-64 and Exp.S0F1-64 are experimental measured as $-3.57$, $-3.21$, $-3.42$ and $-2.89$, as shown in Table 4.

$$3[\text{Ti}] + 2(\text{Al}_2\text{O}_3) = 4[\text{Al}] + 3(\text{TiO}_2) \quad (1)$$
\[ \lg K = \lg \frac{\gamma_{\text{Al}}^3 \gamma_{\text{Al}_{2}O_3}^3}{\gamma_{\text{Ti}}^3 \gamma_{\text{TiO}_2}^3} = \frac{w_{\text{Al}}^3 [\text{Al}_{2}O_3]}{w_{\text{Ti}}^3 [\text{TiO}_2]} \gamma_{\text{TiO}_2}^3 + \frac{f_{\text{Al}}^3 \gamma_{\text{Al}_{2}O_3}^3}{f_{\text{Ti}}^3 [\gamma_{\text{Ti}}]} = -\frac{35300}{T} + 9.94 \] (2)

where \( \gamma_{\text{TiO}_2} \) and \( \gamma_{\text{Al}_{2}O_3} \) are the activities of TiO_2 and Al_{2}O_3 in the slag; \( X_{\text{TiO}_2} \) and \( X_{\text{Al}_{2}O_3} \) are the mole fraction of TiO_2 and Al_{2}O_3 in slag; \( \gamma_{\text{TiO}_2} \) and \( \gamma_{\text{Al}_{2}O_3} \) are the activity coefficients of TiO_2 and Al_{2}O_3 in slag; \( f_{\text{Al}} \) and \( f_{\text{Ti}} \) are the activity coefficients of Al and Ti; \( \frac{f_{\text{Al}}^3 \gamma_{\text{Al}_{2}O_3}^3}{f_{\text{Ti}}^3 [\gamma_{\text{Ti}}]} \) is the activity coefficient of Equation (2).

During the slag-metal reaction experiments, the MgO in slag after experiments was increased to 10% because of MgO crucible being eroded by slag. In order to investigate the thermodynamic equilibrium of SUS321 steel and slag S0-F1(F2) further, the activity coefficients of Ti and Al in steel are calculated by Equation (3) and the value of \( \lg \gamma_{\text{TiO}_2} / \gamma_{\text{Al}_{2}O_3} \) is considered as \(-0.12\). The interaction parameters [24–26] used in present study are listed in Table 5. The activity coefficients of TiO_2 and Al_{2}O_3 in slag are calculated based on Factsage 7.3-FToxid FactPS. The change of activity coefficient of Equation (2) with MgO in Exp.S0F1-82, Exp.S0F2-82, Exp.S0F1-64 and Exp.S0F1-64 are calculated, as shown in Figure 3a. It is clear that the calculated results in Figure 3a are in good agreement with measured results listed in Table 4.

\[
\lg f_i = \sum c' [\% w_j] \]

(3)

### Table 5. Activity interaction coefficient \( c' \) of the constituent in the present work.

| \( c' \) | C | Si | Mn | P | S | Al | Ti | Cr | Ni |
|---|---|---|---|---|---|---|---|---|---|
| Al | 0.091 | 0.056 | 0.035 | 0.033 | 0.035 | 0.08 | 0.004 | 0.03 | - |
| Ti | -0.19 | -0.025 | -0.043 | -0.0064 | -0.27 | 0.0037 | 0.013 | 0.055 | 0.009 |

**Figure 3.** (a) The change of activity coefficient of Equation (2) with MgO, and (b) the change of \( \lg (\gamma_{\text{TiO}_2} / \gamma_{\text{Al}_{2}O_3}^3) \) with CaO in slag calculated by Factsage.

Figure 3a shows that the activity coefficient values of Equation (2) under slag S0:F1 = 8:2, S0:F1 = 6:4, S0:F2 = 8:2 and S0:F2 = 6:4 can be calculated as \(-3.33\), \(-3.20\), \(-2.95\) and \(-2.52\), as listed in Table 6. After obtained the activity coefficient value of Equation (2) in each slag, the slag S0:F1 = 8:2, S0:F1 = 6:4, S0:F2 = 8:2, S0:F2 = 6:4 and corresponding \( \lg (w_{\text{Al}}^3 / w_{\text{Ti}}^3) \) are calculated in Table 6, which will be used as points in Figure 4.
Table 6. The relationship between $\lg (w_{Ti}^3/w_{Al}^4)$ and slag listed in Table 2 determined by experiments.

| Slag     | CaF$_2$ | CaO | MgO | Al$_2$O$_3$ | TiO$_2$ | $\lg (\gamma_{TiO_2}^3/\gamma_{Al_2O_3}^2)$ | $\lg (w_{Ti}^3/w_{Al}^4)$ |
|----------|---------|-----|-----|-------------|---------|--------------------------------------------|--------------------------|
| S0:F1 = 8:2 | 46      | 25  | 4   | 20          | 5       | -3.33                                      | 3.76                     |
| S0:F2 = 8:2 | 46      | 22.5| 4   | 22.5        | 5       | -2.95                                      | 4.04                     |
| S0:F1 = 6:4 | 46      | 25  | 4   | 15          | 10      | -3.20                                      | 5.03                     |
| S0:F2 = 6:4 | 46      | 20  | 4   | 20          | 10      | -2.52                                      | 5.49                     |

Figure 4. The changes of S0:F1 and S0:F2 ratios in slag mixtures with $\lg (w_{Ti}^3/w_{Al}^4)$ in steel.

It is also can be seen that the activity coefficients of Equation (2) in each slag listed in Table 6 are different, it is different CaO content in slag that changes the activity coefficients of TiO$_2$ and Al$_2$O$_3$, which has been studied based on ion and molecular coexistence theory (IMCT) in the previous study [8,9]. The changes of $\lg (\gamma_{TiO_2}^3/\gamma_{Al_2O_3}^2)$ with CaO are calculated based on Factsage software, as shown in Figure 3b. The $\lg (\gamma_{TiO_2}^3/\gamma_{Al_2O_3}^2)$ decreases with the increase of CaO in slag, which means the ratio of $\lg (w_{Ti}^3/w_{Al}^4)$ in slag should increase with the increase of CaO under the condition of fixed $\lg (w_{Ti}^3/w_{Al}^4)$ in slag.

The changes of S0:F1 and S0:F2 ratios in slag mixtures with $\lg (w_{Ti}^3/w_{Al}^4)$ are calculated according to Equations (1)–(3) and Factsage software at the temperature of 1550 °C, as shown in Figure 4. It can be seen that the points listed in Table 6 are in good agreement with the calculated results based on thermodynamics and Factsage software. The slag S0-F1 containing high CaO needs large ratio of $\lg (w_{Ti}^3/w_{Al}^4)$ to guarantee the thermodynamic equilibrium of 3[Ti] + 2(Al$_2$O$_3$) = 4[Al] + 3(TiO$_2$) and the ratio of $\lg (w_{Ti}^3/w_{Al}^4)$ in steel.

If the titanium and aluminum contents in steel are given, the mixture ratios between pre-melted slag S0 and F1(F2) can be acquired according to Figure 4. In order to compare the melting temperature of two slag systems S0-F1 and S0-F2 under the condition of fixing the titanium and aluminum contents in steel, the steel with $\lg (w_{Ti}^3/w_{Al}^4)$ 4.10 and 5.03 combined with corresponding slag systems S0-F1 and S0-F2 are calculated, as shown in Table 7.

Table 7. The slag used for steel with $\lg (w_{Ti}^3/w_{Al}^4) = 5.03$ or 4.10.

| $\lg (w_{Ti}^3/w_{Al}^4)$ | $\lg (\alpha_{TiO_2}^3/\alpha_{Al_2O_3}^2)$ | Slag        | Slag Ratio | CaF$_2$ | CaO | MgO | Al$_2$O$_3$ | TiO$_2$ |
|--------------------------|--------------------------------------------|-------------|------------|---------|-----|-----|-------------|---------|
| 5.03                     | -4.51                                      | S0F1-4      | S0:F1 = 60:40 | 46      | 25  | 4   | 15          | 10      |
| 5.03                     | -4.51                                      | S0F2-4      | S0:F2 = 67:33 | 46      | 20.875 | 4   | 20.875 | 8.25    |
| 4.10                     | -5.44                                      | S0F1-2      | S0:F1 = 76:24 | 46      | 25  | 4   | 19          | 6       |
| 4.10                     | -5.44                                      | S0F2-2      | S0:F2 = 79:21 | 46      | 22.375 | 4   | 22.375 | 5.25    |
Then the melting temperatures of thermodynamic equilibrium slag systems in Table 7 are measured in slag melting experiments, and the results are listed in Table 3.

3.2. Slag Melting Temperature Results

The halfsphere melting temperature and flowing melting temperature results for the slag listed in Table 3 are shown in Figure 5. It is clear that: (i) with a CaO/(Al_2O_3 + TiO_2) ratio = 1, the melting temperature of the slag S0-F1 is lower than slag S0-F2 with a CaO/Al_2O_3 ratio = 1 under the condition of increasing TiO_2 content in slag; (ii) when the TiO_2 content reaches more than 9%, the melting temperatures of slag S0F1-3 and S0F1-4 are much lower than that of slag S0F2-4 and S0F2-5; (iii) the melting temperatures of slag S0F1-4 is much lower than that of slag S0F2-4 in Table 7 under the condition of fixing TiO_2 content, which has been described in detail based on SHTT, SEM and XRD in [3]. As the description of conclusion in [3], TiO_2 addition from 0 to 6.43 mass% inhibited crystallisation behaviour of CaF_2-CaO-MgO-Al_2O_3 ESR type slag, whereas the further TiO_2 addition up to 9.73 mass% greatly enhanced the crystallisation tendency.

![Figure 5. The change of melting temperature with different S0:F1 and S0:F2 ratios: (a) halfsphere temperature, and (b) flowing temperature.](image-url)

The phenomena whereby ‘the melting temperature of the slag S0F2 system decreases first and then increases with the increase of TiO_2 content’ and ‘the melting temperature of the slag S0F1 system decreases with the increase of TiO_2 content’ is further explained according to the phase diagram of CaF_2-CaO-MgO-Al_2O_3-TiO_2 (CaF_2 = 46% and MgO = 4%) calculated by Factsage, as shown in Figure 6. It can be seen that slag S0-F1 is closer to the low melting point region with the increase of F1:S0 ratio. TiO_2 addition from 0 to 6 mass% promotes S0-F2 to approach the low melting point region, whereas the further TiO_2 addition up to 9.73 mass% makes S0-F2 away from the low melting point region.

3.3. The Optimized Low Melting Temperature Slag Used for Steel Containing Ti and Al

It is final goals to acquire the optimized slag with low melting temperature under the condition of fixing the CaO/(Al_2O_3 + TiO_2) ratio between Ti and Al contents in steel. During ESR of steel containing CaO/Al_2O_3 = 5.03 and 4.10, the corresponding isoactivity lines of CaO/TiO_2 = 46:25:4:(25 - x):x, have the low melting temperature property while satisfying the CaF_2-CaO-MgO-Al_2O_3-TiO_2 = 46:25:4:(25 - x):x, have the low melting temperature property while satisfying the CaO/Al_2O_3 = 5.03 and 4.10, and MgO/Al_2O_3 = 4% in steel. The
melting temperature of CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ slag systems would increase with the decrease of CaO content. In addition, with the increase of CaO in slag due to the reaction of 3CaF$_2$ + Al$_2$O$_3$ = 2AlF$_3$ (g) + 3CaO during long term ESR process [27], the melting temperature of slag S0-F1 would be decreased further according to Figure 7.

![Figure 6. The phase diagram of CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ (CaF$_2$ = 46% and MgO = 4%).](image)

![Figure 7. The phase diagram of melting temperature and isoactivity lines of lg(a$_{\text{TiO}_2}$/a$_{\text{Al}_2\text{O}_3}$) in CaF$_2$-CaO-MgO-Al$_2$O$_3$-TiO$_2$ (CaF$_2$ = 46% and MgO = 4%).](image)

**4. Conclusions**

The melting temperature of two slag systems and thermodynamic equilibrium of 3[Ti] + 2(Al$_2$O$_3$) = 4[Al] + 3(TiO$_2$) in resistance furnace have been experimentally carried out based on phase diagram, Factsage, and thermodynamic calculation. The results are as follows:

1. The calculated results of thermodynamic analysis based on Factsage are in good agreement with the slag-metal reaction experimental results in resistance furnace. The changes of S0:F1 and S0:F2 ratios in slag mixtures with different titanium and aluminum contents in steel are determined. The slag S0-F1 containing high CaO needs large ratio of TiO$_2$/Al$_2$O$_3$ to guarantee the thermodynamic equilibrium of 3[Ti] + 2(Al$_2$O$_3$) = 4[Al] + 3(TiO$_2$) and the ratio of Ti/Al in steel.
(2) The melting temperature of slag S0-F1 with a CaO/(Al2O3 + TiO2) ratio = 1 is lower than that of slag S0-F2 with a CaO/Al2O3 ratio = 1. Especially for thermodynamic equilibrium slag containing high TiO2, the melting temperature of S0-F1 slag CaF2:CaO:MgO:Al2O3:TiO2 = 46:25:4:15:10 is much lower than that of S0-F2 slag CaF2:CaO:MgO:Al2O3:TiO2 = 46:20.875:4:20.875:8.25.

(3) The slag mixtures consisting of pre-melted slag S0 (CaF2:MgO:CaO:Al2O3 = 46:4:25:25) and pre-melted slag F1 (CaF2:MgO:CaO:TiO2 = 46:25:25:25), which component is CaF2:CaO:MgO:Al2O3:TiO2 = 46:25:4:25−x, have the desired low melting temperature property while satisfying the concentrations of Ti and Al in steel.

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