The phase composition and microstructural evolution of a novel MgO-C-Al-Si refractory used in bottom-blowing elements at high temperatures in flowing nitrogen

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1. Introduction

A bottom-blowing element, made of MgO-C refractories with carbon contents between 12 and 20 wt% that are installed at the bottom of a top-bottom blowing converter, plays an important role in iron- and steel-making processes. However, bottom-blowing elements are frequently subjected to physical penetration and chemical corrosion by molten slag and air oxidation during the periodic steel-making process [1,2], which causes the work face of the MgO-C refractories to form a decarburized layer with a porous structure and low bonding strength [3]. This decarburization further makes the service life of the bottom-blowing element difficult to synchronize with that of the converter. The decarburized layer can improve the wettability between the MgO-C refractories and molten slag, providing channels for the molten slag to penetrate into the inner parts of the refractories. Therefore, a novel bottom-blowing element should have a low oxidation rate of carbon materials (flake graphite and phenolic resin) and a decarburized layer with low porosity after oxidation to protect the remaining carbon materials from further oxidation.

Introducing metal antioxidants (Al or Si) into the MgO-C refractories is an effective method for overcoming their poor oxidation resistance and low mechanical strength [3-9], which has been one of the research directions of the MgO-C refractories with low carbon content less than 8 wt% in recent years [10]. Compared with Si, Al has a higher activity and is more likely to react with other substances within the MgO-C refractories to form some nonoxides and oxides with high performances, for example, AlN, Al4C3, and MgAl2O4 spinel [4,11]. After reacting with molten slag and air, those nonoxides can be transformed into MgAl2O4 spinel with excellent oxidation resistance and good mechanical strength, protecting the MgO-C refractories from further oxidation and slag corrosion [12-14]. In regard to the MgO-C refractories, the lower the carbon content is, the smaller the oxidation rate, and the higher the strength retention rate [2]. Studies on the MgO-C refractories with low carbon content also indicate that the simultaneous introduction of Al and Si into the MgO-C refractories exhibits better comprehensive performance than the use of only Si or Al after the heat treatment in a coke-embedded atmosphere [15]. Based on the above study results, a novel idea was put forward that Al changed from antioxidants into raw materials, with addition of a small number of Si, and graphite content decreased to below 8 wt% to prepare a novel bottom-blowing element with MgO-MgAl2O4 protective layer after oxidation.
The working environment of the bottom-blowing element is blowing highly pure nitrogen at the early stage and highly pure argon at the middle-later stage, which is greatly different from that of MgO-C refractories used in basic oxygen furnaces, electric arc furnaces and steel ladles. The application environment has a great influence on the reactions between Al/Si and gas components. In a CO(g)/CO₂(g) atmosphere, Al added to MgO-C refractories reacts with CO(g), CO₂(g) and Mg(g) to form Al₂O₃, C and MgAl₂O₄ spinel whiskers [16]. In a carbon-embedded atmosphere, the atmospheric components are 65 vol% N₂(g) and 35 vol% CO(g), in which Al and Si react with other substances to in-situ form many of ceramic phases, such as plate-/whisker-shaped AlN whiskers, Al₄C₃ whiskers, SiC whiskers or MgAl₂O₄ spinel whiskers, improving the mechanical properties of MgO-C refractories [17–21]. Compared with argon, nitrogen can participate in phase reactions. Thus, it is very necessary for the MgO-C refractory to clarify the influence of Al and Si on its phase composition and microstructure in high-temperature nitrogen, which is related to the development and application of bottom-blowing elements with long service lives. In this work, taking the bottom-blowing element with 15 wt% graphite and 1 wt% Al as the research object, a novel MgO-C refractory was prepared that graphite content decreased to 6 wt% and the Al content increased to 5 wt% based on w(Al)/w(C) = 27/12, along with 1 wt% Si. After being treated at 1200–1600°C in flowing nitrogen, the phase composition and microstructure were characterized and analyzed by XRD, SEM and EDS to aim at investigating the influence of Al and Si on the MgO-C refractories. Furthermore, some physical properties are characterized.

2. Experimental

The raw materials were meticulously weighed and mixed based on Table 1, using fused magnesia (w-(MgO) ≥ 98%), flake graphite (w(C) ≥ 99%), silicon powder (w(Si) ≥ 99%) and metal aluminum powder (w(Al) ≥ 99%) as raw materials and a thermosetting phenolic resin as the binding agent. After being mixed for 30 min, the raw materials were pressed into samples with a size of 40 mm×40 mm×120 mm under a pressure of 200 MPa. Then, the samples were dried at 200°C for 24 h. To choose the appropriate heat treatment temperature for the above samples, with the help of FLUENT software (US, the ANSYS Release Version 16.0), the temperature field distribution of the MgO-C refractory along the vertical direction was simulated based on the bottom-blowing element blowing highly pure nitrogen, as shown in Figure 1. It can be seen that the thickness of the bottom-blowing element was less than 20 mm at temperatures from 1600°C to 1200°C, in which the phase composition and microstructure of the corresponding refractory thickness will determine the service performance of the bottom-blowing element. Therefore, 1200°C, 1400°C, 1500°C and 1600°C (at the early stage of steel-making by the converter) were selected as the heat treatment temperatures in this paper. After a heat treatment at 620°C for 6 h in flowing nitrogen, the above samples above were placed in graphite crucibles and held for 3 h at 1200°C, 1400°C, 1500°C and 1600°C, and these samples were named S1200, S1400, S1500 and S1600, respectively. The whole experiment was carried out in a highly pure nitrogen flow (N₂ 99.999 Vol%, O₂ 1 × 10⁻³ Vol%) at a slightly higher pressure than standard atmospheric pressure.

The samples were ground to a fine powder and analyzed by X-ray diffraction (XRD, Japan, Rigaku Corporation, Smartlab) using a CuKα radiation source from 10° to 90°. The morphologies and compositions of the samples were investigated using field emission scanning electron microscopy (SEM, Japan, SU8020) equipped with energy-dispersive X-ray spectroscopy (EDS, Britain, Oxford, X-MAX). Cold bending strength was measured by the 3-point bending test at room temperature with a span of 40 mm and a loading rate of 0.5 mm/min using an electronic digital control system (Shanghai Hengyi Testing Instrument Co., Ltd). The cold crushing strength was also evaluated according to this equipment.

3. Results and discussion

3.1. Phase characterization of the samples after the heat treatment

Refractories generally consist of 60–70 wt% aggregates and 30–40 wt% matrix. The phases from the aggregates usually present sharp diffraction peaks in the X-ray powder diffraction pattern. Figure 2 shows the XRD patterns of the samples after being treated at 1200–1600°C in flowing nitrogen. As shown in Figure 2, the characteristic diffraction peaks of the main phases within samples S1200, S1400, S1500 and S1600 are consistent with those of MgO and graphite. The melting points of Al and Si are approximately 660°C and 1414°C, respectively [22]. As the temperature increases, Al preferentially diffuses along the pores in the refractories above 660°C and reacts with C and MgO to form Al₄C₃ and MgAl₂O₄ spinel, respectively [16]. In regard to MgO-

| Table 1. Ratio of raw materials used for MgO-Al-C-Si refractory. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Raw materials  | Fused magnesia  | Al powder       | Flake graphite  | Si powder       | Phenolic resin  |
| Particle size/ | 5–0 mm          | <0.074          | <0.044          | <0.149          | <0.074          |
| Mass percent/  | wt%             |                 |                 |                 |                 |
|                 | 67              | 18              | 5               | 6               | 1               | 3               |

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C refractories, Al and Si easily react with graphite and resin cracking carbon to form Al$_4$C$_3$ and SiC [17], respectively. The Gibbs free energy of Al$_4$SiC$_4$ changes from a positive value to a negative value at 1106°C. In practice, Al$_4$C$_3$ reacts with SiC to form Al$_4$SiC$_4$ at approximately 1200°C [23]. Therefore, at 1200–1600°C in flowing nitrogen, the Al and Si in the matrix are not stable and will be transformed into Al$_4$C$_3$, SiC, MgAl$_2$O$_4$ spinel and Al$_4$SiC$_4$.

The diffraction peaks of magnesia aggregates are so sharp and prominent that the diffraction information of the matrix phases can be obscured. To characterize and analyze the new phases formed in the matrix, the diffraction patterns of the square selection in Figure 2 were obtained as shown in Figure 3. It can be seen from Figure 3 that after the heat treatment at 1200–1600°C in flowing nitrogen, the samples S1200 and S1400 are composed of
3.2. Microstructural characterization of the samples after the heat treatment

Refractories contain many pores and gaps that can provide sites for gas-gas reactions. When Al and Si are introduced into MgO-C refractories, Al and Si can react with other substances to form Al₄C₃ whiskers, AlN whiskers, SiC whiskers and MgAl₂O₄ spinel whiskers in the pores and gaps based on the gas-gas reactions that occur at high temperatures under coke-embedded conditions [17–20]. Different from the coke-embedded atmosphere, for the bottom-blowing element, nitrogen participates in the reactions between Al/Si and other substances at the early stage of steelmaking by the converter, which affects the microstructural evolution of the matrix as shown in Figures 4, 5, and 7.

Figure 4 SEM images of the sample treated at 1200°C in flowing nitrogen. Based on the XRD and EDS analysis of the selected area in Figure 4(a), it could be found that after heat treatment at 620°C × 6 h and 1200°C × 3 h, Al and Si completely reacted and left behind no residue, and a shell structure composed of AlN and Al₄C₃ was generated on the surface of the Al particles as shown in Figure 4(b). At 1200°C, metal Al diffused in both liquid and gas forms, resulting in the fact that many of flake crystals with a diameter of less than 0.5 μm were observed at around the reacted Al in Figure 4(c). Al(g) and Al₂O(g) [26,27], as well as SiO(g) [28] are the main gas-phase composition of Al and Si at high temperatures, controlling the chemical vapor deposition reaction (CVD) in the pores of the refractory. As could be seen from the reaction area between Al and Si shown in Figure 4(d), the pore structure was improved and Al₄SiC₄ flakes with a diameter of more than 5 μm (Figure 4(e,f)) formed. Among magnesia aggregates, MgAl₂O₄ spinels (Figure 4(g)) by the reaction of Al(l) and MgO [11] were also observed. Besides, the characterization analysis on magnesia aggregates (Figure 4(g)) indicated that their surfaces were modified by SiC (Figure 4(h)), MgAl₂O₄ spinel (Figure 4(i)) and Al₄SiC₄ flakes (Figure 4(k)). Here, SiC formed by the reaction between Si(s) or SiO(g) and resin cracking carbon, MgAl₂O₄ spinel formed by the reaction between Al(l) and magnesia aggregates, and Al₄SiC₄ precipitated out from the melt containing Al, Si and C on the surface of the magnesia aggregates. More in-depth analysis on the contact region between Si and graphite showed some Sic particles (Figure 4(l)) and SiC whiskers (Figure 4(m)) and AlN solid solution fibers.
containing Mg and O in the reacted shell of the Al particles (Figure 4(n)).

After increasing temperature above 1200°C, the transformation driving force of Al(l) and Si(l) into Al₂O(g) and SiO(g) increases [27,28], and different kinds of gas–gas reactants are produced. Figure 5 shows the SEM images of the samples treated at 1400°C and 1500°C in flowing nitrogen. As can be seen from Figure 5(a), metal Al reacted completely and left behind a broken shell structure. The surface morphologies on the graphite (Figure 5(b)) and magnesia particles (Figure 5(c)) were characterized, and some Al₄SiC₄ flakes and MgAl₂O₄ spinels formed on their surface by the reaction between Al(l), Si(l) and C. In the gas–gas reaction system of CO(g), Al(g), Al₂O(g) and SiO(g), the reaction products, such as Al₄SiC₄ flakes (Figure 5(d)), SiC whiskers (Figure 5(e)) and trace amounts of MgAl₂O₄ spinel whiskers (Figure 5(f)) could also be observed. However, different from the sample treated at 1200°C, when the samples were treated at...
temperatures above 1400°C in flowing nitrogen, there were many white whiskers (Figure 5(g)) on the surface of the samples, which had been confirmed as MgO whiskers by EDS. It can be deduced based on the above results that Al, Si and C react with O\textsubscript{2} to decrease the oxygen partial pressure inside the refractories at high temperatures in flowing nitrogen, resulting in the following decomposition reaction

\[ \text{MgO(s)} \rightarrow \text{Mg(g)} + 0.5\text{O}_2(g) \]

and affecting the phase compositions and morphologies of the gas products. For instance, the edges of the Al\textsubscript{4}SiC\textsubscript{4} flakes become round and fuzzy, as shown in Figure 5(h,i), and Mg, O and N elements enter into the Al\textsubscript{4}SiC\textsubscript{4} crystals, as shown in Figure 6. It has been reported that Mg and O can enter the Al\textsubscript{4}SiC\textsubscript{4} lattice to form an Al\textsubscript{4}SiC\textsubscript{4} solid solution [29].

Figure 7 shows the SEM images of the sample treated at 1600°C in flowing nitrogen. Thereinto, Figure 7(a,d) are the two organization morphologies with low magnification. It could be observed from Figure 7(a) that the crystallinity of the Al\textsubscript{4}SiC\textsubscript{4} flakes got worse and their edges and corners (Figure 7(b,c)) became fuzzy within the pores, which were consistent with the results of the sample S1500. Interestingly, at the concurrent area of metal Al and graphite shown in Figure 7(d), many novel flake substances were found, which were different from the Al\textsubscript{4}SiC\textsubscript{4} flakes generated by the liquid-phase crystallization and gas–gas reaction. It was confirmed that these were Al\textsubscript{4}Si\textsubscript{2}C\textsubscript{3} flakes (Figure 7(e,f)) by combining the diffraction results from Figure 3 and EDS analysis. The modified phenomenon of the magnesia aggregates was also easily observed in Figure 7(g,i) where the Al\textsubscript{4}SiC\textsubscript{4} flakes (Figure 7(h,i)) and MgAl\textsubscript{2}O\textsubscript{4} spinels (Figure 6(k)) precipitated out from their surface. In addition, we also found that the precipitated MgAl\textsubscript{2}O\textsubscript{4} spinel presented a classic screw growth morphology (Figure 7(l)) and the Al\textsubscript{4}C\textsubscript{3} by the reaction between Al(l/g) and C was formed on the surface of graphite as shown in Figure 7(m,n). Based on the analysis of S1200, S1400, S1500 and S1600, some conclusions can be drawn that Al and Si show gradient reactivity, and metal Al more easily reacts with MgO to form MgAl\textsubscript{2}O\textsubscript{4} spinel. Metal Al and Si can modify magnesia aggregates by forming MgAl\textsubscript{2}O\textsubscript{4} spinels and Al\textsubscript{4}SiC\textsubscript{4} flakes on the magnesia aggregate surfaces. Mg, N and O enter into the Al\textsubscript{4}SiC\textsubscript{4} crystal lattice to form a solid solution.

### 3.3. Physical properties of the samples after the heat treatment

Table 2 shows the mechanical properties of the samples S1200, S1400, S1500 and S1600. It can be seen from Table 2 that the samples S1200, S1400, S1500 and
3.4. Discussion and analysis

A refractory is a kind of multicomponent and heterogeneous material composed of an aggregate, a matrix and pores. The oxygen partial pressure within the refractory is different from that of the environmental atmosphere. After introducing metal Al into the MgO-C refractories, the oxygen partial pressure is controlled by the metal Al and carbon materials. Taking the oxygen partial pressure corresponding to the decomposition reaction of MgO as the reference point, the equilibrium oxygen partial pressure around the metal Al and carbon materials within the MgO-C refractories is calculated at high temperatures as shown in Table 3. Based on the thermodynamic reaction equations (1)–(10), the relationship diagram of $\log P_\text{O}_2/P^0$ vs $\log P_\text{O}_2/P^0$ is drawn with regard to the oxygen partial pressures determined in Table 3 as shown in Figure 9. Figure 9 shows that as the temperature increases, the oxygen partial pressure continuously increases in the equilibrium reaction zone determined by the metal Al and carbon materials, and the partial pressures of the corresponding gas products also increase accordingly. In the temperature range of 1400–1600°C, the partial pressure of Al(g) has an advantage over that of Al$_2$O(g) by an order of magnitude. Furthermore, this partial pressure difference decreases with increasing oxygen partial pressure. In contrast, the partial pressure of SiO(g) has a clear advantage over that of Si(g) by an
order of magnitude at 1200–1600°C, and their partial pressure difference becomes increasingly larger with an increasing oxygen partial pressure.

Before equilibrium reactions are achieved, the mass transfers of liquid and gas phases concurrently occur in the MgO-C-Al-Si refractories at 1200–1600°C in flowing nitrogen. In the gas-gas reaction equilibrium region determined by metal Al and carbon materials, the main gas composition of the MgO-C-Al-Si refractories is Al₂O(g), Al(g), SiO(g), CO(g) and Mg(g). Due to the existence of metal Al and carbon materials, the oxygen partial pressure within the MgO-C refractories is different from that of the environmental atmosphere. The pores provide gas-gas reaction sites for Al₂O(g), Al(g), SiO(g), CO(g) and Mg(g). The reacted products depend on the amounts and types of substances involved in the gas–gas reactions. Figures 4, Figure 5 and Figure 7

Table 2. Mechanical properties of the samples S1200, S1400, S1500 and S1600.

| Mechanical Properties | S1200 | S1400 | S1500 | S1600 |
|-----------------------|-------|-------|-------|-------|
| Cold bending strength/MPa | 7.6   | 13.2  | 15.4  | 16.7  |
| Cold crushing strength/MPa | 35    | 38    | 45    | 49    |

Figure 7. SEM images of the sample treated at 1600°C in flowing nitrogen (Fig. 7a and 7d are the two organization morphologies with low magnification. Fig. 7b and 7c are the structure expanded view of Al₄SiC₄ in Fig.7a; Fig. 7e and 7f are the structure expanded view of Al₄Si₂C₅ in Fig.7d; Fig. 7g is a modified magnesia particle in Fig. 7a; Fig. 7h is an expanded structure view of Al₄SiC₄ in Fig. 7g; Fig. 7 j and 7k is Al₄SiC₄ and MgAl₂O₄ on the surface of the magnesia aggregate in Fig. 7i, respectively; Fig. 7 l is the spiral growth structure of MgAl₂O₄; Fig. 7 n is the Al₄C₃ formed on graphite in Fig. 7 m).
show that the gas-phase products are $\text{Al}_4\text{SiC}_4$ flakes, in the contact area of metal Al, Si and carbon materials, along with trace amounts of SiC whiskers and $\text{MgAl}_2\text{O}_4$ spinel whiskers in the contact area of Si and Al. According to the thermodynamic reaction data calculated in Table 4, the reacted Gibbs free energy of the SiC whiskers, $\text{MgAl}_2\text{O}_4$ spinel whiskers and $\text{Al}_4\text{SiC}_4$ flakes are all negative in the equilibrium reaction region shown in Figure 9. Therefore, the formation
feasibility of these gas substances can be further proven theoretically.

\[
2\text{Al}(l) + 3\text{MgO}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{Mg}(g)
\]

\[
\Delta G_r = 489811 - 282.58T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{-489811}{3 	imes 2.303T} + \frac{282.58}{3 	imes 2.303T}
\]

\[
\Delta G_r = 609837 - 287.71T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{-609837}{3 	imes 2.303T} + \frac{287.71}{3 	imes 2.303T}
\]

\[
\Delta G_r = -724237 + 201.94T - 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{-724237}{0.5 \times 2.303T} + \frac{201.94}{0.5 \times 2.303T} - 2 \log \frac{P_{\text{MgO}}}{P_{\text{Mg}}}
\]

\[
\Delta G_r = 304640 - 109.50T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{-304640}{2 \times 2.303T} + \frac{109.50}{2 \times 2.303T}
\]

\[
\Delta G_r = -170700 - 49.37T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{-170700}{2 \times 2.303T} + \frac{49.37}{2 \times 2.303T} + 0.5 \log \frac{P_{\text{MgO}}}{P_{\text{Mg}}}
\]

\[
\Delta G_r = -108489 - 79.26T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{-108489}{2 \times 2.303T} + \frac{79.26}{2 \times 2.303T} + 0.5 \log \frac{P_{\text{MgO}}}{P_{\text{Mg}}}
\]

\[
\Delta G_r = 445550 - 144.32T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{445550}{2 \times 2.303T} - \frac{144.32}{2 \times 2.303T}
\]

\[
\Delta G_r = 395400 - 111.38T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{395400}{2 \times 2.303T} - \frac{111.38}{2 \times 2.303T}
\]

\[
\Delta G_r = 651214 - 178.53T + 2.303RT \log \left( \frac{P_{\text{MgO}}}{P_{\text{Mg}}} \right) ^3
\]

\[
\log \frac{P_{\text{MgO}}}{P_{\text{Mg}}} = \frac{651214}{2 \times 2.303T} - \frac{178.53}{2 \times 2.303T}
\]

Driven by the Gibbs free energy in Table 5, liquid Al(l) reacts with O(g) and N(g) to form Al₂O₃ and AlN, respectively, and reacts with C and MgO to form AlC₃ and Al₂O₃, respectively. Subsequently, Al₂O₃ reacts with MgO to form MgAl₂O₄ spinel. Affected by the decomposition of MgO, Mg₃N₂ forms by the reaction Mg(g) + 2N(g) → Mg₃N₂(s). Mg and AlN forms further generated without the coexistence of AlN and Mg₃N₂. The reaction between Si(s) and carbon materials results in the formation of SiC particles. At 1200°C, SiC reacts with Al₂C₃ to form Al₂SiC₄ flakes by the following reaction, SiC + Al₂C₃ → Al₂SiC₄. When the temperature reaches

### Table 4. Gibbs free energy of the SiC, MgAl₂O₄ and Al₂SiC₄ whisker [30,31].

| Thermodynamic reaction equation | Gibbs free energy (J·mol⁻¹·K⁻¹) | Temperature/°C |
|---------------------------------|----------------------------------|----------------|
| SiO(g) + CO(g) → SiC(g) + O₂(g) | 159,125 + 157.88 T               | 727–1412       |
| SiO(g) + CO(g) → SiC(s) + O₂(g) | 155,230 + 170.25 T               | 1412–1727      |
| Mg(g) + 2Al(g) + 4CO(g) → MgAl₂O₄(s) + 4C(s) | -2,582,421 + 1082.35 T | 750–1000       |
| Mg(g) + Al₂O₄(g) + 3CO(g) → Mg₂Al₆O₁₄(s) + 3C(s) | -521,559 + 912.72 T | 750–1000       |
| SiO(g) + 2Al₂O₃(g) + 4CO(g) → Al₂SiC₄(s) + 3SO₂(g) | 919,106 + 362.23 T | 727–1412       |
| SiO(g) + 2Al₂O₃(g) + 4CO(g) → Al₂SiC₄(s) + 3SO₂(g) | 875,211 + 374.8T | 1412–1727      |
| SiO(g) + 4Al(g) + 4CO(g) → Al₂SiC₄(s) + 2SO₂(g) | -640,832 + 701.49 T | 727–1412       |
| SiO(g) + 4Al(g) + 4CO(g) → Al₂SiC₄(s) + 2SO₂(g) | -644,727 + 713.86 T | 1412–1727      |

### Table 5. Gibbs free energy of the reactions between Al, Si and other substances within MgO-C-Al-Si refractory (J·mol⁻¹·K⁻¹) [30,31].

| Thermodynamic reaction equation | Gibbs free energy (J·mol⁻¹·K⁻¹) | Reaction Gibbs free energy |
|---------------------------------|----------------------------------|---------------------------|
| 2Al(l) + 1.5O₂(g) → Al₂O₃(l)    | -1,682,900 + 323.24 T            | <0                        |
| 4Al(l) + 3C(s) → 2Al₂C₃(s)      | -266,520 + 96.23 T               | <0                        |
| Si(l) + 3C(s) → SiC(s)          | -63,764 + 7.15 T                 | <0                        |
| Si(l) + C(s) → SiC(s)           | -114,400 + 37.2 T                | <0                        |
| Al₂C₃(s) + 3C(s) → Al₄C₆(s)     | 341,901–247.93 T                 | <0                        |
| 2Al(l) + 3MgO(s) → Al₂O₃(s) + 3Mg(g) | 489,811–282.58 T     | <0                        |
| Al₂O₃(s) + MgO(s) → MgO₂ • Al₂O₃(s) | -23,604–59.1 T       | <0                        |
| 3Mg(g) + N₂(g) + Mg₃N₂(s)       | -860,668 + 504.87 T             | <0                        |
| Al(l) + 0.5N₂(g) → AlN(s)       | -326,477 + 116.4 T              | <0                        |
Conclusions

MgO, Al, and Si show gradient reactivity at high temperatures, and Al has priority over Si to react with MgO to form MgAl2O4 spinel. The samples are composed of MgO, Al2C3, SiC, Al4SiC4, MgAl2O4, Mg3Al2N4 and Al2O3 at 1200–1400°C, while the samples are composed of MgO, Al2C3, SiC, Al4SiC4, Al4SiC3, MgAl2O4, Mg3Al2N4 and Al2O3 at 1500–1600°C. The higher the temperatures are, the more abundant the products. Al(g), Al2O(g) SiO(g), Mg(g) and CO(g), as the gas–gas reaction substances, react to form many of Al4SiC4 flakes containing Mg, O and N within pores or gaps of the refractory, along with trace amounts of SiC whiskers and MgAl2O4 spinel whiskers.

The samples present the difference in the mechanical properties which result from the phase composition and microstructure of MgO-Al-C-Si specimens at different temperatures. The novel refractory forms a compact decarburized layer with MgAl2O4 spinel as bonding phase. The surface morphology of magnesia particles is modified by MgAl2O4 spinels and Al4SiC3 flakes. The formation of MgAl2O4 spinels and Al4SiC4 flakes on the surface of the magnesia aggregates can be divided into four stages. First, the gas or liquid substances containing Al and Si diffuse into the magnesia aggregates. Second, a supersaturated melt ([C]-[O]-[Mg]-[Al]-[Si]) containing C, O, Mg, Al and Si elements forms on the surface of the magnesia. Third, the crystal nuclei of the MgAl2O4 spinels and Al4SiC4 flakes separate out from the supersaturated melt. Finally, their crystal nuclei continue to grow.

4. Conclusions

A novel MgO-C-Al-Si refractory with low carbon content used in bottom-blowing elements was prepared, and its phase composition and microstructural evolution were investigated by XRD, SEM and EDS after being treated at 1200–1600°C in flowing nitrogen. The results shows that Al and Si react up to 1600°C, SiC and Al4SiC4 react to form Al4Si2C3 flakes. The formation of Al4Si2C3 flakes may be due to the doping of Mg, O and N into their crystals. In addition to the effect of Al and Si on the matrix phases, the surface morphology of the magnesia aggregates is also modified by MgAl2O4 spinels and Al4SiC4 flakes. This phenomenon belongs to the classic V-L-S model that Al and Si diffuse into the magnesia surface in the form of Al(l), Si(l), Al(g), Al2O(g) and SiO(g) at high temperatures, and the solid magnesia, as Mg source, participates in. The formation of MgAl2O4 spinels and Al4SiC4 flakes on the surface of the magnesia aggregates can be divided into four stages as shown in Figure 10. First, the gas or liquid substances containing Al and Si diffuse into the magnesia aggregates. Second, a supersaturated melt ([C]-[O]-[Mg]-[Al]-[Si]) containing C, O, Mg, Al and Si elements forms on the surface of the magnesia. Third, the crystal nuclei of the MgAl2O4 spinels and Al4SiC4 flakes separate out from the supersaturated melt. Finally, their crystal nuclei continue to grow.

Figure 10. Formation model diagrams of MgAl2O4 spinels and Al4SiC4 flakes on the surface of magnesia aggregate.
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Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Jansson S, Brabie V, Jöenngsson P. Corrosion mechanism of commercial MgO-C refractories in contact with different gas atmospheres. Isij Int. 2008;48(6):760–767.
[2] Liu ZY, Yu JK, Yue SJ, et al. Effect of carbon content on the oxidation resistance and kinetics of MgO-C refractory with the addition of Al powder. Ceram Int. 2019;46(3):3091–3098.
[3] Zhang SW, Lee WE. Influence of additives on corrosion resistance and corroded microstructures of MgO-C refractories. J Eur Ceram Soc. 2001;21(13):2393–2405.
[4] Zhu TB, Li YW, Sang SB, et al. Formation of nanocarbon structures in MgO–C refractories: matrix influence of Al and Si additives. Ceram Int. 2016;42(16):18833–18843.
[5] Luz AP, Souza TM, Pagliosa C, et al. In situ hot elastic modulus evolution of MgO-C refractories containing Al, Si or Al-Mg antioxidants. Ceram Int. 2016;42(8):9836–9843.
[6] Gokce AS, Gurcan C, Ozgen S, et al. The effect of antioxidants on the oxidation behaviour of magnesia-carbon refractory bricks. Ceram Int. 2008;34(2):323–330.
[7] Poya-Mehr MR, Nemati A. Effects of aluminum, silicon and ferro silicon antioxidants in MgO-C refractories. J Eng Transactions B: Applications. 2003;16:361–372.
[8] Zhang S, Marriott NJ, Lee WE. Thermochemistry and microstructures of MgO–C refractories containing various antioxidants. J Eur Ceram Soc. 2001;21(8):1037–1047.
[9] Sadrnezhaad SK, Nemati ZA, Mahshid S, et al. Effect of Al antioxidant on the rate of oxidation of carbon in MgO-C refractory. J Am Ceram Soc. 2007;90(2):509–515.
[10] Wei GP, Zhu BQ, Li XC, et al. Microstructure and mechanical properties of low-carbon MgO–C refractories bonded by an Fe nanosheet-modified phenol resin. Ceram Int. 2015;41(1):1553–1566.
[11] Yu JK, Yamaguchi A. Behavior of Al on microstructure and properties of MgO-C-Al refractories. J Ceram Soc Jpn. 1993;101(4):475–479.
[12] Yu C, Zhu HX, Yuan WJ, et al. Synthesis of monophase Al2O3C and the effect of Al2O3C addition to MgO–C refractory. J Alloy Compd. 2013;579(5):348–354.
[13] Yao HB, Xing XX, Wang EH, et al. Oxidation behavior and mechanism of Al6SiC4 in MgO-C-Al6SiC4 system. Coatings. 2017;85(7):1–9.
[14] Lee JW, Duh JG. High temperature MgO-C-Al refractories-metal reactions in high aluminum-content alloy steels. J Mater Res. 2003;18(8):1950–1958.
[15] Bitencourt CS, Luz AP, Pagliosa C, et al. Phase and microstructural evolution based on Al, Si and TiO2 reactions with a MgO-C resin-bonded refractory. Ceram Int. 2016;42(15):16480–16490.
[16] Zhu TB, Li YW, Sang SB, et al. The influence of Al and Si additives on the microstructure and mechanical properties of low carbon MgO-C refractories. J Ceram Soc Technol. 2016;7(1):127–134.
[17] Liu HT, Meng FR, Li Q, et al. Phase behavior analysis of MgO–C refractory at high temperature: influence of Si powder additives. Ceram Int. 2015;41(3):5186–5190.
[18] Rastegar H, Bavand-vandchali M, Nemati A, et al. Phase and microstructural evolution of low carbon MgO-C refractories with addition of Fe-catalyzed phenolic resin. Ceram Int. 2019;45(3):3390–3406.
[19] Zhu TB, Li YW, Sang SB, et al. Formation of hollow MgO-rich spinel whiskers in low carbon MgO-C refractories with Al additives. J Eur Ceram Soc. 2014;34(16):4425–4432.
[20] Zhu TB, Li YW, Sang SB, et al. Mechanical behavior and thermal shock resistance of MgO-C refractories: influence of graphite content. Ceram Int. 2017;43(9):7177–7183.
[21] Cheng Y, Zhu TB, Li YW, et al. Microstructure and properties of MgO-C refractory with different carbon contents. Ceram Int. 2021;47(2):538–2546.
[22] Murray JL, Mcalister AJ, Al-Si T. (aluminum-silicon) system. Bulletin Alloy Phase Diagrams. 1984;5(1):74–84.
[23] Inoue K, Yamaguchi A. Synthesis of Al6SiC4. J Am Ceram Soc. 2006;86(6):1028–1030.
[24] Grijtheim K, Herstad O, Toguri JM. The Aluminum reduction of Magnesium Oxide, I. The vapor pressure of magnesium over the system Al-MgO. Can J Chem. 2011;39(3):443–450.
[25] Hans JM, Strebbe M, Eichele K, et al. Crystal structure and luminescence investigations of the nitridomagnesia-refractories Mg3Al4N12 with n=1, 2, 3. Eur J Inorg Chem. 2017;2017(20):2727–2735.
[26] Yan MW, Liu KQ, Li Y, et al. Thermodynamic analysis of Al2O3(g) and phase and micro-structure evolution of the resin bonded Al–Al2O3–ZrO2 refractories under air embedded in coke breeze. J Alloy Compd. 2021;855(1):1–10.
[27] Luo M, Li YW, Jin SL, et al. Microstructure and mechanical properties of multi-walled carbon nanotubes containing Al2O3–C refractories with addition of polycarbosilane. Ceram Int. 2013;39(5):4831–4838.
[28] Yao GS, Li Y, Ji Q, et al. Formation mechanisms of Si3N4 and Si2N2O in silicon powder nitridation. Solid State Chem. 2017;66:50–56.
[29] Zhou SM, Deng CJ, Yu C, et al. Effect of MgO on synthesis of Al2SiC4 from Al/Si/C. Rare Metal Mater Eng. 2015;44:459–461.
[30] Chase MW, NIST-JANAF thermochemical tables. 4th ed. Washington DC: American Chemical Society and the American Institute of Physics for the National Institute of Standards and Technology; 1998.
[31] Chen YZ. Chemical thermodynamics of refractories. Beijing: Metallurgical Industry Press; 2001.