Effect of $\text{Al}_4\text{SiC}_4$ Addition to Carbon-Containing Refractories

Shaowei ZHANG and Akira YAMAGUCHI
Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya-shi 466

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The behavior and the effect of $\text{Al}_4\text{SiC}_4$, an excellent hydration-resistant compound, as an antioxidant for carbon-containing refractories have been investigated, and the corresponding mechanisms have been discussed. $\text{Al}_4\text{SiC}_4$ added to the refractories initially reacts with CO to form $\text{Al}_2\text{O}_3$, $\text{SiC}$ and $\text{C}$. After the reaction, if the temperatures are below $\sim 1560^\circ\text{C}$, the formed $\text{SiC}$ and $\text{Al}_2\text{O}_3$ will further react with CO to form mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and $\text{C}$. The above reaction processes can form protective layers on the surfaces of the refractories, which inhibit the oxidation of the refractories. From the results obtained, $\text{Al}_4\text{SiC}_4$ was found to markedly inhibit the oxidation of the carbon-containing refractories.

Key-words : $\text{Al}_4\text{SiC}_4$, Antioxidant, Carbon-containing refractory, Oxidation resistance

1. Introduction

In order to improve the resistance to oxidation of carbon-containing refractories, the so-called antioxidants have often been added. Among the antioxidants, Al is the most widely used one. So far, the behavior of Al in the carbon-containing refractories has been extensively studied.1-4) Although Al effectively inhibits oxidation of the carbon-containing refractories, it has a main drawback; namely, the hydration of $\text{Al}_4\text{C}_3$ which is formed from the reaction of Al with C in the refractories.

Owing to the hydration of the residual $\text{Al}_4\text{C}_3$, the carbon-containing refractories to which Al is added will deteriorate gradually (even at room temperature) and thus cannot be used satisfactorily. Therefore, we must select other antioxidants which have the same antioxidant property as Al but not the drawback of Al mentioned above.

In our previous paper,5) the synthesis and properties of $\text{Al}_4\text{SiC}_4$, one of the complex carbides, were reported. It was verified that the hydration resistance property of $\text{Al}_4\text{SiC}_4$ is sufficient for the practical use. Thus, whether $\text{Al}_4\text{SiC}_4$ can be used as a new antioxidant instead of Al will be mainly determined by its behavior under practical conditions of application to the carbon-containing refractories.

Therefore, this paper intends to further investigate the behavior and the effect of $\text{Al}_4\text{SiC}_4$ as an antioxidant on the carbon-containing refractories.

2. Experimental

2.1 Raw materials

The raw materials used in the study were as follows:

(1) C: natural graphite, purity $>99\%$;
(2) Al: $<50\mu\text{m}$, purity $>99\%$;
(3) $\text{Al}_2\text{O}_3$: fused alumina, purity $>99\%$;
(4) MgO: fused magnesia, purity $>99\%$;
(5) $\text{Al}_4\text{SiC}_4$: prepared by the method stated in Ref. 5, $<50\mu\text{m}$, purity $\sim 97\%$;

2.2 Preparation of samples and examination

2.2.1 Changes of $\text{Al}_4\text{SiC}_4$ heated in CO(g)

About 0.5 g-$\text{Al}_4\text{SiC}_4$ powder was placed in an alumina boat then inserted into an alumina tube which was set in an electric furnace. The heating rate of the furnace was $10^\circ\text{C}/\text{min}$. CO gas was pumped into the alumina tube at a rate of 0.21/min. The powder sample was heated at various temperatures for 2h and at 1500°C for various time periods. After heating, the mass change of the sample was measured, and the phase change and the microstructure were examined by X-ray diffraction analyses and scanning electron microscope (SEM), respectively.

2.2.2 Oxidation resistance of carbon-containing refractories

Two types of carbon-containing refractories, MgO-C and $\text{Al}_2\text{O}_3$-C refractories, with the composition shown in Table 1, were prepared using the raw materials stated in Section 2.1. 4 mass% phenolic resin as a binder was added to the refractories.

Samples with size $10 \times 10 \times 10\text{mm}$ cut from the above refractories were heated at 800°C for 5h so
that the resin added to the refractories was carbonized. After the carbonization, the mass changes of the samples in air were examined by a thermogravimetric analysis (TG) at a heating rate of 10°C/min.

Samples with size 25 × 25 × 25 mm cut from the above refractories were heated in air in an electric furnace at 1500°C for 1h (the heating rate and the cooling rate of the furnace were 10°C/min and 5°C/min, respectively). After heating, the average thickness of the decarbonized layer of the sample was determined.

3. Results

3.1 Behavior of Al₄SiC₄ heated in CO atmosphere

The Al₄SiC₄ powder sample was heated in CO gas at various temperatures for 2h and at 1500°C for 2 to 10h. The mass gain and the phase change of the sample are shown in Figs. 1 and 2, respectively.

The mass gain of the sample is observed at temperatures above 1000°C. It increases slowly with increasing temperature from 1000 to 1200°C, rapidly from 1200 to 1500°C, and at 1500°C, it increases slowly with time from 2 to 6h. Mass gain reaches a maximum after heating at 1500°C for 6h, after which the change becomes negligible with time.

Corresponding to the mass gain of the sample, α-Al₂O₃ and SiC phases were identified in the sample at temperatures above 1000°C. With increasing temperature, the intensity of α-Al₂O₃ and SiC increases, while that of Al₄SiC₄ decreases. After heating at 1500°C for 6h, Al₄SiC₄ disappeared and mullite (Al₆Si₂O₁₃) was formed instead; at this point, the intensity of α-Al₂O₃ and SiC begins to decrease.

Figure 3 shows the SEM micrographs of the untreated Al₄SiC₄ powder and that heated in CO at 1500°C for 4h. Numerous spherical and needle-shaped crystals were observed on the surfaces of the Al₄SiC₄ grains heated in CO at 1500°C for 4h. These small crystals were thought to be α-Al₂O₃ grains which were precipitated during the reaction process.

3.2 Effect of Al₄SiC₄ addition on the oxidation resistance of the carbon-containing refractories

Figure 4 shows the TG curves of Al₂O₃-C refractory samples heated in air at the rate of 10°C/min. The mass loss of the sample without additive (A) can be observed from ~530°C, whereas that of the sample containing Al₄SiC₄ (A–ASC) or Al (A–A) can be observed from ~590°C. With increasing temperature, although the mass of all of the samples decreases, the rate of mass loss of the sample containing Al₄SiC₄ or Al is lower than that of the sample without additive. After heating at 1300°C for 30 min, the mass loss of the sample without additive becomes con-

![Figure 1](image1.png)

Fig. 1. Mass gain of the Al₄SiC₄ powder heated in CO gas at various temperatures for 2h and at 1500°C for 2 to 10h.

![Figure 2](image2.png)

Fig. 2. Phase changes of the Al₄SiC₄ powder heated in CO gas at various temperatures for 2h and at 1500°C for 2 to 10h.

![Figure 3](image3.png)

Fig. 3. SEM micrographs of the Al₄SiC₄ powders: (a) untreated; (b) heated at 1500°C for 4h in CO.

![Figure 4](image4.png)

Fig. 4. TG curves of Al₂O₃-C refractory samples heated in air at the rate of 10°C/min.
stant, whereas that of the sample containing Al$_4$SiC$_4$ (M-ASC) or Al (M-A) can be observed from $\sim 620^\circ$C. The rate of mass loss of the sample containing Al$_4$SiC$_4$ is closed to that of the sample containing Al, and both are lower than that of the sample without additive. After heating at $1300^\circ$C for 35 min, the mass loss of the sample without additive becomes constant, whereas that of the sample containing Al$_4$SiC$_4$ or Al becomes constant at $1300^\circ$C for 65 min.

Figure 6 shows the photographs of cross sections of the Al$_2$O$_3$-C and the MgO-C refractory samples heated at $1500^\circ$C for 1h in air. The black areas in the sections are the areas with carbon residues. Figure 7 shows the average thickness of decarbonized layers of the samples shown in Fig. 6. It is found that the thickness of decarbonized layers of the samples containing Al$_4$SiC$_4$ is almost the same as that of the samples containing Al, and both are thinner than those of the samples without additive.

4. Discussion

4.1 Behavior of Al$_4$SiC$_4$ heated in CO (g)

In order to analyze the behavior of Al$_4$SiC$_4$ heated in CO atmosphere by the thermodynamics method, appropriate thermochemical data should be selected. The thermochemical data of Al$_4$SiC$_4$ were initially reported by Beherens and Rinehart in 1984. Later, Yokogawa et al. reported that the errors of Beherens and Rinehart’s data were too large for use. Meanwhile, Yokogawa et al. estimated the value of the Gibbs energy of formation of Al$_4$SiC$_4$ from AlC$_3$ and SiC to be $(-2.0 \text{ TJ} / \text{mol})$. This value was adopted in this study. As for the thermochemical data of the other species such as AlC$_3$ and SiC were obtained from JANAF.

Figure 8 shows the stability domains of the condensed phases in the Al-Si-C-O system. As shown in Fig. 8, if heated under conditions of $P_{CO} = 1.013 \times 10^6$ Pa (1 atm) and temperatures below $\sim 1980^\circ$C, Al$_4$SiC$_4$ will initially react with CO to form Al$_2$O$_3$, SiC and C, as shown in Reaction (1). At a given temperature, owing to the occurrence of Reaction (1),
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$P_{CO}$ over the surfaces of Al$_4$SiC$_4$ grains is kept at a constant value which is lower than that in Reaction (2). Therefore, as long as Al$_4$SiC$_4$ exists, SiC formed from Reaction (1) is in a stable phase. That is to say, only when Al$_4$SiC$_4$ disappears, the formed SiC (and Al$_2$O$_3$) does further react with CO to form mullite (Al$_6$Si$_2$O$_13$) and C, according to Reaction (2) (if temperatures are below 1560°C).

$$\text{Al}_4\text{SiC}_4(s)+6\text{CO}(g)=2\text{Al}_2\text{O}_3(s)+\text{SiC}(s)+9\text{C}(s) \quad (1)$$

$$3\text{Al}_2\text{O}_3(s)+2\text{SiC}(s)+4\text{CO}(g)\rightleftharpoons \text{Al}_6\text{Si}_2\text{O}_{13}(s)+6\text{C}(s) \quad (2)$$

Moreover, it should be noted that the reactions shown in Reactions (1) and (2) take place via the gases formed in the system. Figure 9, as an example, shows the equilibrium partial pressures of the gases formed in the Al-Si-C-O system with $P_{CO}$ at 1700 K.

![Fig. 9. Equilibrium partial pressures of the gases in the Al-Si-C-O system at 1700 K.](image)

Figures 10 and 11 show, respectively, the equilibrium partial pressures of Al(g) in Reactions (3) and (4) and those of SiO(g) in Reactions (5) and (6) at various temperatures when $P_{CO}=1.013 \times 10^5$ Pa (1 atm).

$$\text{Al}_4\text{SiC}_4(s)\rightleftharpoons 4\text{Al}(g)+\text{SiC}(s)+3\text{C}(s) \quad (3)$$

$$2\text{Al}(g)+3\text{CO}(g)\rightleftharpoons \text{Al}_2\text{O}_3(s)+3\text{C}(s) \quad (4)$$

$$\text{SiC}(s)+\text{CO}(g)\rightleftharpoons \text{SiO}(g)+2\text{C}(s) \quad (5)$$

$$3\text{Al}_2\text{O}_3(s)+2\text{SiO}(g)+2\text{CO}(g)\rightleftharpoons \text{Al}_6\text{Si}_2\text{O}_{13}(s)+2\text{C}(s) \quad (6)$$

It is found that the equilibrium partial pressure of Al(g) in Reaction (4) is much lower than that in Reaction (3) at a given temperature, thus Al(g) evaporated from Al$_4$SiC$_4$ according to Reaction (3) will be condensed to form Al$_2$O$_3$ according to Reaction (4). As a result of Reactions (3) and (4), Reaction (1) is obtained. When Al$_4$SiC$_4$ is completely transformed into Al$_2$O$_3$ and SiC according to Reactions (3) and (4) (i.e., Reaction (1)), if temperatures are below ~1560°C, in a similar manner, SiO(g) produced by Reaction (5) will be condensed to form Al$_6$Si$_2$O$_{13}$ according to Reaction (6). As a result of Reactions (5) and (6), Reaction (2) is obtained.

The actual characteristics of the reaction of Al$_4$SiC$_4$ with CO can be observed from the results shown in Fig. 1 to Fig. 3. The obvious reaction of Al$_4$SiC$_4$ with CO is observed when the temperature is above 1000°C. With increasing temperatures from 1000 to 1500°C and increasing time at 1500°C from 2
to 6h, Al₄SiC₄ always exists, thus, similarly to the thermochemical analyses stated above, only Al₂O₃ and SiC were identified. After heating at 1500°C for 6h, however, Al₄SiC₄ disappears and Al₅Si₂O₁₃ is formed instead; at this point, the intensity of SiC and Al₂O₃ begins to decrease, which indicates that the formed SiC and Al₂O₃ from Reaction (1) react further with CO to form Al₅Si₂O₁₃ according to Reaction (2).

It is of note that after heating at 1500°C for 6h, although Al₄SiC₄ disappeared, the observed mass gain (78.0 mass%) is lower than the theoretical one (91.3 mass%). It is probable that part of the Al(g) formed from Reaction (3) escaped from the sample before it was condensed to Al₂O₃ according to Reaction (4). Based on the similar reason, after being heated at 1500°C for 6 to 10h, the mass gain of the sample changed very little upon the formation of Al₅Si₂O₁₃.

4.2 Effect of Al₄SiC₄ addition on the oxidation resistance of the carbon-containing refractories

As shown in Fig. 4 to Fig. 7, Al₄SiC₄ markedly inhibits the oxidation of the carbon-containing refractories. The mechanisms can be given as follows.

Under the oxidizing conditions, as long as carbon exists, the partial pressure of CO(g) around and inside the refractories can be considered to be about 1.013 × 10⁵ Pa (1 atm).³⁹ Under these conditions, Al(g) evaporating from Al₄SiC₄ according to Reaction (3) can diffuse to the surfaces of the refractories and react with CO to form Al₂O₃ and C on the surfaces, according to Reaction (4). After these reactions, if the temperatures are below ~1560°C, SiO(g) formed according to Reaction (5) can further diffuse to the surfaces of the refractories and react with CO and Al₂O₃ to form Al₅Si₂O₁₃ and C on the surfaces, according to Reaction (6). In the above manner, the Al₂O₃-SiO₂ protective layers are formed on the surfaces of the two types of refractories. The protective layers can inhibit the further oxidation of the carbon, that is, they enhance the oxidation resistance of the refractories.

In addition, by comparing the mechanism of Al₄SiC₄ acting as an antioxidant stated above with that of Al analyzed by Yamaguchi,¹ it is found that the former is similar to the latter. It is possible that this similarity contributes to the similarity in the oxidation resistance property of the carbon-containing refractories to which Al₄SiC₄ and Al were added (Fig. 4 to Fig. 7).

4.3 Advantages of Al₄SiC₄ as an antioxidant for carbon-containing refractories

Aside from the effect of inhibiting the oxidation of carbon-containing refractories stated above, the addition of Al₄SiC₄ has the following advantages.

As stated in the introduction, during heating, Al added to carbon-containing refractories reacts with C to form Al₄C₃. Owing to the hydration of the formed Al₄C₃ (even at room temperature), carbon-containing refractories to which Al is added will deteriorate gradually and thus cannot be used satisfactorily. In addition, because the evaporation of Al(g) from Al(l) leads to cracking of the Al₄C₃ shell formed on the Al(l), the so-called "cavity structure" is formed in the refractories² which is disadvantageous to the properties of the refractories.

Al₄SiC₄ has been reported to show an excellent hydration resistance.³⁰ If it is added to the carbon-containing refractories as an antioxidant, the hydration of the refractories to which Al is added could be prevented. Furthermore, as Al₄SiC₄ itself is a carbide, when Al(g) or SiO(g) evaporates from it according to Reactions (3) and (5), C is left behind, thus the cavity structure does not form in the refractories (detailed study on this aspect will be reported elsewhere).

5. Conclusions

The behavior and the effect of Al₄SiC₄ as an antioxidant for the carbon-containing refractories have been investigated and the corresponding mechanisms have been discussed. The conclusions are as follows.

1) Al₄SiC₄ added to the carbon-containing refractories initially reacts with CO to form Al₂O₃, SiC and C. After the reaction, if the temperatures are below ~1560°C, the formed SiC and Al₂O₃ further react with CO to form Al₅Si₂O₁₃ and C. Both reaction processes form Al₂O₃-SiO₂ protective layers on the surfaces of the refractories, and thus the oxidation of the refractories is inhibited.

2) From the results obtained, Al₄SiC₄ was found markedly to inhibit the oxidation proceeds of the carbon-containing refractories.

References