RELATIONSHIP OF THE PROPERTIES OF

HOT-PRESSING C-BC$_4$-SiC COMPOSITE WITH

THE CONTENT OF ADDITIVE Al[①]

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ABSTRACT   The relationship of the properties of hot-pressing C-B$_4$C-SiC composite with the content of additive Al was studied. It is found that the density and strength of the composite increase and the specific resistance decreases by the addition of Al(2.5%~10%) as additive. When the weight content of Al is 2.5%, the properties of the composite are the best, and the higher the content of Al, the worse the properties of the composite. Furthermore, the composite has good heat-shock resistance and why the composite with additive Al has better properties was explained.
Key words   additive Al   C-B$_4$C-SiC composite   hot-pressing   property

1 INTRODUCTION

Carbon material is a good conductor in electricity and heat. It can resist high temperature, corrosion, heat-shock and lubricate itself. But its strength is low and its oxidation resistance is bad, which limits its wide application. In order to increase its strength and oxidation resistance, we can composite it with ceramics whose properties are replenished with carbon. Fibber strengthening[1] and surface coating[2] are two usual methods to prepare carbon/ceramics composite. The technical process of the former is complex and the latter cannot make up the shortages of carbon completely. If we add ceramics directly into carbon, the problem will be solved well. By addition of B$_4$C and other ceramics powders into carbon, Ingki[3, 4] prepared C-B$_4$C, C-B$_4$C-TiC, C-B$_4$C-TaC and C-B$_4$C-NbC composites by hot-pressing, in which the composition of ceramics phases is 30%~50% in volume. The composites are of good properties. By addition of B$_4$C and SiC into carbon, we[5] prepared C-B$_4$C-SiC composite by hot-pressing. For C, B$_4$C and SiC all are high melting-point materials, C-B$_4$C-SiC composite is very difficulty to sinter. For the convenience of sintering, we add additives into the composite and studied the effects of the additives[6, 7]. In this paper, we will study the effects of additive Al on the properties of C-B$_4$C-SiC composite.

2 EXPERIMENTAL

Petroleum cokes that were calcined at 1 350 ℃ and milled for 20 h in a ball mill machine were used as carbon materials. Its density is 2.01 g/cm^3, the average particle size of its powders was about 0.93 μm. B$_4$C and SiC were also milled in the ball mill machine. The average particle size of the B$_4$C, SiC and Al powders were 1.27 μm, 0.88 μm and 1.34 μ, respectively. C, B$_4$C, SiC and Al powders were mixed with the ball mill machine for 8 h. The ratio of mixed powders was C : B$_4$C : SiC= 63.6 : 15.4 : 21.3 (weight) or 70 : 19 : 11 (volume). That is to say the mole ratio of SiC

and B_4C is 1:1, the volume of carbon is 70%. And Al powder with content of 0, 2.5%, 5% and 10% was added to C, B_4C and SiC mixture, respectively. The mixed powders were then heated to 2 000 ℃ for 30 min under a pressure of 25 MPa in a graphite mold, in which the rising rate of temperature is 20~30 ℃/min, N_2 was used to protect the samples from oxidation. Specimens 35 mm in diameter and 25 mm in height were thus obtained. The specimens were then cut to 35 mm × 6 mm × 6 mm slips and ground. And then their density, bending strength and specific resistance were measured by waterdisplacing, three-point bending and four-point bridge method, respectively. Heat-shock resistance is indicated by the bending strength measured after the samples were cooled down quickly in 25 ℃ water from 600 ℃ and dried up. The microstructure was observed by a SIEMENS D5 000 diffractometer and an H-800 analytical electron microscopy.

3 RESULTS AND DISCUSSION

The properties of the samples are given in Talbe 1, in which the results of the bending strength, specific resistance and heat-shock resistance are the average data of five samples. From the table, we can see that by the addition of Al, the density, bending strength increase by a big margin. The specific resistance decreases. Furthermore, the bending strength after heat-shock is even higher than that before heat shock.

Fig. 1 and Fig. 2 are X-ray diffraction patterns of sample 1 and 2, respectively. From them, we can see that the sample with no additive is composed of C, B_4C and SiC, and the samples with additive Al are composed of C, B_4C, SiC and new phase $2Al_4C_3 \cdot SiC$.

It is known that the melting point of Al is 660 ℃. When the temperature is higher than this temperature, Al becomes liquid and disperses around the particles. Due to the high pressure, Al touches closely with the particles. Yamaguchi[8] found that during the sintering process, Al begins to react with C to form Al_4C_3 at 700 ℃, free state Al is decreas-

Table 1 The effect of Al on the properties of $C-B_4C-SiC$ composite

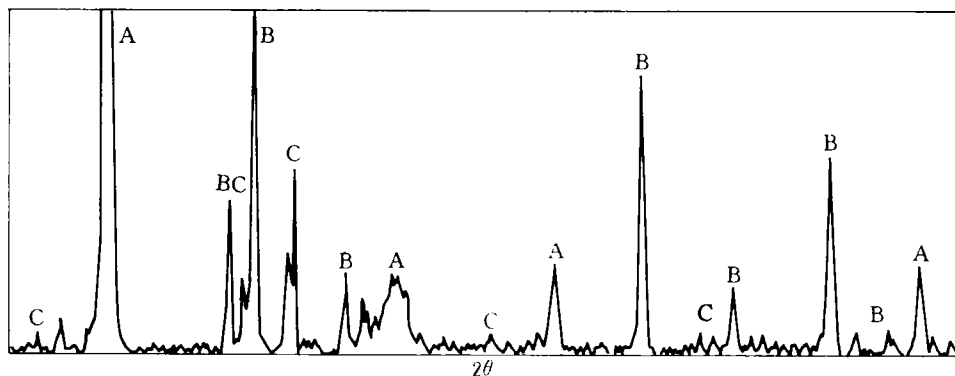| Sample Number	content of Al /%	density /g·cm^{-3}	bending strength /MPa	specific resistance ×10^{-6} Ω·cm	heat-shock resistance /MPa
No. 1	0	1.950	53.4	23.14	72.0
No. 2	2.5	2.103	130.6	12.74	166.5
No. 3	5.0	2.194	103.6	10.56	105.3
No. 4	10	2.249	86.2	10.08	127.7

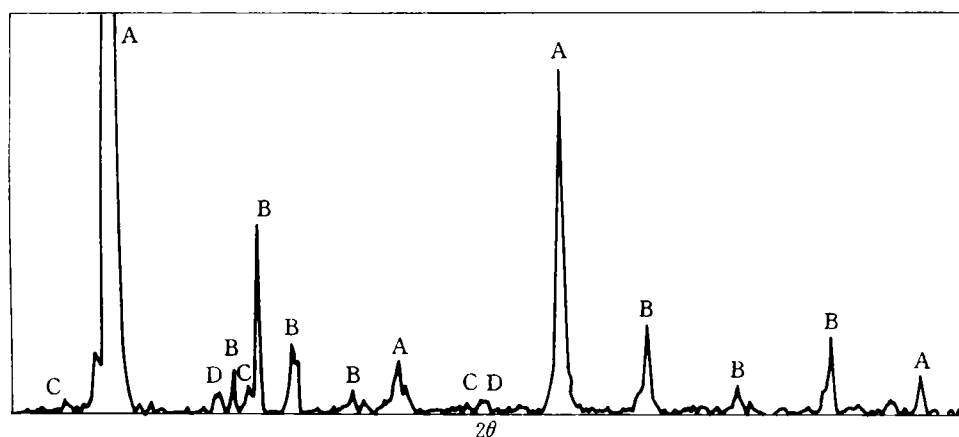**Fig. 1 X-ray diffraction pattern of $C-B_4C-SiC$ composite with no additive**
A—C; B—SiC; C—B_4C

Fig. 2　X-ray diffraction pattern of C-B₄C-SiC composite with additive Al(2. 5%)
A—C; B—SiC; C—B₄C; D—2Al₄C₃·SiC

ing quickly at 800 ℃ and free state Al disappears completely at 900 ℃. As the temperature is rising up, Al_4C_3 is unstable and react with SiC to form $2Al_4C_3$·SiC. It is found that liquid phase that is composed mainly of $2Al_4C_3$ · SiC flows out during the process of hot-pressing and the samples contracts itself greatly at about 1 800 ℃. In order to make surface energy tend to minimum, the liquid phase gather around the particles of carbon and ceramics richly, which decreases the surface energy greatly and accelerates the sintering process. Meanwhile due to the effecting of external pressure and capillary, the shrink of the particles is accelerated. Therefore, the density and the strength of the samples increase, the specific resistance decreases.

The adding amount of Al has strong influence on the properties of the composite. Adding small amount of Al, the properties have greater improvement and the higher the content of Al adding, the smaller the properties are improved. This may be related to the amount of $2Al_4C_3$·SiC phase, when the interfacial film $2Al_4C_3$ · SiC, which wraps up the particles of B₄C and SiC, is thinner, the properties would be better.

The cooling rate and the change of cooling temperature (Fig. 3) of samples thrown to 25 ℃ water from 600 ℃ were measured using

a cooling tester controlled by microcomputer (type BX-01 made in China).

When the C-B₄C-SiC composite is thrown into low temperature T_0 water from high temperature T_1, the shrink rate of the surface layer at the beginning instant is $\alpha(T_1 - T_0)$, where α is expansion coefficient of the material. However, the inside layer which keep on the temperature T_1 is not contract. Therefore, the surface layer suffers an action of a kind of tensile force from the inside layer and the in-
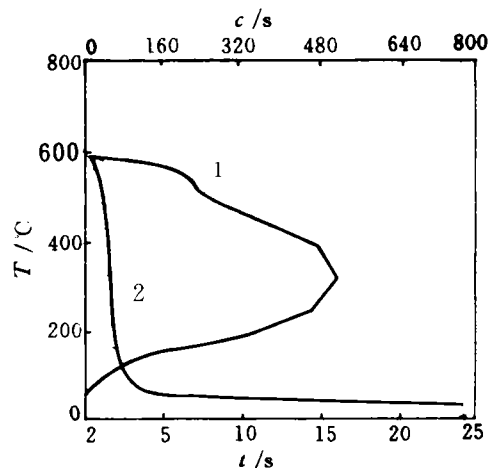

Fig. 3　The cooling process of samples in water(25 ℃)
1—cooling rate; 2—cooling temperature

side layer suffers an action of a kind of compression force from the surface layer. The tensile force that is produced in the surface by quick cooling is as follows:

$$\sigma_s = E_a(T_0 - T_1)/(1 - \gamma)$$

where E is the modules of elasticity, $1 - \nu$ is the part of Poison Ratio which considers the stress resulted by strain.

The stress dispersion by the difference of temperatures at that time is shown in Fig. 4. Soon afterwards, the temperature of the material decreases gradually from the surface to the inside and the thermal stress of both the inside and the surface layer decreases.

The existence of stress has inevitable act on the material. In order to moderate the action of stress, the material would suffer yielding and produce cracks. The size and amount of the cracks are related to the content of gas hole, the hardness, the microstructure and the type of the material. To C-B₄C-SiC composite, the carbon which is around with thin film of additive and ceramics phases is the main phase. Because of its high expansion coefficient and low strength, the carbon would contract itself greatly and microcracks would be formed in it when it is cooled down quickly.

Fig. 4　The dispersion of the stress and the difference of temperature

T —temperature; σ —stress

For the existence of microcracks, parts of energy would be absorbed from the front part of the main cracks when the samples are bending, the breaking energy would increase and so the strength increases. The phenomena is called microcrack strengthening and toughening. Of course, only the microcracks is small, and they will have effects of strengthening and toughening. To all the samples of C-B₄C-SiC, the bending strength has certain increase after 600 ℃ heat-shock.

4　CONCLUSIONS

(1) By the addition of Al, 2Al₄C₃·SiC interfactial film is formed around the particles of C, B₄C and SiC, which accelerates the sintering process. Consequently, the density and the strength of the samples increase by a big margin, and the sepecific resistance decreases.

(2) The adding amount of Al has strong influence on the properties of the composite. Adding small amount of Al, the properties have great improvement. And the higher the content of Al adding, the less the proper.ies are improved. This may be related to the amount of 2Al₄C₃·SiC phase.

(3) C-B₄C-SiC composite has good heat-shock resistance. The strength increases instead when the samples suffer high temperature heat-shock. The phenomena may be caused by the strengthening and toughening of microcracks.

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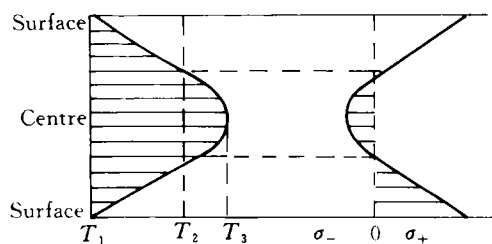9　Zhang Qingchuan. Mechanical Properties of Ceramic Material, Press of Science, 1987.