Research Article

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Oxidizability characterization of slag system on the thermodynamic model of superalloy desulfurization

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Abstract: The oxidizability characterization method of slag system has a decisive influence on the accuracy of the desulfurization model. By carrying out the balance experiments of melting system composed of CaF₂–CaO–Al₂O₃–SiO₂–TiO₂–MgO–FeO slag system and Inconel 718 superalloy, the influence of Al₂O₃ and FeO on desulfurization distribution ratio at 1,773 K was studied. Based on the ion and molecule coexistence theory in slag, the effects of three oxidizability characterization methods, [Fe]–[O] balance, [Al]–[O] balance, and [Fe]–[Al]–[O] balance, on the accuracy of desulfurization thermodynamic model were studied. The results show that the effect of FeO on desulfurization distribution ratio is more significant than that of Al₂O₃ when the FeO content in slag is greater than 0.014%. When the FeO content in the slag is less than 0.014%, the effect of Al₂O₃ on the oxidizability will be greater than that of FeO. The calculated value of [Fe]–[Al]–[O] balance model is closer to the experimental-measured value compared to [Fe]–[O] balance model and [Al]–[O] balance model alone at 1,923 K.

Keywords: ion and molecule coexistence theory, desulfurization, [Fe]–[Al]–[O] balance, slag–metal balance experiment

1 Introduction

Inconel 718 alloy is widely used in aerospace and other fields due to its excellent properties of high temperature resistance, corrosion resistance, and high strength. Sulfur is a harmful element in nickel-based superalloys, which can reduce the tensile plasticity, creep resistance, and high-temperature fatigue life of superalloys [1–4]. In addition, Bricknell et al. [5] indicated that the oxidation of sulfides on the surface of alloys caused by oxygen infiltration could destroy the dense oxide film formed by aluminum and chromium elements, resulting in a brittle substrate surface. Moreover, sulfur can degrade the hot plasticity, hot ductility, and fatigue property and increase the solidification segregation of superalloy [6,7].

The oxidizability of slag has a complex effect on the sulfur content ratio [8]. Li et al. [9] studied the influence of slag system on sulfur in the electroslag remelting process and concluded that reducing the easily oxidized elements in the slag can enhance the desulfurization rate. Geng et al. [10] proposed that unstable oxides (FeO, Cr₂O₃, MnO, SiO₂, etc.) in slag would increase the oxidizability of slag, affecting the dissolved oxygen content in superalloy, and therefore further affecting the desulfurization reaction. Hou et al. [11] showed that slag system containing CaO would lead to enhanced water absorption in the electroslag remelting process, easily causing higher oxygen levels of superalloy and affecting slag desulfurization.

In order to explain the relationship between slag oxidizing and desulfurization ability, scholars used [Fe]–[O] balance and [Al]–[O] balance to characterize the oxygen content in the molten metal and then built a desulfurization thermodynamic model. But the model calculation was not accurate enough. Liu et al. [12] established a mass concentration model of a six-component (CaO–MgO–FeO–CaF₂–SiO₂–Al₂O₃) slag and characterized the dissolved oxygen content based on the [Fe]–[O] balance. However, the oxygen content calculated by the model is lower than the results of industrial tests, which also leads to the inaccuracy of the desulfurization thermodynamic calculation model. Taniguchi et al. [13] characterized the dissolved oxygen content during steelmaking based on [Fe]–[O] balance, but the calculation results also demonstrated a big error with the actual results. Studies have shown that the increase in oxygen content is mainly...
caused by the decomposition of unstable oxides in the slag. In the metallurgical process, the FeO content is usually used to characterize the slag oxidizability. However, the slag temperature in the electroslag remelting process can reach about 2,173 K, which is much higher than the traditional metallurgical process, and the slag system used in the electroslag remelting process usually contains more Al₂O₃ (about 30%). These are conducive to the decomposition of Al₂O₃ and make Al₂O₃ an unstable substance [14]. In addition, the required FeO content in the slag in the electroslag remelting process is very low and usually less than 0.5%. At this time, the effect of Al₂O₃ on the slag oxidizability should not be ignored. Yang et al. [15] conducted the [Al]–[O] balance experiment and concluded that the calculated dissolved oxygen content based on [Al]–[O] balance has a large error with the experimental results. The desulfurization thermodynamic model of Inconel 718 superalloy electroslag remelting process was studied through a slag–metal balance experiment. The [Fe]–[Al]–[O] balance was adopted to characterize the oxidizability of slag. From the thermodynamic point of view, the influence law of slag oxidizability on desulfurization is clarified, which could provide a theoretical basis for precise control of sulfur content in superalloy electroslag remelting process.

In this article, the ion and molecular coexistence theory of slag structure was used to establish the mass–concentration control equations of Inconel 718 superalloy and CaF₂–CaO–Al₂O₃–SiO₂–TiO₂–MgO–FeO slag system. The [Fe]–[O] balance, [Al]–[O] balance, and [Fe]–[Al]–[O] balance were used to build the slag–metal desulfurization thermodynamic model. The effect of three slag oxidizability characterization methods on the desulfurization thermodynamic model was evaluated through experiments.

2 Experiments

The schematic diagram of the experimental device is shown in Figure 1(a). A magnesia crucible with an inner diameter of 60 mm and a height of 100 mm was used in this experiment. The temperature of the MoSi₂ furnace is set to 1,773 K. The Inconel 718 superalloy and slag used in the experiment weight 150 and 50 g, respectively. Table 1 shows the chemical compositions of the Inconel 718 superalloy, and Table 2 shows the compositions of slag. When one component in the slag changes, the remaining components will increase or decrease at the original ratio. In the experiment, chemically pure reagents were used as the components of slag. All used reagents were dried in an oven at 1,073 K for 4 h to remove the water vapor. We refer to the experimental method in Duan’s work [16] wherein the alloy sample was added to the crucible and placed in the constant temperature zone of the MoSi₂ furnace. The temperature was kept at 1,773 K for 20 min to completely melt the sample and then the stopper was pulled up to let the slag flow down, as shown in Figure 1(b) and (c). To avoid the influence of oxygen in the air during the melting process, argon was injected into the furnace with a flow rate of 2.5 L min⁻¹ throughout the experiment. When the reaction time reached 80 min, the molten slag and superalloy samples were sucked up by the quartz tube and then the crucible was removed and cooled by water.
The sulfur content in the slag was analyzed by X-ray fluorescence and determined by a carbon–sulfur analyzer. The measured sulfur content results of the slag and alloy sucked out are listed in Tables 3 and 4, respectively.

### 3 Establishment of mass action concentration equations of CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO slags based on the ion and molecule coexistence theory

The ion and molecule coexistence theory [17–21] of slag structure can be used to describe the reactions between molecules and ions in the molten slags. Complex molecules in the slag are formed by the reactions of simple molecules and simple ions in dynamic balance. Assuming that the slag components follow the mass action law, the activity of each component in the slag can be expressed by a mass action concentration. Combining the currently known thermodynamic data and mass action law, the action concentration of each structural unit in the slag can be predicted more accurately.

#### 3.1 Model of mass action concentrations of structural units and ion couples

According to the ion and molecular coexistence theory, the phase composition of slag is very important for the establishment of the desulfurization thermodynamic model. According to the phase diagrams of CaO–SiO$_2$, CaO–Al$_2$O$_3$, TiO$_2$–Al$_2$O$_3$, TiO$_2$–CaO, CaO–Al$_2$O$_3$–SiO$_2$, CaO–SiO$_2$–CaF$_2$, CaO–Al$_2$O$_3$–CaF$_2$, CaO–SiO$_2$–TiO$_2$, CaO–FeO–SiO$_2$, CaO–MgO–SiO$_2$, and MgO–Al$_2$O$_3$–SiO$_2$ [22], the structural units from 1,473 to 1,973 K [23] are listed in Table 5.

The molten slag was regarded as an ideal solution in dynamic balance reactions between the simple ions and the simple molecules. The weight of the initial slag system was set to be 100 g. To represent the chemical composition of slags, the variables, $b_1 = n_{CaO}^0$, $b_2 = n_{MgO}^0$, $b_3 = n_{CaF_2}^0$, $b_4 = n_{FeO}^0$, $b_5 = n_{SiO_2}^0$, and $b_6 = n_{TiO_2}^0$, were assigned to represent the number of moles of CaO, MgO, CaF$_2$, FeO, SiO$_2$, TiO$_2$, and Al$_2$O$_3$ in the slag system CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO. The ion and molecule coexistence theory hold that each ion couple is electrically neutral and can be dissociated into separate cations and anions. Each ion pair’s balance number of moles is equal to the summation of the cations and the anions in the ion couple.

The total number of balance moles of all structural units in 100 g slag ($\sum n_i$) can be expressed as follows:

$$\sum n_i = 2n_1 + 2n_2 + \ldots + n_7 + n_{Al} + n_{Fe} + \ldots + n_{<30}$$

According to the ion and molecule coexistence theory, the ratio of the balance number of moles of a structural unit $i$ to the total number of moles of all the structural units in the balance system is the mass action concentration of the structural unit $i$ in the molten slag, which is called $N_i$. It can be calculated as follows:

$$N_i = n_i / \sum n_i$$

### Table 1: Chemical composition of Inconel 718 superalloy (wt%)

| Element | C  | Si | Mn | Mo | Ni | Cr | Nb | Al | Ti | S  | Fe |
|---------|----|----|----|----|----|----|----|----|----|----|----|
| Content | 0.04 | 0.24 | 0.19 | 3.08 | 51.96 | 18.53 | 5.67 | 0.67 | 1.11 | 0.013 | Bal. |

### Table 2: Chemical compositions of slags used in the experiment (wt%)

| Slag system | CaF2 | CaO | Al2O3 | SiO2 | TiO2 | MgO | FeO |
|-------------|------|-----|-------|------|------|-----|-----|
| S0          | 49.90 | 20.0 | 20.04 | 3.01 | 4.01 | 3.01 | 0   |
| S1          | 49.80 | 20.0 | 20.00 | 3.00 | 4.00 | 3.00 | 0.20|
| S2          | 49.70 | 19.96| 19.96 | 2.99 | 3.99 | 2.99 | 0.40|
| S3          | 49.55 | 19.90| 19.90 | 2.98 | 3.98 | 2.98 | 0.70|
| S4          | 47.93 | 19.25| 23    | 2.89 | 3.85 | 2.89 | 0.19|
| S5          | 46.69 | 18.75| 25    | 2.81 | 3.75 | 2.81 | 0.18|
| S6          | 45.44 | 18.25| 27    | 2.74 | 3.65 | 2.74 | 0.18|
| S7          | 44.20 | 17.75| 31    | 2.66 | 3.55 | 2.66 | 0.17|
| S8          | 42.95 | 17.25| 31    | 2.59 | 3.45 | 2.59 | 0.17|

### Table 3: The sulfur content in final slag samples (wt%)

| Slags | S0  | S1  | S2  | S3  | S4  | S5  | S6  | S7  | S8  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $w(S)$| 0.0984 | 0.0408 | 0.0361 | 0.0356 | 0.0412 | 0.0399 | 0.0392 | 0.0389 | 0.0387 |
When the system reaches a dynamic balance, each simple molecule and complex molecule can only provide one structural unit. Therefore, the mass action concentrations of all structure units in the form of ions, simple molecules, and complex molecules in CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO slag can be calculated from equation (2). However, mass action concentrations of ion couples, such as ($Ca^{2+} + O^{2-}$), should be calculated as follows:

$$N_{CaO} = \frac{n_{Ca^{2+},CaO} + n_{O^{2-},CaO}}{\sum n_i}$$  \hspace{1cm} (3)

Assuming the conservation of mass and dynamic balances for the reactions of the slag structure units, the activity model of slag can be established. The ions and structural units can form complex molecules through chemical reactions in the slag system CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO. The chemical reactions, the standard molar Gibbs free energies ($\Delta_r G_m^\theta$), and the mass action concentrations of possibly formed complex molecules are shown in Table 6. The standard molar Gibbs free energies for the reactions were cited from the literatures [24,25] or calculated with the FactSage software.

Based on the balance number of moles and mass action concentration of each structural unit of slag, the mass conservation equation is established as follows:

$$b_1 = (0.5N_1 + 3N_{c1} + 2N_{c2} + N_{c3} + 3N_{c4} + 12N_{c5} + N_{c6} + N_{c7} + N_{c8} + 3N_{c13} + N_{c16} + 3N_{c17} + 4N_{c18} + 2N_{c26} + 2N_{c25} + N_{c26} + 2N_{c27} + 3N_{c28} + 3N_{c29} + 11N_{c30} + N_{c31} + 3N_{c32} + N_{c33} + N_{c34})\sum n_i = n_{CaO}^0$$  \hspace{1cm} (4)

$$b_2 = (0.5N_2 + 2N_{c9} + N_{c10} + N_{c11} + N_{c19} + N_{c20} + 2N_{c21} + 2N_{c22} + N_{c26} + N_{c27} + N_{c28} + N_{c31})\sum n_i = n_{MgO}^0$$  \hspace{1cm} (5)

$$b_3 = (1/3N_3 + N_{c29} + N_{c30} + N_{c32})\sum n_i = n_{CaF_2}^0$$  \hspace{1cm} (6)

Table 4: The sulfur content in final alloy samples (wt%)  

| Samples | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------|---|---|---|---|---|---|---|---|---|
| W$_{S}$ | 0.00071 | 0.00063 | 0.00072 | 0.00082 | 0.00075 | 0.00084 | 0.00095 | 0.00106 | 0.00112 |

Table 5: The structural unit and mass action concentrations existed in the balance of the slag system CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO  

| Structural units | Mass action concentrations | Structural units | Mass action concentrations |
|------------------|---------------------------|------------------|---------------------------|
| Ca$^{2+}$ + O$^{2-}$ | N$_1$ | 2FeO-SiO$_2$ | N$_{c15}$ |
| Mg$^{2+}$ + O$^{2-}$ | N$_2$ | CaO-TiO$_2$ | N$_{c16}$ |
| Ca$^{2+}$ + 2F$^-$ | N$_3$ | 3CaO-2TiO$_2$ | N$_{c17}$ |
| Fe$^{2+}$ + O$^{2-}$ | N$_4$ | 4CaO-3TiO$_2$ | N$_{c18}$ |
| SiO$_2$ | N$_5$ | MgO-TiO$_2$ | N$_{c19}$ |
| TiO$_2$ | N$_6$ | MgO-2TiO$_2$ | N$_{c20}$ |
| Al$_2$O$_3$ | N$_7$ | 2MgO-TiO$_2$ | N$_{c21}$ |
| 3CaO-SiO$_2$ | N$_{c1}$ | Al$_2$O$_3$-TiO$_2$ | N$_{c22}$ |
| 2CaO-SiO$_2$ | N$_{c2}$ | 2MgO-Al$_2$O$_3$-SiO$_2$ | N$_{c23}$ |
| CaO-SiO$_2$ | N$_{c3}$ | 2CaO-Al$_2$O$_3$-SiO$_2$ | N$_{c24}$ |
| 3CaO-Al$_2$O$_3$ | N$_{c4}$ | CaO-Al$_2$O$_3$-2SiO$_2$ | N$_{c25}$ |
| 12CaO-7Al$_2$O$_3$ | N$_{c5}$ | CaO-MgO-2SiO$_2$ | N$_{c26}$ |
| CaO-Al$_2$O$_3$ | N$_{c6}$ | 2CaO-MgO-2SiO$_2$ | N$_{c27}$ |
| CaO-2Al$_2$O$_3$ | N$_{c7}$ | 3CaO-MgO-2SiO$_2$ | N$_{c28}$ |
| CaO-6Al$_2$O$_3$ | N$_{c8}$ | 3CaO-3Al$_2$O$_3$-CaF$_2$ | N$_{c29}$ |
| 2MgO-SiO$_2$ | N$_{c9}$ | 11CaO-7Al$_2$O$_3$-CaF$_2$ | N$_{c30}$ |
| MgO-SiO$_2$ | N$_{c10}$ | CaO-MgO-SiO$_2$ | N$_{c31}$ |
| MgO-Al$_2$O$_3$ | N$_{c11}$ | 3CaO-2SiO$_2$-CaF$_2$ | N$_{c32}$ |
| 3Al$_2$O$_3$-2SiO$_2$ | N$_{c12}$ | CaO-SiO$_2$-TiO$_2$ | N$_{c33}$ |
| 3CaO-2SiO$_2$ | N$_{c13}$ | CaO-FeO-SiO$_2$ | N$_{c34}$ |
| FeO-Al$_2$O$_3$ | N$_{c14}$ |


\[ b_4 = (0.5N_5 + N_{14} + 2N_{15} + N_{34}) \sum n_i = n_{SiO_2}^0 \] (7)

\[ b_5 = (N_5 + N_{14} + N_{15} + N_{34} + N_{10} + 2N_{12} + 2N_{13} + 5N_{23} + N_{24} + 2N_{25} + 2N_{26} + 2N_{27} + 2N_{28} + N_{31} + 2N_{32} + N_{33} + N_{34}) \sum n_i = n_{SiO_2}^0 \] (8)

\[ b_6 = (N_5 + N_{15} + 2N_{25} + 3N_{28} + N_{29} + 2N_{30} + N_{33} + N_{34}) \sum n_i = n_{SiO_2}^0 \] (9)

\[ b_7 = (N_7 + N_{16} + 7N_{5} + N_{10} + 2N_{12} + N_{22} + 2N_{23} + N_{25} + 3N_{29} + 7N_{30}) \sum n_i = n_{NiO}^0 \] (10)

Because the sum of the mole fractions of all structural units in slag is 1 under balance conditions, the following formula can be obtained:

\[ N_1 + N_2 + N_3 + N_4 + N_5 + N_7 + N_{11} + N_{12} + \ldots + N_{34} = 1 \] (11)

Table 6: Chemical reaction formulas, standard molar Gibbs free energy, and mass action concentrations of possibly formed complex molecules in the system CaF₂–CaO–Al₂O₃–SiO₂–TiO₂–MgO–FeO at different temperatures

| Reactions | \( \Delta r G_m^{0} \) (J mol⁻¹) | \( N_i \) |
|-----------|---------------------------------|---------|
| 3(Ca²⁺ + O²⁻) + (SiO₂) = (3CaO-SiO₂) | -118,826 to 6.6947 T | N₁ = K₁Ca²⁺NiO |
| 2(Ca²⁺ + O²⁻) + (SiO₂) = (2CaO-SiO₂) | -102,090 to 24.2677 T | N₂ = K₂Ca²⁺NiO |
| (Ca²⁺ + O²⁻) + (SiO₂) = (CaO-SiO₂) | -21,757 to 36.8197 T | N₃ = K₃Ca²⁺NiO |
| 3(Ca²⁺ + O²⁻) + (Al₂O₃) = (3CaO-Al₂O₃) | -21,757 to 29.2887 T | N₄ = K₄Ca²⁺NiO |
| 12(Ca²⁺ + O²⁻) + 7(Al₂O₃) = (12CaO-7Al₂O₃) | 6,17,977 to 612.1917 T | N₅ = K₅Ca²⁺NiO |
| (Ca²⁺ + O²⁻) + (Al₂O₃) = (CaO-Al₂O₃) | 59,413 to 59.4137 T | N₆ = K₆Ca²⁺NiO |
| (Ca²⁺ + O²⁻) + 2(Al₂O₃) = (CaO-2Al₂O₃) | -16,763 to 25.5227 T | N₇ = K₇Ca²⁺NiO |
| (Ca²⁺ + O²⁻) + 6(Al₂O₃) = (CaO-6Al₂O₃) | -22,594 to 31.7987 T | N₈ = K₈Ca²⁺NiO |
| 2(Mg²⁺ + O²⁺) + (SiO₂) = (2MgO-SiO₂) | -16,902 to 3.3477 T | N₉ = K₉Mg²⁺NiO |
| (Mg²⁺ + O²⁺) + (SiO₂) = (MgO-SiO₂) | 23,849 to 29.7067 T | N₁₀ = K₁₀Mg²⁺NiO |
| (Mg²⁺ + O²⁺) + (Al₂O₃) = (MgO-Al₂O₃) | -18,828 to 6.2767 T | N₁₁ = K₁₁Mg²⁺NiO |
| 3(Al₂O₃) + 2(SiO₂) = (3Al₂O₃-2SiO₂) | -435,27 to 10.4677 T | N₁₂ = K₁₂Mg²⁺NiO |
| (Fe²⁺ + O²⁻) + (Al₂O₃) = (FeO-Al₂O₃) | -33272.8 to 6.1028 T | N₁₃ = K₁₃Mg²⁺NiO |
| 2(Fe²⁺ + O²⁺) + (SiO₂) = (2FeO-SiO₂) | -28595.84 to 3.3497 T | N₁₄ = K₁₄Mg²⁺NiO |
| (Ca²⁺ + O²⁻) + (TiO₂) = (CaO-TiO₂) | -79,900 to 3.357 T | N₁₅ = K₁₅Mg²⁺NiO |
| 3(Ca²⁺ + O²⁻) + 2(TiO₂) = (3CaO-2TiO₂) | -2,07,100 to 11.357 T | N₁₆ = K₁₆Mg²⁺NiO |
| 4(Ca²⁺ + O²⁻) + 3(TiO₂) = (4CaO-3TiO₂) | -2,92,880 to 17.5737 T | N₁₇ = K₁₇Mg²⁺NiO |
| (Mg²⁺ + O²⁻) + (TiO₂) = (MgO-TiO₂) | -26376.8 to 3.147 T | N₁₈ = K₁₈Mg²⁺NiO |
| (Mg²⁺ + O²⁺) + (SiO₂) = (MgO-SiO₂) | -27632.9 to 0.63 T | N₁₉ = K₁₉Mg²⁺NiO |
| 2(Mg²⁺ + O²⁺) + (TiO₂) = (2MgO-TiO₂) | -25539.5 to 1.267 T | N₂₀ = K₂₀Mg²⁺NiO |
| (Al₂O₃) + (SiO₂) = (Al₂O₃-SiO₂) | -25,270 to 3.9247 T | N₂₁ = K₂₁Mg²⁺NiO |
| 2(Mg²⁺ + O²⁻) + 2(Al₂O₃) + 5(SiO₂) = (2MgO-2Al₂O₃-5SiO₂) | -14,422 to 14.8087 T | N₂₂ = K₂₂Mg²⁺NiO |
| 2(Ca²⁺ + O²⁻) + (Al₂O₃) + (SiO₂) = (2CaO-Al₂O₃-SiO₂) | -1,16,315 to 38.9117 T | N₂₃ = K₂₃Mg²⁺NiO |
| (Ca²⁺ + O²⁻) + (Al₂O₃) + 2(SiO₂) = (CaO-Al₂O₃-2SiO₂) | -4,184 to 73.6387 T | N₂₄ = K₂₄Mg²⁺NiO |
| (Ca²⁺ + O²⁻) + (Mg²⁺ + O²⁻) + 2(SiO₂) = (CaO-MgO-2SiO₂) | -80,387 to 51.9167 T | N₂₅ = K₂₅Mg²⁺NiO |
| 2(Ca²⁺ + O²⁻) + (Mg²⁺ + O²⁻) + 2(SiO₂) = (2CaO-MgO-2SiO₂) | -73,688 to 63.6397 T | N₂₆ = K₂₆Mg²⁺NiO |
| 3(Ca²⁺ + O²⁻) + (Mg²⁺ + O²⁻) + 2(SiO₂) = (3CaO-MgO-2SiO₂) | -2,05,016 to 31.7987 T | N₂₇ = K₂₇Mg²⁺NiO |
| 3(Ca²⁺ + O²⁻) + 2(Al₂O₃) + (Ca²⁺ + 2F⁻) = (3CaO-3Al₂O₃-CaF₂) | -44,942 to 73.157 T | N₂ₘ = K₂ₙMg²⁺NiO |
| 11(Ca²⁺ + O²⁻) + 7(Al₂O₃) + (Ca²⁺ + 2F⁻) = (11CaO-7Al₂O₃-CaF₂) | -2,28,760 to 155.87 T | N₃₀ = K₃₀Mg²⁺NiO |
| (Ca²⁺ + O²⁻) + (Mg²⁺ + O²⁻) + (SiO₂) = (CaO-MgO-SiO₂) | -124766.6 + 3.6768 T | N₃₁ = K₃₁Mg²⁺NiO |
| 3(Ca²⁺ + O²⁻) + 2(SiO₂) + (Ca²⁺ + 2F⁻) = (3CaO-2SiO₂-CaF₂) | -2,55,180 to 8.207 T | N₃₂ = K₃₂Mg²⁺NiO |
| (Ca²⁺ + O²⁻) + (SiO₂) + (TiO₂) = (CaO-SiO₂-TiO₂) | -1,14,683 + 7.32 T | N₃₃ = K₃₃Mg²⁺NiO |
| (Ca²⁺ + O²⁻) + (Fe²⁺ + O²⁻) + (SiO₂) = (CaO-FeO-SiO₂) | -72996.8 to 29.3169 T | N₃₄ = K₃₄Mg²⁺NiO |
Equations (4)–(11) govern the calculation of the mass action concentrations of structural units or ion couples in slag system CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO. There are eight unknowns as in $N_1$, $N_2$, $N_3$, $N_4$, $N_5$, $N_6$, and $N_7$ and $\sum n_i$ with eight independent equations. Using MATLAB 7.0 to solve these higher order nonlinear equations, the activity of each component in slag was obtained.

3.2 Verification of mass action concentration model

The mass action concentration model of slags is also called the activity model of slag components. Because the measured activity values of slag CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO have rarely been reported, another common slag system studied by researchers [26,27] was used to verify the new model. The components of the common slag system were brought into the model and then the calculated activity values were compared with previous experimental results, as seen in Figure 2.

![Figure 2: Comparison between calculated values of the activity model and the tested values. (a) FeO, (b) CaO, and (c) Al$_2$O$_3$.](image)

Figure 2(a) shows that the FeO activities calculated by the new model are in good agreement with the measured values from Zhou et al. [27]. Meanwhile, our calculation results of the FeO activities are slightly different from Chen’s measurement results [26]. The slight difference might be generated by the differences in thermodynamic values used in the calculation process. The results described in Figure 2(b) and (c) show that the CaO and Al$_2$O$_3$ activities calculated by the model are in good agreement with the results by Chen, which further proved that the model can be used to calculate the activities of slag components accurately.

3.3 Thermodynamic model of desulfurization between slag and metal interface

In the process of establishing the governing equation for calculating the mass action concentration of slag components in the CaF$_2$–CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$–MgO–FeO system, the structure unit $S^2^-$ was ignored because the balance number of
moles of $S^{2-}$ as a structure unit was very small. Therefore, the calculation of mass action concentration of other structural units was not affected by the number of moles of structured unit $S$.  

According to the ion and molecule coexistence theory, only free (Ca$^{2+} + O_2^-$) and (Mg$^{2+} + O_2^-$) ion couples have the ability to desulfurize and participate in the desulfurization reaction. The reaction is expressed as follows:

$$(Ca^{2+} + O_2^-) + [S] = (Ca^{2+} + S^{2-}) + [O]$$

(12)

$$(Mg^{2+} + O_2^-) + [S] = (Mg^{2+} + S^{2-}) + [O]$$

(13)

The equations’ balance constants are expressed as follows:

$$K_{CaS} = \frac{a_{CaS}a_O}{a_{CaO}a_S} = \frac{N_{CaS}a_O}{N_{CaO}a_S} = \frac{2\gamma_{SisiS/M_{Si}}\sum n_i a_O}{N_{CaO}a_{Si/Si}} (14)$$

$$K_{MgS} = \frac{a_{MgS}a_O}{a_{MgO}a_S} = \frac{N_{MgS}a_O}{N_{MgO}a_S} = \frac{2\gamma_{SisiS/M_{Si}}\sum n_i a_O}{N_{MgO}a_{Si/Si}} (15)$$

The sulfur distribution ratio of (Ca$^{2+} + O_2^-$) and (Mg$^{2+} + O_2^-$) ion pairs can be calculated from equations (14) and (15) as follows:

$$L_{S,CaO} = \frac{\omega_{SisiS/Si}}{\omega_{Si/Si}} = \frac{16K_{CaS}N_{CaO}\sum n_i x_f S}{a_O} (16)$$

$$L_{S,MgO} = \frac{\omega_{SisiS/Si}}{\omega_{Si/Si}} = \frac{16K_{MgS}N_{MgO}\sum n_i x_f S}{a_O} (17)$$

In the electroslag remelting (ESR) process, the oxygen content in the molten metal pool is related to the content of FeO or Al$_2$O$_3$ in the slag [13]. According to the following reactions:

$$\begin{align*}
\text{(FeO)} &= [\text{Fe}] + [O] \\
\Delta G^\theta &= 1,21,010 - 52.35 T \text{ (J mol}^{-1}) \text{ (reference 13)} \\
2[\text{Al}] + 3[O] &= (\text{Al}_2\text{O}_3) \\
\Delta G^\theta &= -12,02,000 + 386.30 T \text{ (J mol}^{-1}) \text{ (reference 14)}
\end{align*}$$

The deformations are expressed as follows:

$$\alpha_{FeO}^& = a_{FeO} \exp\left(\frac{\Delta G_{FeO}^G}{RT}\right) \frac{f_i}{f_0}$$

(22)

$$- RT \ln K^\theta = -RT \ln a_{Al_{Oj}}^\theta a_O^\theta = -12,02,000 + 386.30 T$$

(23)

$$\omega_{AlO} = \left(\exp\left(\Delta G_{AlO}^G/RT\right)f_i^\theta a_{Al}^\theta f_O^\theta\right)^{-1} (24)$$

The activity coefficient of the elements in superalloy can be calculated from equation (25). Because Inconel 718 alloy possesses high alloying element contents, the calculated results of the element activity coefficient could be much more accurate if the secondary interaction coefficient between elements was considered. However, the secondary interactions between elements in nickel-base superalloy activity coefficient have been rarely reported, thus this study only considers the primary activity interaction coefficients [28,29], as shown in Table 7.

$$\log f_i = \sum \gamma_i \omega_{ij} + \log \omega_{ij}$$

(25)

Based on the [Fe]–[O] balance, the oxygen content in alloys is described as:

$$L_S = L_{S,CaO} + L_{S,MgO} = \frac{16 \times (K_{CaS}N_{CaO} + K_{MgS}N_{MgO}) \sum n_i x_f S}{a_O} \frac{f_i}{f_0}$$

(26)

Based on the [Al]–[O] balance, the oxygen content in alloys is described as:

$$L_S = L_{S,CaO} + L_{S,MgO} = \frac{16 \times (K_{CaS}N_{CaO} + K_{MgS}N_{MgO}) \sum n_i x_f S}{a_O} \frac{f_i}{f_0}$$

(27)

Based on [Fe]–[Al]–[O] balance, the thermodynamic model of oxygen content in alloys is described as:

$$L_S = L_{S,CaO} + L_{S,MgO} = \frac{16 \times (K_{CaS}N_{CaO} + K_{MgS}N_{MgO}) \sum n_i x_f S}{a_O} \frac{f_i}{f_0}$$

(28)

The total sulfur distribution ratio in the slag system can be calculated using equations (26)–(28). The variable $f_S$ represents the activity coefficient of dissolved sulfur in the nickel-based alloy. A 1% mass fraction was selected as the standard state, and the sulfur content of our experiment was less than 10 ppm. According to the
previous studies of nickel-based alloy solutions, the activity coefficient \(f_s\) of dissolved sulfur is assumed to be 1. Since the entire experiment process was under the protection of argon atmosphere, and the added superalloy had no oxide layer, the oxygen in the molten metal can only be supplied from the slag. The components in slag that can affect the oxygen content in the molten metal are mainly FeO and Al\(_2\)O\(_3\), and the effects of these two components are independent of each other. So the equilibrium oxygen content based on \([\text{Fe}]-[\text{Al}]-[\text{O}]\) can be calculated as the sum of that of \([\text{Fe}]-[\text{O}]\) and \([\text{Al}]-[\text{O}]\) balance. In addition, \(K^\theta_{\text{CaS}}\) and \(K^\theta_{\text{MgS}}\) can be calculated using equation (29).

\[
K^\theta_i = \exp(-\Delta G^\theta_i/RT) \tag{29}
\]

where \(R\) is the gas constant \((8.314 \text{ J mol}^{-1} \text{ K}^{-1})\) and \(T\) is the absolute temperature (K).

### 4 Experimental results and discussion

#### 4.1 Experimental results

The sulfur distribution ratio of experimental slags is shown in Table 8. It has been experimentally determined that as the content of FeO and Al\(_2\)O\(_3\) increases, the desulfurization distribution ratio gradually decreases. By changing the content of FeO and Al\(_2\)O\(_3\) in the experiment, slag desulfurization is affected. The effect of FeO will be more significant than that of Al\(_2\)O\(_3\), which mainly affects the desulfurization effect by affecting the slag oxygen content.

### 4.2 Verification of the desulfurization model

Figure 3 shows the effect of FeO and Al\(_2\)O\(_3\) on the oxygen content in the alloy through theoretical calculation based on ion and molecule coexistence theory and experimental data. It is obvious that the increase in FeO and Al\(_2\)O\(_3\) will increase the oxygen content in the alloy, and the influence of FeO is obviously much greater than that of Al\(_2\)O\(_3\).

Taking the S4 slag system as an example, the calculated oxygen contents according to \([\text{Fe}]-[\text{Al}]-[\text{O}]\) balance, \([\text{Fe}]-[\text{O}]\) balance, and \([\text{Al}]-[\text{O}]\) balance are shown in Figure 4. It can be seen from the figure that the influence of \([\text{Fe}]-[\text{O}]\) balance on oxygen content is much greater than that of \([\text{Al}]-[\text{O}]\) balance, but the influence of \([\text{Al}]-[\text{O}]\) balance cannot be ignored. The \([\text{Fe}]-[\text{Al}]-[\text{O}]\) balance is more comprehensive in characterizing the oxygen content. Figure 5 shows the comparison of sulfur distribution ratios at different FeO contents obtained through three characterization methods and experiments. In Figure 5, \(L_s[\text{Fe}]-[\text{O}],\text{calculated}\) line is the sulfur distribution ratio calculated based on the desulfurization thermodynamic model established by \([\text{Fe}]-[\text{O}]\) balance; \(L_s[\text{Al}]-[\text{O}],\text{calculated}\) line is the sulfur distribution ratio calculated based on \([\text{Al}]-[\text{O}]\) balance; \(L_s[\text{Fe}]-[\text{Al}]-[\text{O}],\text{calculated}\) line is the calculated sulfur distribution ratio based on \([\text{Fe}]-[\text{Al}]-[\text{O}]\) balance; \(L_s[\text{Fe}]-[\text{O}],\text{tested}\) line is the sulfur distribution ratio of slag system S0, S1, S2, and S3 measured by experiment. The sulfur distribution ratio determined by any characterization method or experiment decreases with the increase in FeO content at the basicity of 6.67. When the content of FeO in the slag is less than 0.4%, the variation ratio of sulfur distribution is larger. When the FeO content is between 0.4% and 0.7%, the variation range of sulfur distribution ratio is significantly reduced. With the increase in FeO content, the effect of FeO content on the sulfur distribution ratio becomes smaller, which is mainly because some FeO in the slag combines with Al\(_2\)O\(_3\), SiO\(_2\), and CaO in the slag to form FeO·Al\(_2\)O\(_3\), 2FeO·SiO\(_2\), CaO·FeO·SiO\(_2\), and so on. The molecule [17] reduces the activity of FeO, so that the sulfur distribution ratio tends to be stable with the change in FeO. In Figure 5, the fluctuation range of Al\(_2\)O\(_3\) content is in the range of 19.96–20.04%, so the change trend of sulfur distribution ratio calculated according to \([\text{Al}]-[\text{O}]\) balance is not obvious. Line \(L_s[\text{Fe}]-[\text{O}],\text{calculated}\) and

#### Table 7: The activity interaction coefficients used in the calculation process

| \(e_i^j\) | Ni | Cr | Al | Mo | Ti | O | S |
|---------|----|----|----|----|----|---|---|
| Al      | -0.029 | 0.0096 | 0.045 | - | - | -1.4 | 0.03 |
| O       | 0.003 | -0.0431 | -0.89 | 0.0035 | -0.6 | -0.2 | -0.133 |

#### Table 8: The sulfur distribution ratio of experimental slags

| Slag system | S0 | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 |
|------------|----|----|----|----|----|----|----|----|----|
| \(\ln L_s\) | 4.9316 | 4.1707 | 3.9168 | 3.7707 | 4.0068 | 3.8595 | 3.7221 | 3.6044 | 3.5441 |
Figure 3: Influence of FeO and Al₂O₃ on the oxygen content in the alloy.

Line $L_{\text{Al}:[\text{O}]}$,calculated have an intersection point when the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the [Al]–[O] balance is closer to the experimental value, while the sulfur distribution rate calculated based on [Fe]–[O] balance is closer to the experimental value on the right side of the intersection point. Therefore, we can conclude that the free oxygen released by Al₂O₃ is higher than the free oxygen released by FeO when the FeO content is less than 0.014%. At this time, the [Al]–[O] balance is better than the free oxygen released by FeO when the FeO content is less than 0.014%. At the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%. On the left side of the intersection point, the sulfur distribution rate calculated based on the FeO content is 0.014%.

Figure 4: Calculated oxygen contents based on three oxidizability characterization methods.

Figure 5: Comparison of sulfur distribution ratios at different FeO contents obtained through three characterization methods and experiments.

oxidizability, it will promote the desulfurization reaction. The FeO content in the slag will directly affect the dissolved oxygen content, which in turn affects desulfurization. The experimental and theoretical calculation values of the sulfur distribution ratio in the slag decrease with the increase in the FeO content. When the FeO content is higher than 0.014%, Al₂O₃ will play a weak role. When the FeO content is lower than 0.014%, Al₂O₃ will play a stronger role than FeO. As the content of Al₂O₃ increases gradually, the sulfur distribution ratio changes greatly. However, the sulfur distribution ratio calculated by the desulfurization thermodynamic models has a large deviation from the experimental value, and the theoretical calculation values are higher than the experimental measurement value. In addition, during the experiment, the S0 slag which does not contain FeO still has desulfurization ability and a large sulfur distribution ratio. However, the desulfurization thermodynamic model based...
on the [Fe]–[O] balance cannot explain this phenomenon. This indicates that the dissolved oxygen content in the sample is affected not only by the FeO content but also by other factors such as Al₂O₃. Taniguchi et al. [13] has used the activity of FeO to characterize the dissolved oxygen content in the steelmaking process, but the calculated values of the model and the experimentally determined values are quite different, which further confirms this view. Based on the desulfurization thermodynamic model established by [Fe]–[Al]–[O] balance, L₅₆[Fe]–[Al]–[O], calculated is lower than L₅₆[Fe]–[Al]–[O], calculated and closer to the experimental measurements. In addition, when the FeO content is 0, L₅₆[Fe]–[Al]–[O], calculated is 746.03, and this model can explain the phenomenon that the SO slag system has a large sulfur distribution ratio. And as shown in Figure 6, this also verifies that L₅₆[Fe]–[Al]–[O], calculated is closer to the measured value. Therefore, using the desulfurization thermodynamic model established by [Fe]–[Al]–[O] balance is more reasonable and feasible compared to other models. However, the sulfur distribution ratio calculated by [Fe]–[Al]–[O] balance is still higher than that of the experimental value. This may be due to the insufficient protection of the atmosphere during the experiment. The element Fe in the alloy is oxidized, making the actual FeO content higher than the FeO content used in the model calculation, resulting in a large deviation. It can be seen from Figure 6 that when the FeO or Al₂O₃ content is high, the gap between the model calculated value and the experimental value becomes smaller.

When smelting ultra-pure alloys during electroslag remelting, the sulfur content of the alloy must be strictly controlled. Therefore, the content of FeO and Al₂O₃ must be strictly controlled to be low. In addition, the slag temperature in the electroslag remelting process is usually higher than 1,923 K, and that Al₂O₃ content in the electroslag remelted slag system usually exceeds 25%, so it is necessary to consider the effect of the oxygen released by the decomposition reaction of Al₂O₃ on desulfurization. The desulfurization thermodynamic model established by [Fe]–[Al]–[O] balance is more accurate than the desulfurization thermodynamic model constructed by [Fe]–[O] and [Al]–[O] balance; therefore, this method is more suitable for oxygen content characterization in the process of electroslag remelting. Superalloys have very strict requirements for oxygen, sulfur, and other components. Generally, it is required to control the oxygen content to less than 0.0012% and the sulfur content to less than 0.0020%. Therefore, FeO must be strictly controlled during the electroslag remelting process. According to the calculation results in Figure 5, it is recommended to control the FeO content to less than 0.014%.

5 Conclusion

(1) The desulfurization thermodynamic model established by [Fe]–[Al]–[O] balance to characterize slag oxidizability is more accurate compared to the models established by the [Fe]–[O] balance and [Al]–[O] balance, and it is closest to the experimental results.

(2) When the FeO content in the slag is greater than 0.014%, the effect of FeO on the slag sulfur distribution ratio is significantly higher than Al₂O₃. When the FeO content in the slag is less than 0.014%, the effect of Al₂O₃ on slag oxidizability will be greater than that of FeO. It is recommended to control FeO content to less than 0.014% when smelting superalloys.

Symbol list

| Symbol | Description |
|--------|-------------|
| aᵢ     | Activity of components i; |
| bᵢ     | Mole number of components i in 100 g of slags (mol); |
| fᵢ     | Activity coefficient of component i in nickel-base alloy; |
| Kᵢ     | Chemical balance constant of forming component i or structural unit i; |
| Lₛ     | Sulfur distribution ratio between slags–metal; |
n_i^0 \text{Mole number of components } i \text{ in 100 g of slags (mol);}

n_i \text{balance mole number of structural unit } i \text{ or ion couple } i \text{ (mol);}

R \text{Gas constant (8.314 J mol}^{-1} \text{ K}^{-1});

T \text{Absolute temperature (K);}

\Delta r G_{m,ci} \text{Standard molar Gibbs free energy}

\omega_i \sum n_i \text{Total balance mole number of all structural units (mol);}

\omega_{(i)} \text{Mass percentage of component } i \text{ in slags (%);}

\omega_{(i)}(\text{FeO}) \text{Mass percentage of FeO in nickel-base alloy (%);}

\omega_{(i)}(\text{AlO}_3) \text{Mass percentage of Al}_2\text{O}_3 \text{ in slags (%);}

\omega_{(S)}(\text{CaS}) \text{Sulfur content in slags boned as CaS (%);}

\omega_{(S)}(\text{MgS}) \text{Sulfur content in superalloy boned as MgS (%);}

L_n[\text{Fe}]=\text{[Al]}=\text{[O]}_{\text{calculated}} \text{Calculated sulfur distribution ratio based on [Fe]=[Al]=[O] balance;}

L_n[\text{Fe}]=\text{[O]}_{\text{calculated}} \text{Calculated sulfur distribution ratio based on [Fe]=[O] balance;}

L_n,\text{tested} \text{Tested total sulfur distribution ratio between slag and metal.}

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