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Oxidation Behavior and Mechanism of Al₄SiC₄ in MgO-C-Al₄SiC₄ System

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Abstract: Al₄SiC₄ powder with high purity was synthesized using the powder mixture of aluminum (Al), silicon (Si), and carbon (C) at 1800 °C in argon. Their oxidation behavior and mechanism in a MgO-C-Al₄SiC₄ system was investigated at 1400–1600 °C. XRD, SEM, and energy dispersive spectrometry (EDS) were adopted to analyze the microstructure and phase evolution. The results showed that the composition of oxidation products was closely related to the atom diffusion velocity and the compound oxide layer was generated on Al₄SiC₄ surface. In addition, the effect of different CO partial pressure on the oxidation of Al₄SiC₄ crystals was also studied by thermodynamic calculation. This work proves the great potential of Al₄SiC₄ in improving the MgO-C materials.

Keywords: Al₄SiC₄; oxidation; MgO-C bricks

1. Introduction

Magnesia-carbon (MgO-C) bricks are a kind of typical refractories, and are mainly composed of MgO and graphite. They have been playing a vital role in the fields of converters, electric furnaces and molten steel refining, etc. [1–3], owing to the nice combination of the perfect properties of the corresponding components (i.e., high temperature resistance and great basic slag resistance as well as low wettability to molten steel). Despite these advantages, graphite's susceptibility to oxidation is the major weakness of carbon-containing refractories, leading to the degradation of brick properties in service. To solve this problem, antioxidants such as Al powder, Si powder, and Al-Si alloys as well as borides including B_4C , ZrB_2 , etc. are adopted to decrease the oxygen partial pressure, reducing the detrimental effect of oxidizing gas on the network structure of carbon and graphite. Therefore, the study of antioxidants is as important as the crystallization, composition, and structure of magnesite and graphite in MgO-C. In view of the antioxidants, recent studies have been focused on their form, phase reaction, and structure evolution in MgO-C, as well as the influence of their types on the decarburized layer and the slag corrosion resistance [3–6].

Among these antioxidants, borides are seldom used due to their high costs and potential harmful impact on some steels. Al powder is the most common antioxidant, and it can react with graphite and carbon to form Al_4C_3 during application. Then, this resulting product can improve the strength of MgO-C bricks at high temperature, which is of significant importance for MgO-C in scour resistance of molten steel [7]. However, Al powder as an antioxidant still has certain defects. On one hand, the formation process of Al_4C_3 would bring in a substantial volume effect, limiting the adoption amount

of Al powder at around 3 wt % [8]. On the other hand, Al_4C_3 always easily hydrates to form $Al(OH)_3$, and this reaction also leads to large volume expansion, which is very detrimental to MgO-C bricks [9].

It should also be noted that with the purpose of improving the quality of steel, the carbon content in MgO-C bricks is required to reduce (C \leq 6wt %). The following problem is the great decline of thermal stability, slag penetration resistance, and oxidation resistance, etc. due to high thermal expansion coefficient (14 \times 10⁻⁶ °C) of MgO, which is the most important issue for low-carbon MgO-C bricks [10–12].

To solve the above problems of low-carbon MgO-C bricks, different introduced forms of carbon and brick structures are mainly studied, in which activated carbon and nanocarbon having relatively high specific surface area are the research focus. The introduction of these carbons can reduce the expansion of magnesite particles and improve the thermal stability and slag penetration resistance by enveloping magnesite particles. However, the micronization of carbon leads to weak oxidation resistance [12–15]. In addition, the adoption amount of Al powder is also limited because low-carbon MgO-C bricks cannot stand much of a volume effect brought by the formation of Al₄C₃.

Therefore, it is desirable to solve two important problems of traditional MgO-C bricks. The first is how to introduce the non-metal antioxidants that possess low volume effect and good oxidation resistance. The second is how to realize low carbon while retaining excellent slag penetration resistance.

 Al_4SiC_4 is the most stable and valuable phase in the Al-Si-C system, and has many excellent properties, such as high melting point (around 2080 °C [16]) and great hydration resistance [17–19]. In addition, although Al_4SiC_4 is easily oxidized at high temperature, its oxidation product can form protective layer and prevent subsequent reaction. These advantages make Al_4SiC_4 a prospective modified material in MgO-C bricks.

Some investigations of the effect of Al_4SiC_4 on the properties of MgO-C bricks have been carried out. Zhang et al. [20,21] studied the oxidation behavior of Al_4SiC_4 in CO and the effect of Al_4SiC_4 addition on the carbon-containing refractories. They found that the Al_2O_3 -SiO₂ layer would form on the refractory surface after oxidation, and prevented the further oxidation of internal refractory. Li et al. investigated the properties of Al_4SiC_4 on MgO-C bricks. The results showed that MgO-C bricks were oxidized to generate magnesia-alumina spinel (MgAl₂O₄). During this process, the volume expansion was able to reduce the porosity of MgO-C bricks, and a protective layer was formed. In addition, Al_4SiC_4 could improve the stability of MgO-C bricks from high temperature to room temperature [22]. Wang et al. added Al_4SiC4 powders synthesized by self-propagating chemical method to carbon-containing refractories, which indicated that Al_4SiC_4 could improve the property of original matrix and make up the shortage of Al-containing additives [23].

Although the above works have been conducted, there still remains some unclear questions; i.e., how does the oxidation of Al₄SiC₄ happen in the MgO-C-Al₄SiC₄ system? How do the elements of Al, Si, etc. transfer and diffuse? What will happen between components in diffusion scale and different MgO-C matrixes? The understanding of the above problems is crucial to optimizing and improving the effect of Al₄SiC₄ in MgO-C bricks. Therefore, in this work, the oxidation behavior and mechanism of perfect Al₄SiC₄ crystals in a MgO-C-Al₄SiC₄ system are investigated, laying a solid foundation for the breakthrough of traditional and low-carbon MgO-C bricks.

2. Materials and Methods

2.1. Preparation of Al₄SiC₄ Crystals

During the preparation process, commercial grade Al powder (\geq 99.99 wt %) with an average particle size of 100 µm, Si powder (\geq 99.9 wt %) with an average particle size of 75 µm, and graphite (\geq 99.85 wt %) with an average particle size of 30 µm were used as raw materials. They were all purchased from Sinopharm Chemical Reagent Beijing Co. Ltd., Beijing, China. The powders with a molar ratio of 4:1:4 corresponding to the chemical composition of Al₄SiC₄ were mixed in a planetary ball mill using alcohol as medium at the rate of 100 rpm for 24 h. Then, the mixture was dried at 80 °C for 24 h and pressed into column (Φ 25 mm × 30 mm) under a pressure of 30 MPa. Finally, the

compacted column was placed in a graphite crucible and heated to 1800 °C for 3 h in 99.99% argon with a flow rate of 0.2 mL/min. After cooling to room temperature, large-scale Al_4SiC_4 product was obtained. At last, the Al_4SiC_4 product was ground into powder for the oxidation experiment.

2.2. Evolution of Al₄SiC₄ in MgO-C-Al₄SiC₄ System

Analytically pure MgO powder (wt % > 98%), graphite powder (wt % > 99.85%) and synthesized Al₄SiC₄ crystals were mixed according to mass ratio of 40:15:45. Herein, the relatively higher content of Al₄SiC₄ was chosen to magnify the experiment and better study the oxidation behavior of Al₄SiC₄ in the MgO-C-Al₄SiC₄ system. Besides, 10 wt % phenolic resin was also added as binding agent. Subsequently, the mixture was pressed into column (Φ 25 mm × 30 mm) under a pressure of 30 MPa, followed by drying at 110 °C for 12 h. Then, the dried sample was placed into an electric furnace and calcined at 1400–1600 °C for 4 h under carbon-buried condition in air, respectively. Finally, the sample was cooled naturally for subsequent analysis.

2.3. Characterization

The phase composition of the Al₄SiC₄ crystals and calcined MgO-C-Al₄SiC₄ specimens was characterized using X-ray Diffraction (XRD; D8 Advance, Bruker, Germany) at a scanning rate of 0.02° /min in the scanning range of 10° –90°. The surface microstructure of Al₄SiC₄ crystals and cross-sectional oxidation microstructure of calcined MgO-C-Al₄SiC₄ specimens were analyzed using a scanning electron microscope (SEM, novaTM nano 450, FEI Company, Hillsboro, OR, USA) equipped with an energy dispersive spectrometer (EDS, EDAX-TEAMTM, EDAX, Mahwah, NJ, USA).

3. Results and Discussion

3.1. Characterization of Synthesized Al₄SiC₄ Crystals

Large-scale yellow Al₄SiC₄ powder was obtained in argon at 1800 °C. The reason for the choice of this temperature is that lower synthesis temperatures would introduce SiC as an impurity phase while higher ones could lead to the decomposition of Al₄SiC₄ [24]. The corresponding XRD pattern of Al₄SiC₄ is given in Figure 1. From Figure 1, it can be seen that the peaks are sharp, and the main characteristic peaks correspond well to Al₄SiC₄ (PDF card no. 35–1072), indicating the synthesis of highly pure Al₄SiC₄. Meanwhile, it should be noted that the peak intensity at (0010, $2\theta = 41.62^{\circ}$) of the synthesized sample is far higher than standard spectral line, which is attributed to the special orientation distribution in Al₄SiC₄ crystals. Figure 2 shows the micromorphology of the synthesized Al₄SiC₄. It can be observed that Al₄SiC₄ nuclei grow to form a hexagonal crystal structure that has smooth surfaces and intercrosses each other. The plate-like Al₄SiC₄ crystals have diameters of 10–30 µm and thickness of 2–3 µm.



Figure 1. XRD pattern of Al₄SiC₄ powders and corresponding standard spectral line.



Figure 2. SEM image of Al₄SiC₄ powders.

3.2. Evolution of Al₄SiC₄ in the MgO-C-Al₄SiC₄ System

Carbon-buried oxidation experiments of the MgO-C-Al₄SiC₄ bricks carbon-buried at different temperatures were conducted in order to analyze the evolution of Al₄SiC₄ in the MgO-C-Al₄SiC₄ system, and the XRD patterns of oxidized products are illustrated in Figure 3. It can be seen that with increasing oxidation temperature, the relative intensity of the characteristic peaks of Al₄SiC₄ decreased. Meanwhile, a new MgAl₂O₄ phase appeared and its relative intensity of characteristic peaks gradually increased, indicating that the oxidation products of Al₂O₃ and MgO react with each other to generate MgAl₂O₄. Besides, a small amount of SiC peaks can also be detected at 1600 °C, suggesting the formation of SiC in MgO-C-Al₄SiC₄ at higher temperature. To get more knowledge of the phase composition, quantitative analysis using X-ray diffraction Rietveld refinement method in the TOPAS software was also carried out, and the results of different phase contents are given in Table 1. As can be seen, the phase amount of Al₄SiC₄ decreased while the MgAl₂O₄ content increased with increasing temperature.



Figure 3. XRD patterns of the MgO-C-Al₄SiC₄ bricks reacted at different temperature: (**a**) 1400 °C; (**b**) 1500 °C; (**c**) 1600 °C.

Micromorphologies of Al₄SiC₄ oxidized at different temperature in MgO-C-Al₄SiC₄ system are depicted in Figure 4, in which middle parts (marked by a green point), two outer layers (marked by a red point), and outmost parts (marked by a blue point) represent unreacted Al₄SiC₄ crystals, oxide layer, and MgAl₂O₄ particles existing in the matrix, respectively. With the combination of EDS results at different areas, it can be seen that the oxidation of Al₄SiC₄ took place at all temperatures and the oxidation thickness increased with increasing temperature, suggesting more severe oxidation of Al₄SiC₄ in MgO-C system at higher temperature.

Table 1. Phase compositions of the oxidized samples at different temperature calculated based on Rietveld.

Temperature	Phase Content (wt %)				
	MgO	С	Al ₄ SiC ₄	MgAl ₂ O ₄	SiC
1400 °C	25.78	10.44	8.23	55.55	_
1500 °C	4.21	11.26	6.94	77.59	-
1600 °C	-	11.75	4.95	77.72	5.58



Figure 4. Structure evolution of Al₄SiC₄ crystals at different temperature: (**a**) 1400 °C; (**b**) 1500 °C and (**c**) 1600 °C.

To further understand the oxidation process of Al_4SiC_4 crystals, the cross-section and element distribution of the samples after oxidation at 1600 °C was investigated, as shown in Figure 5. After reaction at 1600 °C, the oxidation of Al_4SiC_4 crystal was obvious. The outer oxide layers were mainly composed of Mg, Al, and O, while the internal crystals mainly consisted of C, Si, and a lesser amount of Al. This shows that Al_4SiC_4 is unstable, accompanied with a rapid migration of Al from interior to exterior. Compared with the Al element, the migration rate of Si is relatively smaller. Such migration behaviors led to the formation of Al_2O_3 and SiO_2 on the surface of Al_4SiC_4 . At the same time, some MgAl₂O₄ phase generated by Al_2O_3 and MgO also appeared on the Al_4SiC_4 surface due to abundant MgO in the MgO-C matrix. This can explain why no mullite was detected in XRD while massive MgAl₂O₄ particles exist on the surface of Al_4SiC_4 .



Figure 5. Cont.



Figure 5. The energy dispersive spectrometry (EDS) mapping analysis of the cross-section oxide scale of Al_4SiC_4 crystal at 1600 °C. (a) the enlarged SEM image of the cross-section; (b)~(f) the distribution of respective element with different color.

The micromorphological evolution of $MgAl_2O_4$ in the MgO-C- Al_4SiC_4 system was also observed, and the results are shown in Figure 6. With increasing temperature, both the amount and grain size of $MgAl_2O_4$ increased. These $MgAl_2O_4$ particles not only increase the density of samples by filling in the pores, but also provide benefit to the improvement of slag corrosion and permeation resistance, which is in line with the previous report [22].



Figure 6. Morphology of product MgAl₂O₄ in MgO-C-Al₄SiC₄ system reacted at different temperature: (a) 1400 °C; (b) 1500 °C and (c) 1600 °C.

3.3. Thermodynamic Analysis of the Oxidation Process

Under carbon-buried conditions at high temperature, Al_4SiC_4 in the MgO-C-Al_4SiC_4 system is mainly confronted with CO, N₂, and less Mg(g). When CO exists, Al_4SiC_4 is always oxidized according to the following equations:

$$Al_4SiC_4(s) + 6CO(g) = 2Al_2O_3(s) + SiC(s) + 9C(s)$$
 (1)

$$3Al_2O_3(s) + 2SiC(s) + 4CO(g) = Al_6Si_2O_{13}(s) + 6C(s)$$
(2)

To identify the possibility of the above reactions, the stability region of the solidification phase of Al₄SiC₄ according to thermodynamic data of Al₄SiC₄ and JANAF (Joint Army-Navy-NASA-Air Force)

data under different CO partial pressure is depicted as shown in Figure 7 [25,26]. From Figure 7, it can be concluded that the product of Al₄SiC₄ is dependent on temperature and CO partial pressure. In addition, under the condition of low oxygen partial pressure, the reaction of MgO may also take place as follows:

$$2MgO(s) = 2Mg(g) + O_2(g)$$
 (3)

$$2C(s) + O_2(g) = 2CO(s)$$
 (4)

$$MgO(s) + C(s) = Mg(g) + CO(g)$$
(5)

As is known to all, open and closed pores simultaneously exist in MgO-C bricks. The oxidation behavior of Al_4SiC_4 crystals at different positions may be different. To clarify this, oxidation experiments of Al_4SiC_4 under both open-pore and closed-pore systems were conducted.



Figure 7. Stability region of solidification phase of Al₄SiC₄ oxidized under different conditions.

Under an open-pore system, according to Equation (4), oxygen in the air accompanied with excessive carbon will mostly transfer to CO at temperature above 1000 °C. So, the total partial pressure of CO and N₂ is close to 1 atm while the content of Mg(g) is negligible; i.e., $P_{CO} + P_{N2} = 10^5$ Pa. Thus, the equilibrium gas composition is as follows:

$$\varphi(\text{CO}) = \frac{P_{\text{CO}}}{P} \times 100, \, \varphi(\text{N}_2) = \frac{P_{\text{N}_2}}{P} \times 100$$
 (6)

Besides,

$$\frac{n_N}{n_O} = \frac{\varphi(N_2)}{\varphi(O_2)} = \frac{79}{21} = \frac{2n_{N_2}}{2n_{CO}} = \frac{2\varphi(N_2)}{\varphi(CO)} = 3.76$$
(7)

Combining Equations (6) and (7) obtains $\varphi(CO) = 34.72$; i.e., $\frac{P_{CO}}{P} = 0.3472$.

From the red line in Figure 7, when the CO partial pressure was 0.3472, the abscissa was -0.46 and corresponding temperature was 1483 °C. Below 1483 °C, Al₄SiC₄ stayed in the Al₆Si₂O₁₃-C phase area, indicating the entire transformation of Al₄SiC₄ to mullite. However, the characteristic peaks of mullite could not be detected in XRD (Figure 3), which is possibly attributed to two points. That is, (1) little amount or poor crystalline (glass phase) of mullite; (2) massive MgAl₂O₄ particles on the product surface weaken the intensity of mullite. When the temperature was above 1483 °C, phase equilibrium was in the Al₂O₃-SiC-C area and Al₄SiC₄ was oxidized to Al₂O₃ and SiC. Under this condition, the SiC was stable, suggesting the decrease of oxygen partial pressure above 1483 °C.

As for the closed pores in samples, they are a relative concept because the refractory itself is not a very dense material. With increasing temperature, the air in the pores will be replaced with CO(g) and $CO_2(g)$. In this situation, equilibrium gas composition is almost determined by specific material components. In such a closed system that is at high temperature with excessive carbon, the gas in the pores mainly originates according to Equations (3)–(5). In the gas composition, the content of oxygen is rather smaller than that of CO(g) and Mg(g).

Assuming the total pressure as *P*, one can obtain,

$$P_{\rm CO} + P_{\rm Mg} = P \tag{8}$$

Substituting Equation (8) into Equation (5) yields $P_{CO}/P = 0.50$, and the corresponding abscissa is -0.301. At the same temperature, the CO partial pressure in closed pores is higher than that in open pores. Besides, Figure 7 also shows that the stable region of Al₂O₃ and SiO₂ in closed pores was above 1516 °C, which is nearly same as the open system. Therefore, in closed pores, the oxidation products are Al₂O₃ and SiC at 1600 °C, while they are Al₆Si₂O₁₃ and Al₂O₃ at 1400–1500 °C.

From the above, after oxidation at 1600 °C, SiC will be generated in both open and closed pores and can be detected in XRD. Meanwhile, at 1500 °C, SiC forms only in open pores, and lower temperature is not good for its formation, resulting in no characteristic peak shown in XRD.

In the MgO-C-Al₄SiC₄ system, open and closed pores have no obvious influence on the oxidation behavior of Al₄SiC₄, owing to little difference in CO partial pressure. Importantly, Al₂O₃ will have a priority to form on the Al₄SiC₄ surface and further react with MgO to generate MgAl₂O₄. As a result, MgAl₂O₄ can fill in the pores in materials, which provides a benefit to the improvement of the properties of MgO-C bricks.

4. Conclusions

Al₄SiC₄ crystals with diameter of 10–30 μ m and thickness of 2–3 μ m were synthesized at 1800 °C using Al, Si, and graphite powders as raw materials. The oxidation behavior and mechanism of Al₄SiC₄ in MgO-C-Al₄SiC₄ system was investigated. At high temperature, Al₄SiC₄ was unstable where the migration rate of Al element was greater than that of Si. Thus, at first, Al₂O₃ would form on the Al₄SiC₄ surface and then react with MgO existing in the matrix to generate massive MgAl₂O₄ particles. Si element exists either in the form of SiC within Al₂O₃ scale or in the form of Al₆Al₂O₁₃ on the Al₄SiC₄ surface. Thermodynamic calculation was also carried out to further analyze the oxidation mechanism, verifying a slight influence of open and closed pores on the oxidation of Al₄SiC₄ in MgO-C materials.

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