Synthesis of CA₆/AlON composite with enhanced slag resistance

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Abstract: Different amounts of AlON have been introduced in calcium hexaaluminate (CA₆) using two approaches, that is, one-step and two-step methods, to improve the slag resistance of CA₆. A one-step method can directly sinter the mixtures combining Al₂O₃, CaCO₃, and Al in flowing nitrogen, in which AlON clusters are always formed because of the poor wettability of Al by Al₂O₃, leading to the high porosity of CA₆/AlON composite. In a two-step method, CA₆ and AlON are prepared separately and then mixed and sintered in flowing nitrogen. Compared with the sample prepared by the one-step method, CA₆ and AlON in composite by the two-step method are more uniformly distributed, and the optimized amount of AlON added is 10wt%. The slag corrosion and penetration test shows that the CA₆/AlON composite using the two-step method exhibits superior slag corrosion protection. The promoted effect of AlON on slag penetration and corrosion resistance is also discussed.

Keywords: CA₆/AlON composite; two-step method; wettability; slag resistance

1. Introduction

Calcium hexaaluminate (CaAl₁₂O₁₉, usually denoted as CA₆) is widely used as a high-temperature ceramic because of its excellent properties, including high melting point, good alkaline resistance, high stability in a reducing atmosphere, and low thermal conductivity [1–4]. However, CA₆ possesses a magnetoplumbite structure and belongs to the hexagonal crystal system (space group P6₃/mmc) [5–8]. The specific structure can result in the anisotropic growth of CA₆ platelet-shaped grains, which cannot obtain dense bulk CA₆. Consequently, the obtained CA₆ usually has high porosity up to more than 20% sintered at 1750°C [9–10]. This porous structure accelerates the penetration and chemical attack of molten slag when used as ladle furnace lining’s refractories [11–12].

The addition of a second phase is an effective approach to increase the densification of matrixes [12–19]. For example, Yao et al. [15] introduced 20wt% SiO₂ into Cr₂O₃ during sintering in a buried carbon atmosphere. The results showed that the crystal growth of Cr₂O₃ was significantly limited, and the densification of the bulk composite was increased to a large extent. Luo et al. [16] proposed that MnO can improve the densification of Ca₃Mg₂Al₅O₁₄ ceramic, and the results showed that apparent porosity was decreased to 8.4% with the addition of 3wt% MnO. Xu et al. [12–13,17] found that ZrO₂, Y₂O₃, and TiO₂ can greatly decrease the porosity and pore sizes of the MgAl₂O₄–CaAl₂O₆–CaAl₂O₆ composite, thereby improving the slag resistance of the composite.

Al₂O₃N₂ (usually denoted as AlON) as the solid solution of Al₂O₃ and AlN belongs to the cubic crystal system (space group Fd-3m) [20]. Different from the large plate-like crystal morphology of CA₆, AlON always exists in small cubic or near-spherical structures, which cannot fill the voids formed among CA₆ grains. Meanwhile, AlON possesses the characteristics of nitrogen oxide, and its metal and oxide melts have poor wettability [20–26]. Based on previous reports, the addition of AlON can improve the slag resistance of some matrixes such as Al₂O₃–C and Al₂O₃–SiC–C [25–26]. Furthermore, no significant solid solution and any chemical reaction are found between CA₆ and AlON sintered at 1750°C, which is conducive for maintaining respective properties [27]. Therefore, AlON could be a potential additive for the improvement of densification and slag resistance of CA₆.

In this study, the CA₆/AlON composite has been prepared using one-step and two-step methods for the first time. The former includes the sintering of Al₂O₃, CaCO₃, and Al mixtures with different proportions as raw materials in a flowing nitrogen atmosphere. In the latter, a pre-synthesized mixture of CA₆ and AlON is sintered at 1650°C in a flowing nitrogen atmosphere. In this study, the obtained CA₆/AlON composite is characterized using X-ray diffraction (XRD) and
scanning electron microscopy (SEM) combined with energy-dispersive spectrometry (EDS). The bulk density and apparent porosity were also measured. The slag penetration and corrosion resistance tests of the CA₆/AlON composite with pure CA₆ as the control sample were conducted. Furthermore, the promoted effect of AlON on the slag resistance of CA₆/AlON composite was discussed.

2. Experimental

2.1. Raw materials

The main raw materials for the preparation of CA₆/AlON composite used in this work were analytically pure Al₂O₃ and CaCO₃ (Sinopharm Chemical Reagent Co., Ltd., 99wt% purity, average grain size < 44 µm), with Al fine powders (Shanghai Aladdin Reagent Co., Ltd., 99wt% purity, average grain size < 58 µm). MgO, CaO, and SiO₂ powders (Sinopharm Chemical Reagent Co., Ltd., 99wt% purity, average grain size of < 44 µm) were adopted to prepare the refining slag. Al₂O₃, SiO₂, CaO, and MgO powders were pre-calcined in a muffle furnace (5*2-5-13A, Zhengzhou Xinhan Instrument Equipment Co., LTD., China). The resulting CA₆ block was further crushed with the same size as AlON powder. The obtained AlON and CA₆ powders were further mixed, ball-milled, dried, pressed, and then sintered at 1650°C for 2 h in flowing N₂ gas in the same furnace mentioned in Section 2.2.1.

Notably, the amount of AlON incorporated during the two abovementioned methods was 5wt%, 10wt%, 15wt%, and 20wt%. Therefore, the CA₆/AlON composite prepared by the one-step method and two-step method was labeled as S1-x and SII-x, respectively, where x denotes the mass percent of AlON (Table 1).

| Table 1. Compositions of the designed CA₆/AlON composites wt% |
|---------------------------------------------------------------|
| Composite prepared by one-step method | Composite prepared by two-step method | CA₆ | AlON |
| S1-5 | SII-5 | 95 | 5 |
| S1-10 | SII-10 | 90 | 10 |
| S1-15 | SII-15 | 85 | 15 |
| S1-20 | SII-20 | 80 | 20 |

2.2. Preparation of CA₆/AlON composite

2.2.1. One-step method

In view of the one-step method, the pre-fired Al₂O₃ and CaCO₃ powders and Al powder with different proportions were wet ball-milled for 24 h in absolute ethanol. The resulting slurry was dried in a vacuum-drying cabinet (DZF-6020, Zhongyi Guoke Technology Co., LTD., China) at 100°C for 12 h, ground in a mortar, and filtrated through nylon sieves with screen mesh of 120. Subsequently, the obtained mixture was uniaxially pressed under 20 MPa into φ25 mm × 25 mm cylinders. Based on the stability region of AlON reported by Willems et al. [28], the AlON phase will form at above 1625°C. High sintering temperature contributed to the purity of AlON. Combining the capacity of the experimental furnace (RV281P8ANT, Nabatherm Company, Germany), the specimens were sintered from 1650 to 1750°C with 50°C intervals for 3 h in flowing N₂ gas (99.999%).

2.2.2. Two-step method

The two-step method includes the preparation of single CA₆ and AlON phases and the sintering of CA₆/AlON composite. Regarding the preparation of the AlON phase, aluminothermic reduction nitridation was herein adopted [29–31]. First, the pre-fired Al₂O₃ and Al powders with a mass ratio of 88:12 were wet milled for 24 h and dried in a vacuum at 100°C for 10 h. Afterward, the dried powder mixture was uniaxially pressed into a 50 mm block under 30 MPa and then sintered at 1750°C for 3 h in a graphite crucible under flowing N₂ atmosphere using a chamber electric furnace (5*2-5-13A, Zhengzhou Xinhan Instrument Equipment Co., LTD., China). The obtained AlON ceramic block was pulverized to a particle size of 45 µm for later use. Likewise, based on the stoichiometric ratio of n(CaO) : n(Al₂O₃) = 1:6, the pre-fired Al₂O₃ and CaCO₃ as raw materials were mixed and sintered at 1550°C for 2 h in the air to prepare the single CA₆ phase [3] in a chamber electric furnace (5*2-5-13A, Zhengzhou Xinhan Instrument Equipment Co., LTD., China). The resulting CA₆ block was further crushed with the same size as AlON powder. The obtained AlON and CA₆ powders were further mixed, ball-milled, dried, pressed, and then sintered at 1650°C for 2 h in flowing N₂ gas in the same furnace mentioned in Section 2.2.1.

The slag penetration and corrosion test shown in Fig. 1 was adopted to evaluate the slag penetration and corrosion resistance of the CA₆/AlON composite [11–12,32]. This method has two main purposes. On the one hand, it can assess the wettability between the molten slag and the composite. On the other hand, it can provide a direct way to observe the coupling effect of penetration and corrosion of molten slag on the composite.

Fig. 1. Schematic diagram of the slag–composite interface in the reaction test.

Herein, the slags were pressed into a cylinder with 30 mm in diameter and 5 mm in height at 30 MPa. Then, the cylindrical slag was placed on the polished surfaces (the minimum abrasive size was 1200 grit using a SiC sandpaper) of the cylindrical CA₆/AlON composite and pure CA₆ with 50 mm in diameter and 30 mm in height, followed by a thermal treatment in a chamber electric furnace with carbon buried at 1550°C for 0.5 h. The slag composition used herein is illustrated in Table 2. In addition, the viscosity of the slag was calculated to be 0.978 at 1550°C based on FactSage software. This kind of slag was selected because of two reasons. First, the slag components originating from a typical Landle furnace (LF) slag are commonly applied during the refining of
different steels using an aluminum-deoxidized process [1,33]. Second, CA₆ generally exhibits outstanding corrosion resistance to high basicity steel slag (≥4). The selected LF slag with a basicity (the ratio of CaO/SiO₂) of 3.42 can test the effect of an addition on the slag penetration resistance of CA₆. The evaluation of slag penetration depth of the tested composite was based on the following steps. First, the tested composites were cut along the vertical axis. The penetration depth was then measured on the basis of different grayscale values between the unreacted composite and corrosion zone, where the corrosion zone was defined via the degradation of the sample.

Table 2. Chemical composition of model slag

| Oxide content / wt% | C/S |
|--------------------|-----|
| CaO                | 59.1|
| Al₂O₃              | 19.3|
| SiO₂               | 17.3|
| MgO                | 4.3 |
|                    | 3.42|

Note: C/S—Ratio of CaO/SiO₂ in the slag, which can reflect the basicity of the slag.

2.4. Characterization

The crystalline phases of the synthesized samples were examined by using an XRD analyzer (Cu Kα radiation, MAC Science Co. Ltd., Japan) from 10° to 90° at a step of 0.02°. Based on the Rietveld theory, structure refining was conducted using GSAS software. The surface and cross-sectional morphologies and chemical analysis of the samples were characterized by SEM (JSM-840A, JEOL, Japan) in combination with EDS analysis. In addition, the bulk density and apparent porosity were evaluated on the basis of the Archimedes law. Considering the potential hydration problem of a small amount of possible AlN in composite [34], distilled kerosene was used as the immersion fluid.

2.5. Molecular dynamics (MD) simulation approach

MD simulation was conducted to investigate the wetting behavior of molten slag by CA₆ and AlON using the Large-scale Atomic/Molecular Massively Parallel Simulator package [35]. For the slag system, Miyake potential [36–37] was used to describe the force among slags, and Lennard–Jones potential [38] was used for the slag–CA₆ and slag–AlON interactions. The substrates (CA₆ or AlON) were fixed; thus, no potential function was used for the atoms. During the simulation, the Nose–Hoover thermostat was used to maintain the number of particles (N), temperature (T), and volume (V).

3. Results and discussion

3.1. Preparation and characterization of CA₆/AlON composite by the one-step method

Fig. 2 shows the typical XRD patterns of SI-10 prepared by the one-step method at different sintering temperatures. The main phase of the sample sintered at 1650°C is CA₆ with a small amount of Al₂O₃ and AlN. When the temperature rises up to 1700°C, new characteristic peaks corresponding to AlON can be observed. Meanwhile, the relative intensities of the characteristic peaks of Al₂O₃ are significantly reduced, indicating that high sintering temperature can enhance the solid–solid reaction of Al₂O₃ and AlN to form AlON. This phenomenon is consistent with the results reported in the literature [28,39]. Further increasing the sintering temperature to 1750°C, the main phases of the sintered products transform into CA₆ and AlON. The phase evolutions for SI-5, SI-15, and SI-20 are almost similar to that of SI-10; therefore, they are herein not described for brevity.

![Fig. 2](image-url)  
Fig. 2. XRD patterns of SI-10 sintered at different temperatures for 3 h using the one-step method.

The fracture surface morphologies of the CA₆/AlON composite sintered at 1750°C using the one-step method were further observed. The representative SEM images of SI-10 and SI-20 are illustrated in Fig. 3. As shown in Fig. 3(a), the SI-10 is composed of two typical morphologies, that is, plate-like structure and clusters. Combined with EDS analysis (Table 3), such morphologies are determined to be hexagonal plate-like CA₆ as marked by the green arrows and AlON as marked by the yellow dotted lines. The formation of AlON clusters is closely related to the characteristic of Al powders

![Fig. 3](image-url)  
Fig. 3. SEM images of typical fracture surfaces of (a) SI-10 and (b) SI-20 sintered at 1750°C for 3 h using the one-step method.
with a low-melting-point of 659°C. During sintering, liquid Al has bad wettability on Al₂O₃; thus, it will tend to aggregate on the surface of Al₂O₃. Meanwhile, these liquid tiny Al droppings can be further nitridized into fine AlN particles with high activity [28,30]. When the temperature further increases to the critical point, approximately 1650°C, where the reaction between AlN and Al₂O₃ starts to occur [40], the AlON phase is generated in situ, and it gradually forms clusters as shown in Fig. 3. When the amount of AlON is increased up to 20wt%, the morphology of SI-20 is nearly unchanged; however, AlON clusters characterized by more amount and larger size are formed (Fig. 3(b)). In addition, the apparent porosity of the obtained pure CA₆ ceramic blocks are 2.2 g·cm⁻³ and 29%, respectively.

### 3.2. Preparation and characterization of CA₆/AlON composite by the two-step method

#### 3.2.1. Preparation of single CA₆ and AlON phases

Fig. 4 illustrates the XRD structure refinement and fracture surface SEM image of a single CA₆ phase sintered at 1550°C for 2 h in air. As shown in Fig. 4(a), the predominant peaks correspond to the CA₆ phase (JCPDS: No. 76-0665), indicating the high purity of the obtained material. The lattice parameters of CA₆ are calculated to be \(a = b = 0.55623\) nm and \(c = 2.19134\) nm, which are consistent with the result reported in the literature [41]. In addition, the fracture surface (Fig. 4(b)) exhibits CA₆ grains with a plate-like shape and high porosity. The bulk density and apparent porosity of the obtained pure CA₆ ceramic blocks are 2.2 g·cm⁻³ and 29%, respectively.

The XRD structure refinement and SEM analysis of the single AlON phase sintered at 1750°C for 2 h in a flowing nitrogen atmosphere are shown in Fig. 5. Fig. 5(a) shows that the obtained AlON phase (JCPDS: No. 80-2171) has good crystallinity and high purity. Similarly, the lattice parameters of AlON are determined to be \(a = b = c = 0.79437\) nm, showing a good agreement with the result reported in the literature [42]. Fig. 5(b) displays that the AlON grains have relatively small sizes ranging from 0.5 to 3 µm. In addition, the bulk density and apparent porosity of the obtained AlON composite are 2.5 g·cm⁻³ and 35%, respectively.

#### Table 3. EDS analysis for phases illustrated in Fig. 3

| Area | Ca / at% | Al / at% | O / at% | N / at% | Possible phase |
|------|----------|----------|---------|---------|----------------|
| 1    | 0.13     | 41.69    | 49.14   | 9.04    | AlON           |
| 2    | 3.52     | 41.89    | 54.59   | —       | CA₆            |

Fig. 4. (a) XRD structure refinement (“×” represents experimental data; solid red curve represents fitting data, green curve represents the background of diffraction profile, and blue curve represents the difference between the experimental data and the fitting data. The weighted profile R-factor, \(R_{wp} = 8.95\%\)) and (b) fracture surface SEM image of CA₆ sintered at 1550°C for 2 h in air.

Fig. 5. (a) XRD structure refinement (“×” represents experimental data; solid red curve represents fitting data, green curve represents the background of diffraction profile, and blue curve represents the difference between the experimental data and the fitting data. The weighted profile R-factor, \(R_{wp} = 9.80\%\)) and (b) fracture surface SEM image of AlON sintered at 1750°C for 2 h in flowing nitrogen atmosphere.
density and apparent porosity of the obtained pure AION ceramic blocks are 2.85 g·cm$^{-3}$ and 21%, respectively.

3.2.2. Preparation of the CA$_6$/AION composite

CA$_6$/AION composite added with different amounts of AION has been prepared on the basis of the procedures provided in Section 2.2.2, and the corresponding fracture surface SEM images are shown in Fig. 6. Bulk density and apparent porosity have also been characterized (Fig. 7) to quantify the effects of an addition on the CA$_6$/AION composite. Fig. 6(a) and (b) and EDS analysis (Table 4) show that AION with an average size of approximately 0.5 µm is uniformly distributed around larger CA$_6$ grains with an average size of approximately 20 µm.

As shown in Fig. 7, with the increase of the amount of AION added, the bulk density gradually increases, whereas the porosity decreases. The changing trends are evident when the amount of AION added is below 10wt%. When the amount of AION added is up to 10wt% (Fig. 6(c) and (d)), the newly added AION fills the voids among CA$_6$ grains, thereby increasing densification. The bulk density and apparent porosity for SII-10 are 2.3 g·cm$^{-3}$ and 20%, respectively (Fig. 7). However, the further decrease in porosity is not evident in SII-15 and SII-20 with the addition of more AION (Fig. 7). This phenomenon indicated that some excessive AION grains can be distributed on the surface rather than the voids among CA$_6$ grains (Fig. 6(e)–(h)).

Based on the abovementioned results, the optimized amount of AION in CA$_6$/AION composite is determined to be 10wt%. Notably, the densification of CA$_6$/AION composite can be further increased at higher temperatures or greater forming pressure. In this work, we mainly focused on composite powder.

![Fig. 6. SEM images of fracture CA$_6$/AION composite added with different amounts of AION and sintered at 1650°C for 2 h: (a) SII-5, (c) SII-10, (e) SII-15, and (g) SII-20. (b), (d), (f), and (h) are local enlarged views of (a), (c), (e), and (g), respectively.](image-url)
3.3. Slag penetration and corrosion test

Fig. 8 shows the different views of pure CA$_6$ and SII-10 after slag penetration and corrosion. As shown in Fig. 8(a) and (c), the contacting surface between pure CA$_6$ and the slag is completely corroded and penetrated, with no slag remaining on the upper surface (Fig. 8(e)). By contrast, SII-10 exhibits poor wettability in the molten slag (Fig. 8(b)), and some flowing slags can be observed on the side surface (Fig. 8(d)). This phenomenon is not only related to the decrease in porosity (Fig. 7), but also attributed to the intrinsic characteristic of AlON, which could increase the interfacial tension between the molten slag and SII-10 and wetting angle. In addition, Fig. 8(f) shows that the slag penetration in SII-10 is lower than that in the pure CA$_6$ sample. A clear slag layer can be observed on the upper surface of SII-10, indicating better slag penetration and corrosion resistance.

The wetting behavior of molten slag to CA$_6$ and AlON has been studied by MD simulation to verify whether or not AlON addition can decrease the wettability of composite to
slag. The simulated models for slag–CA$_6$ and slag–AlON systems are shown in Fig. 9(a) and (b), respectively, and each system contains approximately 50000 atoms. The molten slag model is constructed on the basis of the chemical composition shown in Table 2. An important parameter for observing the wetting phenomenon of liquid on the solid surface is the contact angle $\alpha$. As shown in Fig. 9(c) and (d), after simulation of 50 ps at 1550°C, the contact angle $\alpha$ values of slag–CA$_6$ and slag–AlON are approximately 96° and 104°, respectively. The larger the contact angle $\alpha$, the worse the wettability of the liquid in the substrate. Therefore, the addition of AlON can decrease the wettability of SII-10 in the slag.

Typical back-scattered electron (BSE) analysis of the cross-sections of pure CA$_6$ and SII-10 has been compared (as shown in Figs. 10 and 11, respectively) to investigate the promoted effects of AlON addition on the slag penetration and corrosion resistance. Fig. 10(a) shows the EDS maps for the cross-sections of pure CA$_6$ after the slag penetration and corrosion test. No evident boundary between the corrosion zone and unaltered composite is found. Based on the enlarged image (Fig. 10(b)) in combination with EDS analysis (Table 5), the corrosion zone is composed of CA$_6$ and CaO·2Al$_2$O$_3$ (CA$_2$) distributed crossly. These species penetrate the sub-
strate and spread in the reaction zone, probably as low-melting-point silicates, spinel, and/or glass, which result in the low intensity of signals corresponding to Si and Mg. Fig. 10(c) shows that the unaltered substrate is CA$_6$ with high porosity.

Fig. 11 shows the BSE images and corresponding element distributions of the cross-sections of SII-10 after the slag penetration and corrosion test. The cross-section (Fig. 11(a)) can be clearly divided into three parts, that is, slag layer, corrosion zone, and unaltered composite. Based on the EDS results shown in Table 5, some low-melting-point phases, including CaMgAl$_2$SiO$_7$ (CMAS) and Ca$_2$Al$_2$SiO$_7$ (C$_2$AS), are formed via the interface reaction between the composite and the slag in the slag layer (Fig. 11(b)), which is consistent with the results reported in literature [11,43–46]. Meanwhile, some high melting point phases consisting of CA, CA$_2$, and MgO·Al$_2$O$_3$ (MA) can also be observed, which is in accordance with the results reported by Chen et al. [1]. The thickness of the corrosion zone is approximately 345 μm. The whole phase composition in this zone is the same; that is, CA$_2$ and C$_2$AS, represented by pale and bright areas, respectively (Fig. 11(c) and (d)). The differences are mainly the following two points. First, a gradient distribution of the C$_2$AS phase is found along the corrosion direction. Second, the CA$_2$ phase close to the unaltered composite is denser and more continuous. These results suggest that the CA$_2$ layer can effectively slow down the penetration of the low-point-melting phase, thereby hindering further corrosion.

Table 5. EDS analysis for phases illustrated in Figs. 10 and 11

| Area | Ca / at% | Al / at% | O / at% | Si / at% | Mg / at% | Possible phases          |
|------|----------|----------|----------|----------|----------|--------------------------|
| 4    | 3.45     | 40.74    | 55.63    | 0.05     | 0.13     | CA$_6$                   |
| 5    | 10.08    | 38.33    | 50.98    | 0.55     | 0.06     | CA$_3$                   |
| 6    | 3.31     | 40.55    | 55.94    | 0.07     | 0.13     | CA$_6$                   |
| 7    | 0.17     | 35.30    | 48.12    | 0.00     | 16.41    | MA                       |
| 8    | 15.79    | 30.96    | 52.50    | 0.65     | 0.10     | CA                       |
| 9    | 15.97    | 18.59    | 55.83    | 8.23     | 1.38     | C$_2$AS and CMAS         |
| 10   | 9.87     | 38.24    | 51.23    | 0.52     | 0.15     | CA$_2$                   |
| 11   | 17.64    | 18.27    | 55.36    | 8.38     | 0.35     | C$_2$AS                  |
| 12   | 9.79     | 38.93    | 50.83    | 0.14     | 0.31     | CA$_2$                   |
| 13   | 8.83     | 39.10    | 51.73    | 0.13     | 0.21     | CA$_2$                   |
| 14   | 13.29    | 17.11    | 60.93    | 8.10     | 0.57     | C$_2$AS                  |
The reaction between the molten slag and the composite is a process accompanied by ion diffusion. Based on the ionic structure model for the molten slag [47], the CaO with the highest proportion in the slag used in this work (Table 2) will release a large amount of Ca$^{2+}$ and O$^{2-}$. Oishi et al. [48] reported that O$^{2-}$ ions are always more mobile than any of the cations in the molten slag, and their effect on the diffusion coefficient of these cations is small. Therefore, only the movement of cations is discussed herein. As documented in the literature [1,49–51], the movement driving force of ions is related to the chemical potential gradient. The selected slag with high basicity of 3.42 indicates that the proportion of Ca$^{2+}$ ions is higher than other positive ions. In this case, Ca$^{2+}$ should have a stronger driving force to diffuse and react with the composite. Consequently, on the one hand, when CA$_6$ in SII-10 and/or pure CA$_6$ comes into contact with the molten slag, it can react with Ca$^{2+}$ and O$^{2-}$ to form the corrosion product of CA$_6$ as referred to Eq. (1). On the other hand, AION can be oxidized by O$^{2-}$ ions to form more Al$_2$O$_3$ (Eq. (2)). Subsequently, based on the FactSage calculation results [47], the newly formed Al$_2$O$_3$ will react with Ca$^{2+}$ and O$^{2-}$ to preferentially generate CA$_6$ as referred to Eq. (3), followed by further transformation into CA$_6$ as described in Eq. (1). Therefore, the continuous and dense CA$_6$ is gradually formed in the corrosion zone, and it further improves the slag penetration and corrosion resistance of SII-10.

$$2\text{Ca}^{2+} + 2\text{O}^{2-} + \text{CaAl}_{12}\text{O}_{19}\text{composite} \rightarrow 3\text{CaAl}_4\text{O}_7$$  \(1\)

$$2\text{Al}^{3+} + 2\text{O}^{2-} + \text{N}_2\text{composite} + 15\text{O}^{2-} \rightarrow 23\text{Al}_2\text{O}_3 + 5\text{N}_2$$  \(2\)

$$\text{Ca}^{2+} + 2\text{O}^{2-} + 6\text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_6\text{O}_{19}$$  \(3\)

Therefore, the addition of AION reduces the apparent porosity of CA$_6$ and decreases the wettability of composite to slag, which significantly improves the slag penetration resistance of CA$_6$. Moreover, AION can contribute to the formation of a continuous and dense CA$_6$ layer, improving the slag corrosion resistance of CA$_6$. Based on the abovementioned synergetic effect, the CA$_6$/AION composite exhibits remarkable slag resistance.

### 4. Conclusion

In this work, CA$_6$/AION composite added with different amounts of AION has been prepared using one-step and two-step methods. The phase distribution in composite using the two-step method is more uniform compared with that using the one-step method. Furthermore, the optimized amount of AION added is 10wt% (SII-10), in which the apparent porosity of CA$_6$/AION composite (20%) is lower than that of pure CA$_6$ (29%). The addition of AION can also reduce the wettability of CA$_6$/AION composite in the molten slag to a great extent. Meanwhile, AION oxidized by O$^{2-}$ ions released from the molten slag can generate Al$_2$O$_3$, which can further react with Ca$^{2+}$ and O$^{2-}$ ions to form a dense and continuous CA$_6$ layer. This layer can effectively inhibit further penetration and corrosion of molten slag, thereby improving the slag resistance of CA$_6$/AION composite.

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### Conflict of Interest

The authors declare no financial/commercial interests.

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