Reaction Mechanism of CA$_6$, Al$_2$O$_3$ and CA$_6$-Al$_2$O$_3$ Refractories with Refining Slag

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Abstract: In this study, to clarify the corrosion mechanism of CA$_6$ based refractory by refining slag, the static crucible tests for CA$_6$, CA$_6$-Al$_2$O$_3$, and Al$_2$O$_3$ refractory, were carried out and the detail reaction processes were analyzed from the perspective of thermodynamic simulation and structural evolution. From the results, CaAl$_2$O$_7$ plays a vital role in the slag corrosion resistance of the three refractories. Regarding CA$_6$ refractory, the double pyramid module in CA$_6$ crystal structure was destroyed very quickly, leading to the rapid collapse of its structure to form the denser CaAl$_2$O$_7$ in high amounts. As a result, a reaction layer mainly composed of CaAl$_2$O$_7$ formed, which effectively inhibited the slag corrosion, so CA$_6$ refractory exhibits the most excellent slag corrosion. Meanwhile, the formation of CaAl$_2$O$_7$ can also avoid CA$_6$ particles entering the molten steel to introduce exogenous inclusions. For Al$_2$O$_3$ refractory, the generation of CaAl$_2$O$_7$ is much slower than that of CA$_6$ and CA$_6$-Al$_2$O$_3$ refractory, and the amount generated is also quite small, resulting in its worst slag corrosion among the three crucibles. Therefore, CA$_6$ based refractory has excellent application potential in ladle refining and clean steel smelting.

Keywords: corrosion resistance; refining slag; refractory; thermodynamic simulation

1. Introduction

During the ladle refining process, the refractory is corroded severely due to the continuous reaction of the refining slag [1–3]. The slag corrosion will destroy the structure of the refractory and reduce the service life [4–7]. More importantly, under the continuous scouring effect of molten steel, the dislodged refractory and the corrosion products would enter the molten steel to form exogenous large size inclusions [8–17], which will have a fatally harmful effect on the purity of the molten steel and the quality of the final products [17–20]. Therefore, in order to eliminate the introduction of exogenous inclusion and to increase the service life of the refractories, it is absolutely essential to study corrosion behavior between the refractory and refining slag.

At present, the primary materials for the refining ladle are Al$_2$O$_3$ system refractories, due to their high density and stable high temperature properties. Many researches have been conducted to investigate the corrosion process between Al$_2$O$_3$ refractories and the refining slag [21–23], and many achievements have been obtained. It was found that the slag corrosion degree of Al$_2$O$_3$ refractories is influenced by factors such as temperature and refining slag composition [24–27]. Some scholars pointed out that [28,29] a small amount of CaAl$_2$O$_7$ generated on the surface of Al$_2$O$_3$ refractories can prevent further corrosion effectively, which is a critical mechanism. After years of development, an understanding of...
the corrosion resistance of Al$_2$O$_3$ refractories has been profound, but there are few reports on the introduction and control of inclusions. So far, as Al$_2$O$_3$ refractories, the problem of introducing inclusions into molten steel is still unavoidable. With the development of cleanliness steel smelting, the effect of refractories on inclusions has attracted more and more attention. In order to prepare refractory materials with excellent corrosion resistance and less introduction of inclusions, in our previous work [30–34] we have synthesized the pure dense CA$_6$ (calcium hexaaluminate, CaAl$_{12}$O$_{19}$) base raw material and studied the slag corrosion resistance. After that, some researchers focused on optimizing CA$_6$ structure and tried to dope N$^{3-}$ or Zr$^{4+}$ into CA$_6$ [35,36], trying to improve performance further and achieve expected results. Besides that, from our recent experiments, the CA$_6$-based refractories not only have excellent slag corrosion resistance but can also reduce the size of inclusions and absorb sulfur in steel. Researches on the preparation and structural improvement of CA$_6$ refractory are consummate. However, its slag corrosion mechanism is not clear, and the effect on the exogenous inclusion is not confirmed, which cannot provide strong support for promotion and application. Therefore, it is essential and meaningful to study the slag corrosion of CA$_6$-based refractory, which has a great significance on refining ladle and even on the whole steelmaking process.

In this study, the reaction mechanism between two CA$_6$-based refractory (pure CA$_6$ and CA$_6$-Al$_2$O$_3$ composite) and refining slag was investigated and analyzed, and the Al$_2$O$_3$ refractory commonly used in the refining ladle was also used as a comparison. The microstructure and distribution of elements in the corrosion area were characterized, and the corrosion process was deduced and simulated by the thermodynamic software. The results of this work proved that CA$_6$ refractory has a great application prospect in the metallurgical industry due to excellent and distinctive slag corrosion resistance.

2. Materials and Methods

2.1. Preparation of the Crucibles and Refining Slag

The CA$_6$, Al$_2$O$_3$, and CA$_6$-Al$_2$O$_3$ crucibles were prepared with CA$_6$ powder (purity > 98 wt%, particle size ≤ 74 µm, Shengchuan, Shandong), Al$_2$O$_3$ powder (purity > 98 wt%, particle size ≤ 74 µm, Shengchuan, Shandong), and the CA$_6$ and Al$_2$O$_3$ powder (mass ratio CA$_6$: Al$_2$O$_3$ = 1:1), respectively. The static crucible method was adopted for the corrosion resistance test. Firstly, the dried powder was pressed under 30 MPa into 80 × 80 × 80 mm$^3$ cubes. Secondly, cylindrical holes with a diameter and height of 40 mm were drilled in the cubes as slag holes. Finally, the crucibles were fired at 1650 ºC for 3 h.

The properties of the crucibles are shown in Table 1.

| Crucible      | Bulk Density/(g/cm$^3$) | Apparent Porosity(%) |
|---------------|------------------------|----------------------|
| CA$_6$        | 2.93                   | 19.23                |
| Al$_2$O$_3$   | 2.92                   | 24.41                |
| CA$_6$-Al$_2$O$_3$ | 2.68          | 28.93                |

The chemical composition of the refining slag is shown in Table 2. The refining slag was prepared using analytically pure CaO (Sinopharm Chemical Reagent, purity > 99 wt%, particle size ≤ 74 µm), Al$_2$O$_3$ (Sinopharm Chemical Reagent, purity > 99 wt%, particle size ≤ 74 µm), MgO (Sinopharm Chemical Reagent, purity > 99 wt%, particle size ≤ 40 µm) and SiO$_2$ (Sinopharm Chemical Reagent, purity > 99 wt%, particle size ≤ 74 µm).

|            | CaO  | Al$_2$O$_3$ | MgO  | SiO$_2$ |
|------------|------|-------------|------|---------|
| Wt (%)     | 40   | 39          | 10   | 11      |
2.2. Experimental

The static crucible method was used to investigate the slag corrosion behavior of the three refractories. Put 70 g refining slag into the crucibles and then heat the crucibles to 1600 °C at a heating rate of 5 °C/min in the box furnace (KSL-1700X-M). After holding for 3h, the furnace stopped working and the crucible was taken out when it cooled to room temperature. The crucibles were cut along the center, and the corrosion area was made into a mosaic sample and then polished.

2.3. Characterization

The composition of the refining slag was analyzed by X-ray fluorescence spectrometry (XRF, Shimadzu, Japan). The micro-morphology of the slag-refractory interface was observed by scanning electron microscopy (SEM, FEI Nova nano 450, USA). The elemental distribution at the slag-resistant material interface was analyzed by SEM equipped with Energy Dispersive Spectrometer (EDS, EDAX Team, USA).

2.4. Thermodynamic Simulation

During the corrosion test, only the final result can be determined clearly and the intermediate process cannot be observed directly. Therefore, thermodynamic simulation for the slag corrosion process is necessary.

In this work, Factsage7.0 was used to simulate the corrosion process of three crucibles. The calculation mechanism is shown in Figure 1. The left side is refining slag and the right side is refractory, and the concentration of the refining slag and refractory at the interface area changes in the reverse cross between 0~1. During the calculations, the interface area is considered as a composition of multiple cross sections and the corrosion process of the refractory is simulated by predicting the generation of each section.

![Figure 1. Thermodynamic calculation mechanism of the corrosion process.](image)

The variable <X> in the Equilib module is used to calculate the inverse crossover interdiffusion, based on which to simulate the corrosion process of the refractory from thermodynamic aspect. When X = 0, the refining slag is all the composition of the system. When x = 1, the refractory is all the composition of the system. At the beginning of the reaction, X was defined as 1. With the decrease of X, more and more slag is involved in the reaction. The oxide data included in the calculation are available in the FIToxid module. The calculated temperature was set at a constant 1873 k and the pressure was 1atm.

3. Results and Discussion

3.1. Composition Changes of Refining Slag

The composition of slag always changed due to the reaction with refractory. Figure 2 shows the variations of the refining slag composition after the corrosion test. As can be seen from Figure 2, the content of the CaO and MgO in the refining slag decreased, and the content of the Al₂O₃ increased in all three crucibles. It indicates that the CaO and MgO in
the slag reacted with or entered into the refractories, and Al₂O₃ in the refractories diffused into the slag during the corrosion process. The content of the SiO₂ in the slag remained almost unchanged, which is due to the large ionic radius of the silicate ion. The composition of the slag variation shows that the three crucibles were corroded by the refining slag in varying degrees.

![Figure 2. Composition variation of the refining slag.](image)

**3.2. Microstructure and Element Distribution**

**3.2.1. Corrosion of CA₆ Crucible**

The microstructure results of the CA₆ crucible after slag corrosion are shown in Figure 3. The left side is the slag layer and the right side belongs to the original brick layer, and the reaction layer is in the middle, as shown in the red dotted area. It can be seen that many pores exist in the original brick layer. The average diameter of the pores ranged from 12 to 180 μm. In general, the higher porosity, the more severe corrosion of the crucible. However, the CA₆ crucible shows excellent slag resistance. At the slag-crucible interface, the width of the reaction layer is 50–60 μm, which is the thinnest of the three crucibles (Figures 5 and 7).

![Figure 3. SEM image of CA₆ crucible after corrosion.](image)

The EDS results show that CaAl₄O₇ generated at the slag-refractory interface (reaction layer), and most of the components in the reaction layer are CaAl₄O₇ (such as the EDS results of area 1). At the experimental temperature, liquid slag penetrated into the refractory through the pores and reacted with refractory to form CaAl₄O₇, which is the
main reaction during the corrosion test. The corrosion of the refractory by the liquid slag was effectively inhibited due to the high viscosity of the CaAl$_2$O$_7$. As the time increased, CaAl$_4$O$_7$ continued to react with CaO in the liquid slag to form CaAl$_2$O$_4$ in the reaction layer. In addition, a very small amount of slag phase of Al$_2$O$_3$-CaO-SiO$_2$-MgO was found in the reaction layer. It can be clearly found that the microstructure of the reaction layer was denser than that of the original bricklayer. One of the reasons is the gaps and pores in the reaction layer were filled by CaAl$_4$O$_7$ and CaAl$_2$O$_4$, which is also an important reason for preventing further corrosion of the refining slag. To reveal the penetration degree of the refining slag, area 2 was selected randomly for EDS analysis. The very limited Mg and Si were detected, indicating that the CaAl$_4$O$_7$ layer effectively prevents the penetration of the refining slag.

Figure 4 gives the element distribution result from the slag layer to the original brick layer. It can be seen that the amount of Al in the original brick layer is significantly more than that in the refining slag, while the amount of Ca was the opposite. Thus, it can be deduced that the Ca in the slag diffused into the refractory during the reaction, while Al diffused from the refractory to the refining slag. The amount of Mg and Si in the refractory was minimal, which can also be proved by the EDS result of area 2, indicating that only a very limited Mg and Si in the refining slag penetrate into the crucible through the pores or the gaps between grains.

![Figure 4. Element mapping of the slag-crucible interface of CA$_6$ crucible.](image1)

**3.2.2. Corrosion of Al$_2$O$_3$ Crucible**

Figure 5 exhibits the microstructure of the Al$_2$O$_3$ crucible after the static crucible test. As can be seen from Figure 5, from left to right are the slag layer, reaction layer, penetration layer, and original brick layer, respectively. The width of the reaction layer was 300 μm, and the maximum width of the penetration layer was more than 880 μm that was the widest among the three crucibles.

![Figure 5. The SEM image of the Al$_2$O$_3$ crucible after corrosion by slag.](image2)

The EDS results show MgO·Al$_2$O$_3$ generated in the reaction layer and it was formed by the reaction between MgO in the refining slag and Al$_2$O$_3$ in the refractory, which is the main component in the reaction layer. Some researchers [4,27] pointed out that the
presence of MgO-Al₂O₃ at the interface has some hindrance to the penetration of slag. Meanwhile, trace amounts of Ca₆Al₂O₇ were also detected in the reaction layer, but its generation mechanism is different from the CA₆ crucible. The Al₂O₃ in the refractory and CaO in the slag reacted to form CaAl₁₂O₁₉ first, and then the CaAl₁₂O₁₉ continued to react with CaO in the slag to form CaAl₄O₇ in the reaction layer. Compared with the CA₆ crucible, EDS results (area 3) show that the content of Mg in the reaction layer increased obviously and the amount of Ca decreased. It is confirmed again that the main phase was MgO-Al₂O₃ and the content of CaAl₄O₇ was limited in the reaction layer. Meanwhile, it can be noticed that the liquid slag phase was found in the reaction layer, and its content is more than that in the CA₆ crucible. In the penetration layer, except for the Al₂O₃ particles, the CaAl₁₂O₁₉ is also found in this area, proving that the Ca in the refining slag gradually penetrated into the refractory through the pores or cracks and reacted with the refractory. In addition, some of slag phase of Al₂O₃-CaO-SiO₂-MgO was found in the penetration layer, proving that the reaction layer does not have an advantage in preventing slag penetration. The EDS results of area 4 show that the content of Mg and Si in the penetration layer is more than that of CA₆ and CA₆-Al₂O₃ crucibles, indicating the Al₂O₃ crucible has the worst slag corrosion resistance of the three crucibles.

Figure 6 is the element distribution result of the slag-crucible interface. It can be seen that the content of Al in the crucible was more than that in slag and Ca was detected in the slag at higher amounts. The element of Ca in the refractory mainly came from the multistep reaction of Al and CaO in the refining slag. Of course, a tiny part of CaAl₄O₇ found from the EDS results, and it is quite possibly generated by the reaction between CA₆ and CaO in the slag to form CaAl₄O₇. Meanwhile, trace amounts of CaAl₄O₇ were also detected in the reaction layer, but its generation mechanism is different from the CA₆ crucible. The Al₂O₃ in the refractory and CaO in the slag reacted to form CaAl₁₂O₁₉ first, and then the CaAl₁₂O₁₉ continued to react with CaO in the slag to form CaAl₄O₇ in the reaction layer. Compared with the CA₆ crucible, EDS results (area 3) show that the content of Mg in the reaction layer increased obviously and the amount of Ca decreased. It is confirmed again that the main phase was MgO-Al₂O₃ and the content of CaAl₄O₇ was limited in the reaction layer. Meanwhile, it can be noticed that the liquid slag phase was found in the reaction layer, and its content is more than that in the CA₆ crucible. In the penetration layer, except for the Al₂O₃ particles, the CaAl₁₂O₁₉ is also found in this area, proving that the Ca in the refining slag gradually penetrated into the refractory through the pores or cracks and reacted with the refractory. In addition, some of slag phase of Al₂O₃-CaO-SiO₂-MgO was found in the penetration layer, proving that the reaction layer does not have an advantage in preventing slag penetration. The EDS results of area 4 show that the content of Mg and Si in the penetration layer is more than that of CA₆ and CA₆-Al₂O₃ crucibles, indicating the Al₂O₃ crucible has the worst slag corrosion resistance of the three crucibles.

3.2.3. Corrosion of CA₆-Al₂O₃ Crucible

Figure 7 shows the SEM image of the CA₆-Al₂O₃ crucible after the slag corrosion. From left to right are the slag layer, reaction layer, penetration layer, and original brick layer, respectively. From Figure 6, the reaction layer was generated between the refining slag and CA₆-Al₂O₃ crucible, and its width was about 200 μm, which was wider than that of the CA₆ crucible and thinner than that of the Al₂O₃ crucible. The microstructure of the reaction layer was denser compared to the original brick layer. In the reaction layer, CaAl₄O₇ is found from the EDS results, and it is quite possibly generated by the reaction between CA₆ in the refractory and CaO in the refining slag. Of course, a tiny part of CaAl₄O₇ may also come from the multistep reaction of Al₂O₃ in the refractory and CaO in the refining slag. In the CA₆ crucible, the CaAl₄O₇ can inhibit further corrosion of the refining slag. However, the content of CaAl₄O₇ in the CA₆-Al₂O₃ crucible was lower than that in the CA₆ crucible due to the limit of raw materials, which is one of the reasons for the wider reaction layer than that of the CA₆ crucible. In the reaction and penetration layer, a similar position to that of the CA₆ and Al₂O₃ crucibles was selected for EDS analysis. The results show the content of Ca in the reaction layer is less than that in the CA₆ crucible but more than in the
Al₂O₃ crucible, so it can be deduced that the amount of CaAl₄O₇ in the reaction layer is between the other two crucibles. In the penetration layer, the amount of Mg and Si was decreased compared with the Al₂O₃ crucible, indicating the slag corrosion resistance of the CA₆-Al₂O₃ crucible is better than the Al₂O₃ crucible but worse than the CA₆ crucible.

![Figure 7](image_url) The results of the CA₆-Al₂O₃ crucible after corrosion by slag.

Figure 8 is the element distribution result of the CA₆-Al₂O₃ crucible. From Figure 8, the content of Al in the crucible was more than that in slag and Ca was detected in the refractory at higher amounts. The Mg and Si were also detected in the crucible and the content was less than that of the Al₂O₃ crucibles, which was also confirmed by the EDS result of area 6, proving the slag resistance of the CA₆-Al₂O₃ crucible was worse than the CA₆ crucible but better than Al₂O₃ crucible.

![Figure 8](image_url) Element mapping of the slag-crucible interface of CA₆-Al₂O₃ crucible.

Through the above analysis, it can be found that the CA₆ crucible shows the best slag corrosion resistance, followed by the CA₆-Al₂O₃ crucible, and the Al₂O₃ crucible is the worst. The reaction mechanism of the CA₆ and Al₂O₃ crucible with the refining slag is shown in Figure 9. It can be seen from Figure 9a–c that the CA₆ particles reacted with the refining slag to form CaAl₄O₇ that can fill the pores or the gaps between the particles. Due to the high viscosity of CaAl₄O₇, the slag-refractory interface will be denser and has a positive effect on inhibiting the slag corrosion. At the same time, it should be noticed that the probability of CA₆ particles entering the molten steel is greatly reduced due to the formation reaction layer, so the introduction of exogenous inclusions from the refractory is greatly reduced. In our recent work, it has been proved that the reaction product of the CA₆ refractory and refining slag can decrease the number and size of the inclusions. For the Al₂O₃ crucible, in addition to reacting with the Al₂O₃ particles at the interface, the refining slag also reacts with the inside Al₂O₃ crucible by penetrating into the refractory through the pores and the gaps between the Al₂O₃ particles, as shown in Figure 9d. During the corrosion process, the Al₂O₃ particles gradually dissolve or fall off into the refining slag, causing the more serious corrosion of the crucible, which is shown in Figure 9e,f. In addition, the fall-off particles can enter the molten steel and increase the number of inclusions in steel, which has a negative influence on the quality of steel production. Regarding the CA₆-Al₂O₃ crucible, the
CaAl$_4$O$_7$ is generated faster and the content is more due to the CA$_6$ raw materials compared with the Al$_2$O$_3$ crucible. Therefore, the slag corrosion resistance of the CA$_6$-Al$_2$O$_3$ crucible is better than that of the Al$_2$O$_3$ crucible.

![Figure 9](image)

**Figure 9.** Reaction mechanism of the slag corrosion on the CA$_6$ and Al$_2$O$_3$ crucible. (a-e): The corrosion process of the CA$_6$ crucible; (d-f): The corrosion process of the Al$_2$O$_3$ crucible.

3.3. Thermodynamic Simulation of Corrosion of Crucibles by Refining Slag

The results of the thermodynamic simulation of the corrosion process of the CA$_6$ crucible are shown in Figure 10a. The corrosion process can be divided into the following steps according to the variation of X.

![Figure 10](image)

**Figure 10.** The thermodynamic simulation results of three crucibles: (a) CA$_6$ crucible, (b) Al$_2$O$_3$ crucible, and (c) CA$_6$-Al$_2$O$_3$ crucible.
From Figure 10a, when 1.0 < X < 0.76, four phases of CaAl\(_4\)O\(_7\), Ca\(_2\)Mg\(_2\)Al\(_2\)O\(_{46}\), CaAl\(_{12}\)O\(_19\), and liquid slag were obtained. With the decrease of X, the content of CaAl\(_4\)O\(_7\), Ca\(_2\)Mg\(_2\)Al\(_2\)O\(_{46}\), and liquid slag increased while the content of CaAl\(_{12}\)O\(_19\) decreased sharply. When X = 0.76, the content of Ca\(_2\)Mg\(_2\)Al\(_2\)O\(_{46}\) reached a maximum of 40.95% and the content of CaAl\(_{12}\)O\(_19\) was zero. Ca\(_2\)Mg\(_2\)Al\(_2\)O\(_{46}\) and CaAl\(_4\)O\(_7\) generated by the reaction of Equations (1) and (2):

\[
2\text{CaAl}_{12}\text{O}_{19} + 2\text{MgO} + 2\text{Al}_2\text{O}_3 = \text{Ca}_2\text{Mg}_2\text{Al}_{28}\text{O}_{46}
\]

\[
\text{CaAl}_{12}\text{O}_{19} + 2\text{CaO} = 3\text{CaAl}_4\text{O}_7
\]

When 0.76 < X < 0.7, a new phase of CaMg\(_2\)Al\(_{16}\)O\(_{27}\) appeared and increased with decreasing X, while the content of Ca\(_2\)Mg\(_2\)Al\(_2\)O\(_{46}\) gradually decreased until the content was zero at X = 0.7, indicating that Ca\(_2\)Mg\(_2\)Al\(_2\)O\(_{46}\) gradually transformed into CaMg\(_2\)Al\(_{16}\)O\(_{27}\) and CaAl\(_4\)O\(_7\) following the Equations (3) and (4) respectively:

\[
\text{Ca}_2\text{Mg}_2\text{Al}_{28}\text{O}_{46} = 2\text{CaAl}_4\text{O}_7 + 2\text{MgO} + 10\text{Al}_2\text{O}_3
\]

\[
\text{Ca}_2\text{Mg}_2\text{Al}_{28}\text{O}_{46} + 2\text{MgO} + 2\text{Al}_2\text{O}_3 = 2\text{CaMg}_2\text{Al}_{16}\text{O}_{27}
\]

When 0.7 < X < 0.6, the spinel phase appeared in the system at X = 0.66 through the reaction of Equation (5). The content of CaMg\(_2\)Al\(_{16}\)O\(_{27}\) decreased gradually, and the content of CaAl\(_4\)O\(_7\) increased gradually with the decrease of X, which indicated the CaMg\(_2\)Al\(_{16}\)O\(_{27}\) continues to be converted to the CaAl\(_4\)O\(_7\) by the equation (6). When X = 0.6, the content of CaMg\(_2\)Al\(_{16}\)O\(_{27}\) was zero, while the content of CaAl\(_4\)O\(_7\) and spinel reached the maximum content of 49.04% and 8.91%, respectively:

\[
\text{Al}_2\text{O}_3 + \text{MgO} = \text{MgAl}_2\text{O}_4
\]

\[
\text{CaMg}_2\text{Al}_{16}\text{O}_{27} = \text{CaAl}_4\text{O}_7 + 2\text{MgO} + 6\text{Al}_2\text{O}_3
\]

When 0.6 < X < 0.47, the content of the CaAl\(_4\)O\(_7\) decreased sharply and the liquid slag increased rapidly. When X = 0.47, the content of CaAl\(_4\)O\(_7\) was zero. When 0.47 < X < 0.14, two phases of liquid slag and spinel were in the system, and the content of spinel decreased to zero at X = 0.14. When 0.14 < X < 0, the liquid slag was the only phase in the system.

The results of the thermodynamic simulation of the Al\(_2\)O\(_3\) crucible and CA\(_6\)-Al\(_2\)O\(_3\) crucible are shown in Figure 10b,c, respectively. The trends of the thermodynamic simulation results for the Al\(_2\)O\(_3\) and CA\(_6\)-Al\(_2\)O\(_3\) crucibles are roughly similar to the CA\(_6\) crucible. However, significant differences existed in the beginning stage of the corrosion. For the Al\(_2\)O\(_3\) crucible, when 1 < X < 0.76, the Al\(_2\)O\(_3\) converted to CaAl\(_{12}\)O\(_19\) gradually by Equation (7), and the Ca\(_2\)Mg\(_2\)Al\(_{28}\)O\(_{46}\) can also be generated through Equation (8). When X = 0.76, the phase of CaAl\(_4\)O\(_7\) generated in the system and its content reached the maximum of 34.18% when X = 0.48, which is lower than that of the CA\(_6\) and CA\(_6\)-Al\(_2\)O\(_3\) crucible. For the CA\(_6\)-Al\(_2\)O\(_3\) crucible, the Al\(_2\)O\(_3\) converted to CaAl\(_{12}\)O\(_19\) first, and then CaAl\(_{12}\)O\(_19\) started to react with the refining slag to form CaAl\(_4\)O\(_7\) at X = 0.86. And the maximum content of CaAl\(_4\)O\(_7\) is 40.11% when X = 0.54, which is higher than that of the Al\(_2\)O\(_3\) crucible but lower than that of the CA\(_6\) crucible:

\[
\text{CaO} + 6\text{Al}_2\text{O}_3 = \text{CaAl}_{12}\text{O}_{19}
\]

\[
2\text{CaO} + 2\text{MgO} + 14\text{Al}_2\text{O}_3 = \text{Ca}_2\text{Mg}_2\text{Al}_{28}\text{O}_{46}
\]

From the analysis of thermodynamic simulation, it can be found that the high melting point phase CaAl\(_4\)O\(_7\) is the critical point in enhancing the slag resistance of the crucible [37–40]. The maximum content of the CaAl\(_4\)O\(_7\) of the CA\(_6\), Al\(_2\)O\(_3\), and CA\(_6\)-Al\(_2\)O\(_3\) crucible is 49.04%, 34.18%, and 40.11%, respectively, through the thermodynamic simulation results, which the trend is consistent with the EDS results. The CaAl\(_4\)O\(_7\) was formed at the beginning of the reaction for the CA\(_6\) crucible. For the Al\(_2\)O\(_3\) and the CA\(_6\)-Al\(_2\)O\(_3\) crucible, the CaAl\(_4\)O\(_7\) was
formed at \(X = 0.54\) and 0.86, respectively. Therefore, the \(\text{CaAl}_2\text{O}_7\) generated fastest and the amount was the most during the corrosion process of the \(\text{CA}_6\) crucible, which had a great benefit on the slag resistance corrosion.

3.4. Crystal Structure Analysis of the Refractories

The results of the EDS analysis and thermodynamic simulations show that the \(\text{CA}_6\) crucible can rapidly generate a higher amount of \(\text{CaAl}_2\text{O}_7\) by reacting with the refining slag, while the \(\text{Al}_2\text{O}_3\) crucible generates the \(\text{CaAl}_2\text{O}_7\) through a series of reactions. In this section, the crystal structure of the \(\text{CA}_6\) and \(\text{Al}_2\text{O}_3\) is analyzed, and the reason for the difference in the \(\text{CaAl}_2\text{O}_7\) generation rate and quantity between the \(\text{CA}_6\) and \(\text{Al}_2\text{O}_3\) is also explained.

Figure 11 shows the crystal structure of the \(\text{CA}_6\) and \(\text{Al}_2\text{O}_3\). It can be seen that one \(\text{Al}\) and five \(\text{O}\) combined to form the double pyramid module in the mirror layer of the \(\text{CA}_6\) crystal structure, as shown in the area circled red dotted line. The double pyramid module is the active site of \(\text{CA}_6\) and is unstable during the reaction process. When the refining slag reacts with the crucible, the active site will be destroyed quickly, resulting in the rapid collapse of the \(\text{CA}_6\) crystal structure to form the denser \(\text{CaAl}_2\text{O}_7\). The crystal structure of \(\text{CaAl}_2\text{O}_7\) is more stable and can effectively inhibit the further corrosion of slag, which is one of the reasons for the excellent slag corrosion resistance of the \(\text{CA}_6\) crucible. \(\text{Al}_2\text{O}_3\) crystal is an octahedral structure and more stable compared to \(\text{CA}_6\), so the reaction rate with \(\text{Ca}\) in the refining slag is very slow, resulting in a low content of \(\text{CaAl}_2\text{O}_7\) in the reaction layer and poor corrosion resistance. More importantly, \(\text{Al}_2\text{O}_3\) particles with high stability may directly enter the refining slag and molten steel, resulting in the generation of exogenous inclusions, which has a negative impact on the control of inclusions. At this point, the \(\text{CA}_6\) refractory can well avoid this problem. So, the excellent slag corrosion resistance of the \(\text{CA}_6\) crucible has a great application prospect in the ladle refining process, especially for the smelting clean steel.

![Figure 11](image-url) 

**Figure 11.** The crystal structure of \(\text{CA}_6\), \(\text{CA}_2\), and \(\text{Al}_2\text{O}_3\).

4. Conclusions

Three crucibles (\(\text{CA}_6\) crucible, \(\text{Al}_2\text{O}_3\) crucible, and \(\text{CA}_6\)-\(\text{Al}_2\text{O}_3\) crucible) were selected to investigate the corrosion resistance of the refining slag through laboratory experiments and thermodynamic simulations. The following conclusions were obtained.

(1) The three crucibles show different slag corrosion resistance; \(\text{CA}_6\) crucible has the best corrosion resistance, followed by the \(\text{CA}_6\)-\(\text{Al}_2\text{O}_3\) crucible. The \(\text{Al}_2\text{O}_3\) crucible shows the worst slag corrosion resistance.

(2) The addition of \(\text{CA}_6\) to the raw materials has a positive effect on improving the slag corrosion resistance of the \(\text{Al}_2\text{O}_3\) crucible.

(3) The generation of high melting point \(\text{CaAl}_2\text{O}_7\) is the critical factor for inhibiting the further corrosion of the \(\text{CA}_6\) and \(\text{CA}_6\)-\(\text{Al}_2\text{O}_3\) crucible. The \(\text{CaAl}_2\text{O}_7\) was also detected in the \(\text{Al}_2\text{O}_3\) crucible, but \(\text{Al}_2\text{O}_3\) in the refractory reacts with \(\text{CaO}\) in the refining slag to produce...
CaAl$_2$O$_9$ firstly, and then the CaAl$_2$O$_9$ reacted with slag to form CaAl$_4$O$_7$. Therefore, the generation of CaAl$_4$O$_7$ in Al$_2$O$_3$ crucible is slower than that of CA$_6$ crucible and the amount generated is relatively less, which results in a worse slag corrosion resistance of Al$_2$O$_3$ crucible compared to CA$_6$ crucible and CA$_6$-Al$_2$O$_3$ crucible.

(4) When the refining slag reacts with the crucible, the double pyramid module of CA$_6$ will be destroyed quickly, resulting in the rapid collapse of the CA$_6$ crystal structure to form the denser CaAl$_2$O$_7$, which is an essential reason for the excellent slag corrosion resistance. At the same time, it also avoids CA$_6$ particles entering the molten steel to introduce exogenous inclusions, so CA$_6$ has great application potential in ladle refining and clean steel smelting.

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**References**

1. Chen, J.; Chen, L.; Wei, Y.; Li, N.; Zhang, S. Corrosion and penetration behaviors of slag/steel on the corroded interfaces of Al$_2$O$_3$-C refractories: Role of Ti$_2$AlC$_2$. *Corros. Sci.* 2018, 143, 166–176. [CrossRef]
2. Xu, L.; Chen, M.; Wang, N.; Yin, X.L. Corrosion mechanism of MgAl$_2$O$_4$–CaAl$_2$O$_7$–CaAl$_2$O$_9$ composite by steel ladle slag: Effect of additives. *J. Eur. Ceram. Soc.* 2017, 37, 2737–2746. [CrossRef]
3. Berjonneau, J.; Prigent, P.; Poirier, J. The development of a thermodynamic model for Al$_2$O$_3$–MgO refractory castable corrosion by secondary metallurgy steel ladle slags. *Ceram. Int.* 2009, 35, 623–635. [CrossRef]
4. Riaz, S.; Mills, K.; Bain, K. Experimental examination of slag/refractory interface. *Ironmak. Steelmak.* 2022, 29, 107–113. [CrossRef]
5. Zou, Y.; Huang, A.; Gu, H. Novel phenomenon of quasi-volcanic corrosion on the alumina refractory-slag-air interface. *J. Am. Ceram. Soc.* 2020, 103, 6639–6649. [CrossRef]
6. Mills, K.C.; Su, Y.; Fox, A.B.; Li, Z.; Thackray, R.P.; Tsai, H. A review of slag splashing. *ISIJ Int.* 2005, 45, 619–633. [CrossRef]
7. Liu, C.; Huang, F.; Wang, X. The effect of refining slag and refractory on inclusion transformation in extra low oxygen steels. *Metall. Mater. Trans. B* 2016, 47, 999–1009. [CrossRef]
8. Huang, A.; Wang, Y.; Gu, H.; Zou, Y. Dynamic interaction of refractory and molten steel: Effect of alumina-magnesia castables on alloy steel cleanliness. *Ceram. Int.* 2018, 44, 22146–22153. [CrossRef]
9. Jones, P.T.; Vleugels, J.; Volders, I.; Blanpain, B.; van der Bist, O.; Wollants, P. A study of slag-infiltrated magnesia-chromite refractories using hybrid microwave heating. *J. Eur. Ceram. Soc.* 2002, 22, 903–916. [CrossRef]
10. Ali, M.; Sayet, T.; Gasser, A.; Blond, E. Transient Thermo-Mechanical Analysis of Steel Ladle Refractory Linings Using Mechanical Homogenization Approach. *Ceramics 2020*, 3, 171–189. [CrossRef]
11. Deng, Z.; Zhu, M.; Sichen, D. Effect of refractory on nonmetallic inclusions in Al-killed steel. *Metall. Mater. Trans. B* 2016, 47, 3158–3167. [CrossRef]
12. Deng, Z.; Chen, L.; Zhu, M. Effect of Refractory on Nonmetallic Inclusions in Si–Mn-Killed Steel. *Steel Res. Int.* 2019, 90, 1900268. [CrossRef]
13. Li, Y.; Yang, W.; Zhang, L. Formation mechanism of MgO containing inclusions in the molten steel refined in MgO refractory crucibles. *Metals 2020*, 10, 444. [CrossRef]
14. Beskow, K.; Tripathi, N.N.; Nzotta, M.; Sandberg, A.; Sichen, D. Impact of slag–refractory lining reactions on the formation of inclusions in steel. *Ironmak. Steelmak.* 2004, 31, 514–518. [CrossRef]
15. Brabie, V. Mechanism of reaction between refractory materials and aluminum deoxidised molten steel. *ISIJ Int.* 1996, 36, S109–S112. [CrossRef]
16. Shin, J.; Chung, Y.; Park, J. Refractory–Slag–Metal–Inclusion Multiphase Reactions Modeling Using Computational Thermodynamics: Kinetic Model for Prediction of Inclusion Evolution in Molten Steel. *Metall. Mater. Trans. B* 2016, 48, 46–59. [CrossRef]
17. Du, G.; Li, J.; Wang, Z. Effect of initial large-sized inclusion content on inclusion removal during electroslag remelting of H13 die steel. *Ironmak. Steelmak.* 2018, 45, 919–923. [CrossRef]
18. Lei, Z.; Hong, Y.; Xie, J.; Sun, C.; Zhao, A. Effects of inclusion size and location on very-high-cycle fatigue behavior for high strength steels. *Mater. Sci. Eng. A.* 2012, 558, 234–241. [CrossRef]

19. Holappa, L.; Helle, A. Inclusion control in high-performance steels. *J. Mater. Process. Technol.* 1995, 53, 177–186. [CrossRef]

20. Karr, U.; Sandaiji, Y.; Tanegashima, R.; Murakami, S.; Schoenbauer, B.; Fitzka, M.; Mayer, H. Inclusion initiated fracture in spring steel under axial and torsion very high cycle fatigue loading at different load ratios. *Int. J. Fatigue* 2020, 134, 105525. [CrossRef]

21. Zhang, S.; Rezae, H.R.; Sarpoollaky, H.; Lee, W.E. Alumina dissolution into silicate slag. *J. Am. Ceram. Soc.* 2000, 83, 897–903. [CrossRef]

22. Choi, J.Y.; Lee, H.G.; Kim, J.S. Dissolution rate of Al₂O₃ into molten CaO-SiO₂-Al₂O₃ slags. *ISIJ Int.* 2002, 42, 852–860. [CrossRef]

23. Yan, P.; Weberl, B.A.; Pistorius, P.C.; Fruehan, R.J. Nature of MgO and Al₂O₃ Dissolution in Metallurgical Slags. *Metall. Mater. Trans. B* 2015, 46, 2414–2418. [CrossRef]

24. de Bilbao, E.; Poirier, J.; Dombrowski, M. Corrosion of high alumina refractories by Al₂O₃-CaO slag: Thermodynamic and kinetic approaches. *Metall. Res. Technol.* 2015, 112, 607–621. [CrossRef]

25. Fernández, B.; Almanza, J.; Rodríguez, J.; Cortes, D.; Escobedo, J.; Gutiérrez, E. Corrosion mechanisms of Al₂O₃/MgAl₂O₄ by V₂O₅, NiO, Fe₂O₃ and vanadium slag. *Ceram. Int.* 2011, 37, 2973–2979. [CrossRef]

26. Song, J.; Liu, Y.; Li, X.; You, Z. Corrosion Behavior of Al₂O₃ Substrate by SiO₂–MgO–FeO–CaO–Al₂O₃ Slag. *J. Mater. Res. Technol.* 2020, 9, 314–321. [CrossRef]

27. Tang, H.; Wu, G.; Wang, Y.; Li, J.; Lan, P.; Zhang, J. Comparative evaluation investigation of slag corrosion on Al₂O₃ and MgO-Al₂O₃ refractories via experiments and thermodynamic simulations. *Ceram. Int.* 2017, 43, 16502–16511. [CrossRef]

28. Wang, W.; Xue, L.; Zhang, T.; Zhou, L.; Chen, J.; Pan, Z. Thermodynamic corrosion behavior of Al₂O₃, ZrO₂ and MgO refractories in contact with high basicity refining slag. *Ceram. Int.* 2019, 45, 20664–20673. [CrossRef]

29. Fu, L.; Huang, A.; Gu, H.; Lu, D.; Lian, P. Effect of nano-alumina sol on the sintering properties and microstructure of microporous corundum. *Mater. Des.* 2016, 89, 21–26. [CrossRef]

30. Chen, J.; Yan, M.; Su, J.; Li, B.; Chou, K.C.; Hou, X.; Chen, M.; Zhao, B. Controllable Preparation of Al₂O₃-MgO-Al₂O₃-CaO-6Al₂O₃(AMC) Composite with Improved Slag Penetration Resistance. *Int. J. Appl. Ceram. Technol.* 2016, 13, 33–40. [CrossRef]

31. Li, B.; Li, G.; Chen, H.; Chen, J.; Hou, X.; Li, Y. Physical and mechanical properties of hot-press sintering ternary CM₂₈₉₅₆₆₁₅₁₆₁₄₁₈₁₂₂₀₄₆₁₉₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆1. [CrossRef]

32. Li, B.; Chen, H.; Chen, J.; Wang, E.; Hou, X.; Li, Y. Preparation, growth mechanism and slag resistance behavior of ternary Ca₂Mg₂Al₂O₆(C₂M₂A₁₄) ceramics. *Adv. Ceram.* 2018, 7, 229–236. [CrossRef]

33. Chen, J.; Chen, H.; Mi, W.; Cao, Z.; Li, B.; Liang, C.; Vance, L. Substitution of Ba for Ca in the Structure of CaAl₂O₁₉. *J. Am. Ceram. Soc.* 2017, 100, 413–418. [CrossRef]

34. Chen, J.; Chen, H.; Mi, W.; Cao, Z.; Li, B.; Li, G. Synthesis of CaO₂MgO·8Al₂O₃ (CM₂₈₉₅₆₆₁₅₁₆₁₄₁₈₁₂₂₀₄₆₁₉₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆₁₄₁₈₁₂₂₀₆1. [CrossRef]

35. Xu, L.; Wang, E.; Hou, X.; Chen, J.; He, Z.; Liang, T. Effect of incorporation of nitrogen on calcium hexaaluminate. *J. Eur. Ceram. Soc.* 2020, 40, 6155–6161. [CrossRef]

36. Guo, C.; Wang, E.; Hou, X.; Kang, J.; Yang, T.; Liang, T.; Bei, G. Preparation of Zr₄⁺ doped calcium hexaaluminate with improved slag penetration resistance. *J. Am. Ceram. Soc.* 2021, 104, 4854–4866. [CrossRef]

37. Xiao, J.; Chen, J.; Li, Y.; Cheng, Y.; Nath, M.; Zhang, Y.; Zheng, L.; Wei, Y.; Zhang, S.; Li, N. Corrosion mechanism of cement-bonded Al₂O₃–MgAl₂O₄ pre-cast castables in contact with molten steel and slag. *Ceram. Int.* 2022, 48, 5168–5173. [CrossRef]

38. Darban, S.; Reynaert, C.; Ludwig, M.; Prorok, R.; Jastrzębska, I.; Szczepańska, J. Corrosion of Alumina-Spinel Refractory by Secondary Metallurgical Slag Using Coating Corrosion Test. *Materials* 2022, 15, 3425. [CrossRef]

39. Wang, X.; Zhao, P.; Chen, J.; Zhao, H.; He, K. Corrosion resistance of Al–Cr-slag containing chromium-corundum refractories to slags with different basicity. *Ceram. Int.* 2018, 44, 12162–12168. [CrossRef]

40. Yin, H.; Gao, K.; Wan, Q.; Xin, Y.; Tang, Y.; Yuan, H. A comparative study on the slag resistance of dense corundum-spinel refractory and lightweight corundum-spinel refractory with density gradient. *Ceram. Int.* 2021, 47, 2130–21318. [CrossRef]