Antioxidation Behavior and Effect of $\text{Al}_8\text{B}_4\text{C}_7$ Added to Carbon-Containing Refractories

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炭素含有耐火物への $\text{Al}_8\text{B}_4\text{C}_7$ 添加の耐酸化効果と挙動

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The behavior of $\text{Al}_8\text{B}_4\text{C}_7$ in CO(g) and its effect as an antioxidant in both $\text{Al}_2\text{O}_3\text{-C}$ and MgO-C have been investigated, and the corresponding mechanisms have been discussed. $\text{Al}_8\text{B}_4\text{C}_7$ markedly inhibits the oxidation of the carbon-containing refractories. The added $\text{Al}_8\text{B}_4\text{C}_7$ reacts with CO(g) quickly above 1400°C to give B_2O_3 . The B_2O_3 further reacts with MgO or Al_2O_3 in the refractories to form $\text{Mg}_3\text{B}_2\text{O}_6$ or $\text{Al}_{18}\text{B}_4\text{O}_{33}$. $\text{Mg}_3\text{B}_2\text{O}_6$ is stable till 1400°C in air, but $\text{Al}_{18}\text{B}_4\text{O}_{33}$ begins to decompose above 1300°C . $\text{Al}_8\text{B}_4\text{C}_7$ is more effective as an antioxidant in MgO-C refractories than in $\text{Al}_2\text{O}_3\text{-C}$ refractories, due to the different stability characteristics of $\text{Mg}_3\text{B}_2\text{O}_6$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

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1. Introduction

Owing to its excellent properties (high chemical stability, non-wettability by molten slags and metals, high thermal conductivity etc.), the use of carbon has been responsible for a considerable improvement in the properties of refractory bricks. But carbon is susceptible to oxidation, and measures are therefore required to reduce its oxidizing shedding under operational conditions. The latest development in this field is the use of substances known as antioxidants, such as metals (Al, Si), alloy (Mg–Al, Al–Si) and carbides (B_4C , SiC). Although it has been clear that Al can effectively inhibit the oxidation of carbon-containing refractories, and its behavior in the refractories has been extensively studied,^{1)–4)} the drawback of Al is as distinct as its advantage. The refractories can be deteriorated during reheating due to the hydration of Al_4C_3 that formed at high temperature. Based on this consideration, it is important to develop new Al-containing antioxidants with excellent hydration and oxidation prevention properties.

A new idea, that is, combining Al with carbides to produce some complex compounds such as $\text{Al}_8\text{B}_4\text{C}_7$, Al_4SiC_4 , has been raised up to overcome the drawback.⁵⁾ The synthesis processes of $\text{Al}_8\text{B}_4\text{C}_7$ and Al_4SiC_4 have been investigated,^{6),7)} and both of them show excellent hydration-resistance.⁸⁾ Al_4SiC_4 has also been found to markedly inhibit the oxidation of carbon-containing refractories.⁹⁾

MgO-C and $\text{Al}_2\text{O}_3\text{-C}$ refractories are main carbon-containing refractories that are widely used in iron and steel making process, and therefore the effect of $\text{Al}_8\text{B}_4\text{C}_7$ addition on the oxidation resistance of them is investigated in this study.

Whether $\text{Al}_8\text{B}_4\text{C}_7$ can be used as a new antioxidant instead of Al is mainly determined by its behavior and effect in carbon-containing refractories under practical condition. The purpose of this work is to clarify the chemical process occurring and hence the effect and mechanism of antioxidation by $\text{Al}_8\text{B}_4\text{C}_7$ in both MgO-C and $\text{Al}_2\text{O}_3\text{-C}$ refractories.

2. Experimental

2.1 Raw materials

The raw materials used in this study were as follows:

(1) C: natural; graphite, purity > 99%

(2) Al powder: purity > 99%

(3) B_4C powder: purity > 97%

(4) Al_2O_3 : fused and sintered alumina, purity > 99%

(5) MgO : fused and sintered magnesia, > 99%

(6) $\text{Al}_8\text{B}_4\text{C}_7$: prepared by the method stated in Ref. 6, < 50 μm

2.2 Preparation of samples and examination

2.2.1 Behavior of $\text{Al}_8\text{B}_4\text{C}_7$ heated in CO(g)

An alumina boat containing about 1.0 g $\text{Al}_8\text{B}_4\text{C}_7$ powder was inserted into an alumina tube with size of $\phi 42\text{ mm} \times 600\text{ mm}$. The tube was placed in an electric furnace, which was heated at different temperatures for various lengths of time. The heating rate was 10°C/min . Ar gas was flowed at first and then converted to CO gas when the furnace reached the set temperature, and converted back to Ar again after a definite time. The flow rate of the gases was 0.2 l/min. The powder was heated at 1000, 1200 and 1400°C for up to 8 h. The heated samples were analyzed by X-ray diffraction (XRD).

2.2.2 Oxidation resistance of carbon-containing refractories

Two types of carbon-containing brick samples, $\text{Al}_2\text{O}_3\text{-C}$ and MgO-C , with the composition shown in Table 1 were prepared using the raw materials stated above. 4 mass % of phenol resin was used as binder.

Samples with the size of $20\text{ mm} \times 20\text{ mm} \times 20\text{ mm}$ cut from the brick samples were quenched at different temperatures (The bricks were heated at 230°C for 24 h in order to

Table 1. Composition of the Carbon-Containing Refractory Samples (mass%)

Sample No.		1	2	3	4	5	6	7
Al_2O_3	Fused Al_2O_3	< 3mm	65	65	65	65	65	
	Sintered Al_2O_3	< 45 μm	20	20	20	20	20	
MgO	Fused MgO	< 3mm						60
	Sintered MgO	< 45 μm						20
C	Graphite	180-300 μm						10
		< 180 μm	15	15	15	15	10	10
$\text{Al}_8\text{B}_4\text{C}_7$	Al	< 50 μm		4				4
		< 74 μm			2.52	2.52		
		< 45 μm				0.64	0.64

Fig. 1. Schematic cross section of the oxidized sample, describing the determining method of the thickness of the decarbonized layer.

make the resin added to the refractories solidified before being received from the Company). The quenched samples were cut in the middle, and the average thickness of the decarbonized layers was determined by measuring the side length of black core at two different positions, as shown in Fig. 1, after holding the samples at different temperatures for 3 h.

2.2.3 Stability of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and $\text{Mg}_3\text{B}_2\text{O}_6$ compounds in air

$\text{Al}_{18}\text{B}_4\text{O}_{33}$ was fabricated by well mixing Al_2O_3 and B_2O_3 (molar ratio = 9 : 2), pressing the mixture at 73.5 MPa before heating at 1000°C for 6 h, and then 1200°C for 2 h.

MgO and B_2O_3 was mixed (molar ratio = 3 : 1) before pressing. The shaped mixture was heated at 1000°C for 6 h, and then at 1400°C for 2 h.

XRD results showed that the compounds obtained by the above method were absolutely $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and $\text{Mg}_3\text{B}_2\text{O}_6$, respectively.

The isothermal weight changes of the compounds in air were monitored using an electro-balance whose accuracy was ± 1 mg. About 300 mg compound was placed in a platinum basket, which was suspended by a platinum wire from the balance, so that the basket was located at the center of the reaction tube. The weight loss was recorded at an interval of 30 s at different temperatures for about 7 h, and the remnants were analyzed by XRD.

3. Results and discussion

3.1 Behavior of $\text{Al}_8\text{B}_4\text{C}_7$ powder in CO gas

The partial pressure of CO(g) inside the carbon-containing refractories during using or heating process is 1.013×10^5 Pa.¹⁰⁾ The behavior of $\text{Al}_8\text{B}_4\text{C}_7$ powder in CO atmosphere is therefore investigated in order to clarify its reaction mechanism in carbon-containing refractories. Figure 2 illustrates the phase changes of $\text{Al}_8\text{B}_4\text{C}_7$ powder heated at 1000, 1200 and 1400°C in CO(g) for 2 to 8 h. The intensity of $\text{Al}_8\text{B}_4\text{C}_7$ decreased sharply with the increasing of temperature, while the intensity of Al_2O_3 , C and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ increased. The oxidation went slowly at 1000 and 1200°C, but became quickly since 1400°C. The process can be described by the following two reactions:

According to the reactions, all of $\text{Al}_2\text{O}_3(\text{s})$ should have reacted with $\text{B}_2\text{O}_3(\text{l})$ to form $\text{Al}_{18}\text{B}_4\text{O}_{33}$, and $\text{B}_2\text{O}_3(\text{l})$ should be left under the experimental condition. But actually, $\text{Al}_2\text{O}_3(\text{s})$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}(\text{s})$ co-existed. This can be explained by the formation of large amount of C (35.4 mass% in theory), which greatly reduced the contacting chance of $\text{Al}_2\text{O}_3(\text{s})$ and $\text{B}_2\text{O}_3(\text{s})$. $\text{B}_2\text{O}_3(\text{l})$ could not be identified because it did not crystalline or too little in amount.

Fig. 2. Phase changes of $\text{Al}_8\text{B}_4\text{C}_7$ powder heated in CO(g) at 1000 °C, 1200 °C and 1400 °C for 2 to 8 h.

Fig. 3. Stability domains of the condensed phases in Al-B-C-O system. (1) $\text{Al}_4\text{C}_3(\text{s}) + 6\text{CO}(\text{g}) = 2\text{Al}_2\text{O}_3(\text{s}) + 9\text{C}(\text{s})$; (2) $\text{B}_4\text{C}(\text{s}) + 6\text{CO}(\text{g}) = 2\text{B}_2\text{O}_3(\text{l}) + 7\text{C}(\text{s})$.

Figure 3 shows the stability domains of the condensed phases in Al-B-C-O system. Since the thermodynamic data of $\text{Al}_8\text{B}_4\text{C}_7$ is not clear, it is substituted by the data of Al_4C_3 and B_4C . Thermodynamically, $\text{Al}_8\text{B}_4\text{C}_7$ initially reacts with CO(g) according to Reaction (3) under the conditions $P_{\text{CO}} = 1.013 \times 10^5$ Pa (1 atm) and temperature below 1977°C:

Reaction (4) occurs when temperature is lower than 1580 °C:

At a given temperature, 1400°C, for an example, P_{CO} is 50.12 Pa when $\text{Al}_8\text{B}_4\text{C}_7$ still exists, but 1.2×10^4 Pa when $\text{Al}_8\text{B}_4\text{C}_7$ runs up and B_4C becomes stable.

It can be deduced from Reactions (3) and (4) that $\text{Al}_2\text{O}_3(\text{s})$ initially came out during the process accompanied by the yielding of large amount of C(s).

It should also be noticed that Reaction (1) is achieved via the gases that formed in the system. Partial pressures of the gases in Al-B-C-O system has been calculated in detail and the process of Reaction (1) has been described in Ref. 11, which proves that Al(g) and $\text{B}_2\text{O}_2(\text{g})$ have relatively high partial pressure. The partial pressure of Al(g) , $\text{B}_2\text{O}_2(\text{g})$ and $\text{B}_2\text{O}_3(\text{g})$ at different temperatures are calculated when Reactions (3) and (4) reach balance, respectively, as shown in Fig. 4. The partial pressure of Al(g) decreases as the balance transfers from Reactions (3) to (4), while $\text{B}_2\text{O}_2(\text{g})$ and $\text{B}_2\text{O}_3(\text{g})$ increase. Combining Ref. 11 with the calculat-

Fig. 4. Partial pressures of some main gases as a function of temperature in Al-B-C-O system when different reactions reach balance.

ed results, the whole process can be considered to proceed in the following sequence:

Al(g) evaporates at first and $\text{B}_4\text{C(s)}$ and C(s) are left:

As Al(g) diffuses to the surroundings where the partial pressure of CO(g) is high enough, it reacts with CO and condenses:

Reaction (3) is obtained from Reactions (5) and (6): (5) + (6) $\times$ 4.

When $\text{Al}_8\text{B}_4\text{C}_7$ disappears, $\text{B}_4\text{C(s)}$ reacts with CO(g) to form $\text{B}_2\text{O}_2(\text{g})$ and C(s) :

The formed $\text{B}_2\text{O}_2(\text{g})$ further reacts with CO(g) to form $\text{B}_2\text{O}_3(\text{l})$ and condenses:

As a result of Reactions (7) and (8), Reaction (4) is obtained: (7) + (8) $\times$ 2.

3.2 Effect of $\text{Al}_8\text{B}_4\text{C}_7$ addition on the oxidation resistance of the carbon-containing refractories

Figure 5 shows the photographs of cross sections of the MgO-C and $\text{Al}_2\text{O}_3\text{-C}$ refractory samples with $\text{Al}_8\text{B}_4\text{C}_7$ addition heated at 1400°C for 3 h in air. The black areas were those with carbon residue. Figure 6 tells the comparison of the average decarbonized layers' thickness of the refractory samples without any and with different additives. It can be seen from the figure that the carbon-remaining area of the sample containing $\text{Al}_8\text{B}_4\text{C}_7$ is bigger than that of the sample without additive. On the other hand, the result shows that Al is far more effective than other additives at 1200°C , but the difference is not so big at high temperatures. Figure 7 illustrates the difference of the decarbonized layers' thickness between $\text{Al}_2\text{O}_3\text{-C}$ and MgO-C samples with $\text{Al}_8\text{B}_4\text{C}_7$ addition heated at various temperatures for 3 h in air. The thickness of the decarbonized layer of the $\text{Al}_8\text{B}_4\text{C}_7$ -adding $\text{Al}_2\text{O}_3\text{-C}$ samples is thicker than that of MgO-C samples, while almost the same as that with Al and $\text{Al+B}_4\text{C}$ as additives.

Al is widely used as an antioxidant in MgO-C refractory.

Fig. 5. Photographs of the cross sections of the $\text{Al}_2\text{O}_3\text{-C}$ and MgO-C refractory samples heated at 1400°C for 3 h in air. A: $\text{Al}_2\text{O}_3\text{-C}$; A-A: $\text{Al}_2\text{O}_3\text{-C} + \text{Al}$; A-A+B: $\text{Al}_2\text{O}_3\text{-C} + \text{Al} + \text{B}_4\text{C}$; A-B: $\text{Al}_2\text{O}_3\text{-C} + \text{B}_4\text{C}$; A-ABC: $\text{Al}_2\text{O}_3\text{-C} + \text{Al}_8\text{B}_4\text{C}_7$ and M-ABC: $\text{MgO-C} + \text{Al}_8\text{B}_4\text{C}_7$.

Fig. 6. Thickness of the decarbonized layers of the refractory samples heated at different temperatures for 3 h in air.

Fig. 7. Comparison of the decarbonized layers' thickness of the $\text{Al}_2\text{O}_3\text{-C}$ and MgO-C samples with $\text{Al}_8\text{B}_4\text{C}_7$ addition heated at different temperatures for 3 h in air.

Fig. 8. Partial pressure of Al(g) over different reactions at various temperatures.

The mechanism lies on one hand that it reduces CO(g) to C(s) and therefore controls the loss of carbon. On the other hand, the formed $\text{Al}_2\text{O}_3(\text{s})$ may react with MgO to give MgAl_2O_4 . The large volume expansion accompanied with the reaction promotes the formation of a dense protective layer near the surface of the refractory.¹⁾ In the Al_2O_3 -C refractory, however, the mechanism seems different. The effectiveness of Al may attribute to its higher partial pressure inside the material. The escaped Al(g) reacts with oxygen to form Al_2O_3 , which condenses near the surface of the material and makes the surface layer denser. This can be demonstrated by thermodynamic calculation. The behavior of Al added in carbon-containing refractories has been studied.¹²⁾ The Al either, evaporates or reacts with C or reduces CO(g) to C, among which the partial pressure of Al(g) through the evaporation from Al(s,l) is the highest, as shown in Fig. 8. The reason that Al shows better effect than $\text{Al}_8\text{B}_4\text{C}_7$ lies in that the reaction between $\text{Al}_8\text{B}_4\text{C}_7$ and CO(g) becomes fast above 1400°C (Fig. 2), and the partial pressure of Al(g) over $\text{Al}_8\text{B}_4\text{C}_7$ is expected to be relatively low.⁶⁾

In the investigation of using B_4C as an antioxidant in MgO-C refractory, the behavior was explained by the formation of a liquid borate layer, which protects the carbon against oxygen ingress.¹³⁾ But for Al_2O_3 -C sample, the B_4C addition is no better, or even worse than that without additive.

Comprehensively, the mechanism of suppressing the oxidation of carbon in carbon-containing refractories by additives is the formation of dense layer near the surface of the materials. Thus, the oxidation should be closely related to the property of the formed protective layer, especially the stability.

It has been clarified that the protective layer forms near the black core,¹⁴⁾ As mentioned, $\text{B}_2\text{O}_3(\text{l})$ is formed during the oxidation process of $\text{Al}_8\text{B}_4\text{C}_7$. $\text{B}_2\text{O}_3(\text{g})$, when encountering MgO, reacts with MgO to form $\text{Mg}_3\text{B}_2\text{O}_6$, which engenders liquid phase when co-exists with MgO at above 1333°C (the eutectic point between $\text{Mg}_3\text{B}_2\text{O}_6$ and MgO).¹⁵⁾ $\text{Al}_8\text{B}_4\text{O}_{33}$ can also be formed when Al_2O_3 reacts with B_2O_3 in the Al_2O_3 -C refractory, and the compound is reported to be stable till 1965°C.¹⁶⁾ But the big difference of the decarbonized layer's thickness between Al_2O_3 -C and MgO-C samples implies that the stability of the formed compounds, $\text{Al}_8\text{B}_4\text{O}_{33}$ and $\text{Mg}_3\text{B}_2\text{O}_6$, is quite different under the experimental condition. Figures 9 and 10 illustrate the loss tendency of B_2O_3 from $\text{Al}_8\text{B}_4\text{O}_{33}$ (~13.1 mass% B_2O_3) and $\text{Mg}_3\text{B}_2\text{O}_6$ (~36.5 mass% B_2O_3) under isothermal condition

Fig. 9. Isothermal mass loss tendency of B_2O_3 from $\text{Al}_8\text{B}_4\text{O}_{33}$ at different temperatures in air.

Fig. 10. Isothermal mass loss tendency of B_2O_3 from $\text{Mg}_3\text{B}_2\text{O}_6$ at 1400 and 1500°C in air.

at different temperatures, respectively, assuming that Al_2O_3 and MgO do not evaporate under the condition. $\text{Al}_8\text{B}_4\text{O}_{33}$ decomposed and B_2O_3 evaporated considerably at 1300°C, and almost all B_2O_3 evaporated after 400 min at 1500°C. This also well explains that the B_4C addition is of no effect in Al_2O_3 -C refractories. As discussed above, $\text{Al}_8\text{B}_4\text{C}_7$ reacted with CO(g) quickly above 1400°C when $P_{\text{CO}} = 1.013 \times 10^5$ Pa, and the oxidation of graphite is also very fast since 1000°C.⁵⁾ Thus, it is believed that the evaporation of B_2O_3 controls the oxidation process. It can also be deduced that the Al_2O_3 -C sample with $\text{Al}_8\text{B}_4\text{C}_7$ additive will be wholly oxidized after about 7 h at 1500°C in air. $\text{Mg}_3\text{B}_2\text{O}_6$ was quite stable until 1400°C, and the loss of B_2O_3 was very little even at 1500°C.

Figure 11 shows the phase changes of $\text{Al}_8\text{B}_4\text{O}_{33}$ heated at different temperatures for about 7 h in air. The remnant was almost Al_2O_3 at 1500°C. Figure 12 presents the XRD results of $\text{Mg}_3\text{B}_2\text{O}_6$ heated at various temperatures. Although the intensity of $\text{Mg}_3\text{B}_2\text{O}_6$ slightly decreased with the increasing of temperature, MgO could not be identified until 1500°C. This implies that the MgO-C sample with $\text{Al}_8\text{B}_4\text{C}_7$ additive has a perfect antioxidant property at about 1400°C. The conclusion is also reflected by Fig. 7, in which the decarbonized layer is the thinnest at 1400°C. The formed $\text{Mg}_3\text{B}_2\text{O}_6$ existing as a continuous liquid layer near the surface of the material does not decompose nor evaporate until

Fig. 11. Phase changes of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ heated at different temperatures for 7 h in air.

Fig. 12. XRD results of $\text{Mg}_3\text{B}_2\text{O}_6$ heated at different temperatures for 7 h in air.

1400°C, and greatly prevents the ingress of oxygen. The fact that the decarbonized layer is thicker at 1500°C may attribute to, as one factor, the unstability of $\text{Mg}_3\text{B}_2\text{O}_6$.

The facts demonstrate that the formation of protective layer plays an important part on antioxidation of the material, and therefore the stability of the compounds should be significantly considered. It can be concluded that $\text{Al}_8\text{B}_4\text{C}_7$ is more effective in MgO-C refractory as an antioxidant than in $\text{Al}_2\text{O}_3\text{-C}$ refractory because the stability of $\text{Mg}_3\text{B}_2\text{O}_6$

that formed in MgO-C refractory is superior to that of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ in the $\text{Al}_2\text{O}_3\text{-C}$.

4. Conclusions

The behavior of $\text{Al}_8\text{B}_4\text{C}_7$ in CO(g) and its effect as an antioxidant in both $\text{Al}_2\text{O}_3\text{-C}$ and MgO-C refractories have been investigated, and the corresponding mechanisms have been discussed. Following conclusions are obtained.

(1) The $\text{Al}_8\text{B}_4\text{C}_7$ addition into the carbon-containing refractories markedly inhibits their oxidation.

(2) $\text{Al}_8\text{B}_4\text{C}_7$ reacts with CO(g) quickly above 1400°C to give Al_2O_3 , B_2O_3 and C . The B_2O_3 further reacts with MgO and Al_2O_3 in the refractories to form $\text{Mg}_3\text{B}_2\text{O}_6$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}$, respectively.

(3) $\text{Al}_8\text{B}_4\text{C}_7$ is more effective in MgO-C refractory as an antioxidant than in $\text{Al}_2\text{O}_3\text{-C}$ refractory due to the different stability of $\text{Mg}_3\text{B}_2\text{O}_6$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

(4) $\text{Mg}_3\text{B}_2\text{O}_6$ is stable till 1400°C in air, only a little B_2O_3 evaporates after 7 h even at 1500°C. $\text{Al}_{18}\text{B}_4\text{O}_{33}$ begins to decompose since 1300°C, the B_2O_3 almost runs up at 1500°C for 7 h.

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