

Effect of Carbon Content on Mechanical Properties of SiC/B₄C Prepared by Reaction Sintering

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Abstract: SiC/B₄C composite was obtained by reaction sintering with Si infiltration, and the effects of carbon content on mechanical properties and the microstructure were investigated. The results showed that the mechanical properties of the SiC/B₄C composite improved firstly and then worsened with increasing carbon content. The optimum comprehensive properties of the composite were obtained by addition of 10vol% carbon. The hardness, bending strength, and fracture toughness of the composite were 19.63 GPa, 358 MPa and 3.96 MPa·m^{1/2}, respectively. In addition, at carbon levels below 10vol%, the microstructure became more uniform as the carbon content increased. However, at carbon levels above 10vol%, the addition of carbon led to a fracture mode transformation, from combination of intergranular and transgranular to transgranular, which contributed to a change in the mechanical properties of the SiC/B₄C composite.

Key words: SiC/B₄C composite; reaction sintering; infiltration of Si; fracture mode

Cubic B₄C has long been considered as a choice for light armor applications because of its high hardness, low density and good ballistic resistance^[1]. On the other hand, B₄C is an excellent nuclear shielding material because of its higher neutron absorption cross section and corrosion resistance. However, poor fracture toughness and sintering difficulties have now limited the extending use of the B₄C-based armor^[2].

The addition of SiC to B₄C ceramic material is an effective way to improve not only the compactness and fracture toughness of the sintered body but also its mechanical and physical properties. Thus, SiC/B₄C ceramic material can be widely used as wear and corrosion-resistant materials, which are particularly attractive for vehicle armor and nuclear shielding.

Recently, hot-press sintering, pressureless sintering, and reaction sintering have all been used in the preparation of SiC/B₄C composite. However, high costs and size demands have limited the use of this method. Meanwhile, high sintering temperatures and mass production difficulties have rendered pressureless sintering impracticable. In contrast, reaction sintering has been considered as an alternative method for preparing SiC/B₄C composite due to its lower sintering temperatures, shorter sintering time, and

low cost for obtaining higher densities^[3], especially for the net-shape molding at lower temperatures.

Hayun, *et al*^[4] added free carbons to B₄C through the pyrolysis of sugar and fabricated the composite by reaction sintering with molten Si. However, the process of adding carbons may have caused lower compactness. Zhang, *et al*^[5] also reported the preparation of SiC/B₄C by reaction sintering, but the effect of carbon content on mechanical properties was not systematically studied. In this study, we developed the material components to study the effect of carbon content in reaction sintering processes on mechanical properties of the SiC/B₄C composite and provided a theoretical formulation different from the above studies.

1 Experimental procedure

1.1 Preparation process

B₄C powder (~5 μm, Jin Ma Co.) and carbon powder (Yi Jia Chemical Co.), along with a certain amount of binders, were mixed in various proportions. The mixtures were wet ball milled in ethanol with agate balls in a plastic bottle for 24 h. They were then dried at 65°C for 12 h and compacted at 100 MPa. The compacts

were infiltrated with liquid silicon at 1650°C for 2 h under a vacuum of 1×10^{-3} Pa. At this sintering temperature, the effect of carbon content on mechanical properties was studied.

1.2 Characterization

Density and porosity were measured using the Archimedes method. Microhardness values were determined using Vickers hardness testing (SHA-10A) with 98 N load and 9–12 points were tested under each condition. Flexural strength was measured on 3 mm×4 mm×36 mm samples using three-point bending method and mechanical properties were measured using ceramic material testing system (CMT-4340), and 3–5 samples were tested under each condition. Fracture toughness was measured using an indentation method. Fracture toughness can be measured based on the indentation surface crack size. Microstructure and distribution of phases were observed using optical microscope (OM 2000). Fracture morphology of samples was observed using scanning electron microscope (SEM).

2 Results and discussion

2.1 Composition design

In the reaction-bonded SiC/B₄C composite, B₄C and Si at experimental temperature are inert because the wetting angle of Si to B₄C is 0°. Its reaction-bonding mechanism is the same as that for the reaction bonded silicon carbide (RBSC). The process of the reaction-bonded SiC/B₄C is shown in Fig. 1.

In the preparation of the composite without any obstruction of infiltrating Si, the main reaction involved is $C + Si \rightarrow SiC$. The atomic weights of C and SiC are known, and the volume ratio of SiC/C in the ingredients can be determined from theoretical densities of C and SiC, as follows:

$$\frac{V'_{SiC}}{V_C} = \frac{\frac{M_{SiC}}{\rho_{SiC}}}{\frac{M_C}{\rho_C}} = \frac{\frac{40}{3.21 \text{ g/cm}^3}}{\frac{12}{2.26 \text{ g/cm}^3}} = 2.33 \quad (1)$$

Based on this calculation, the equation can be de-

veloped as

$$V'_{SiC} = 2.33V_C \quad (2)$$

Normally, a sintered body of RBSC consists only of SiC and Si without pores and carbon residue. Considering the mass conservation law, if the volume of a green body is equal to that of a sintered body, the equation obtained is as follows:

$$V_C + V_\pi = V'_{SiC} + V'_\pi \rightarrow V_C + V_\pi = 2.33V_C + V' \quad (3)$$

$$1.33V_C = V_\pi - V'_\pi \quad (4)$$

Ideally, the composite is free of residual silicon. Based on the testing, V_π is 0.35, and the volume fraction of carbon is calculated

$$V_C = \frac{V_\pi - V'_\pi}{1.33} = \frac{0.35}{1.33} = 26.32\% \quad (5)$$

Namely, the carbon content of the reaction-bonded SiC/B₄C system formulations should theoretically range from 0 to 26.32vol%. However, as carbide content increases excessively the mechanical performance worsens. Thus, the carbon content is finally set between 0 and 20vol%. The compositions of the samples in this study are shown in Table 1.

2.2 Microstructure characterization

Figure 2 shows OM images of the composite with different carbon contents. In Fig. 2, the areas of different phase distributions gradually became smaller and more uniform as carbon content ranging from 0 to 10vol%. In the larger-sized, gray-colored^[6] B₄C phase without addition of carbon powder, the areas of different phase distributions were observed to be non-uniform. This phenomenon may be due to the difficulty of B₄C sintering, which may lead to lower strength.

In Fig. 2(c), the addition of 10vol% carbon can be seen to produce a phase distribution with better continuity and no large silicon spots. This may contribute to the effect of sintering aid carbon. The result is a more uniform microstructure with improved hardness and strength of the composite, similar to the study done by Kim^[7]. In Kim's study, Al₂O₃ was used as the sintering aid, and the sinterability of B₄C was greatly improved.

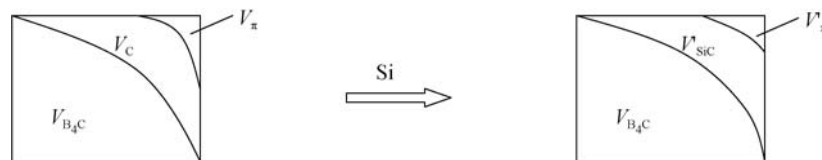
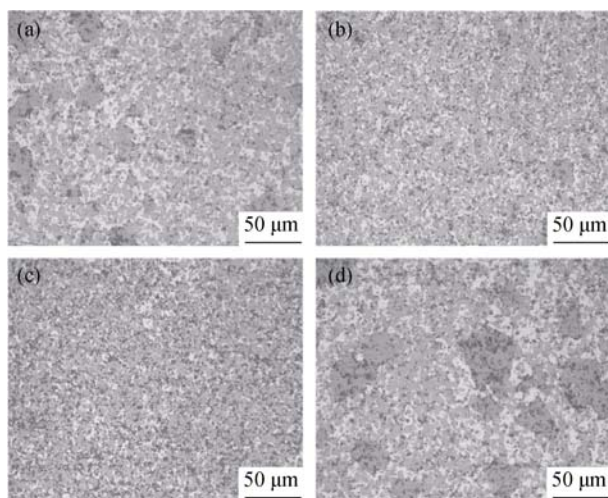


Fig. 1 Schematic of the reaction-bonded SiC/B₄C

V_π is the pore volume of a green body while V'_π is the pore volume of a sintered body

Table 1 Formulation of SiC/B₄C system

Samples	0#	1#	2#	3#	4#
C/vol%	0	5	10	15	20
B ₄ C/vol%	100	95	90	85	80

Fig. 2 OM images of the SiC/B₄C composite with different C contents

(a) 0; (b) 5vol%; (c) 10vol%; (d) 15vol%

When carbon content is more than 10vol%, adding more carbon produces a less uniform phase distribution, and externally larger-sized individual phases can be observed. In Figure 2(d), microstructures with larger sizes come from aggregation of SiC generated in the reaction. Due to further addition of carbon powder, according to Trunec^[8], hardness drops as grain size increases, which confirms the results of this study. Large-sized, gray-colored Si spots have also formed along the larger phase, and homogeneity of the microstructure is poor, leading to lower hardness and strength. Meanwhile, larger-sized microstructures may decrease the toughness because the poor dispersion of particles influences the sintered microstructures, as well as the mechanical properties, just like the study of Paik^[9]. Moreover, according to the research of Monteverde^[10], the composite can be toughened with ultrafine SiC particulates, which may contribute to the correctness of the results.

2.3 Mechanical properties

Figures 3, 4 and 5 show the hardness, flexural strength, and porosity of composite with different carbon contents. The mechanical properties, including hardness, flexural strength, and fracture toughness, of the composite present a peak with carbon content increase.

According to the report^[7], the hardness of the com-

posite has a close relationship with compactness. In general, the higher the compactness the greater the hardness is. With an increase in the carbon content ranging from 0 to 10vol%, porosity decreases slightly, resulting in an increase in hardness and flexural strength. This is because of the fewer defects that are associated with higher compactness. As the carbon content continues to increase, higher porosity can be observed, and hardness decreases with the increased porosity which associated with poor compactness. Meanwhile, higher porosity may contribute to more defects so as to decrease the strength. Furthermore, because of the relatively poor correlation between porosity and toughness, this study will later analyze the toughness and fracture modes.

According to Fig. 3, 4 and 5, when the carbon content is 10vol%, the flexural strength and hardness of the composite reach their maximum. When the addition of carbon ranges from 5vol% to 15vol%, the values of fracture toughness are similar. To obtain the optimal comprehensive performance, carbon should be 10vol%. The optimal hardness, flexural strength, and fracture toughness are 1963 MPa, 358 MPa, and 3.96 MPa·m^{1/2}, respectively.

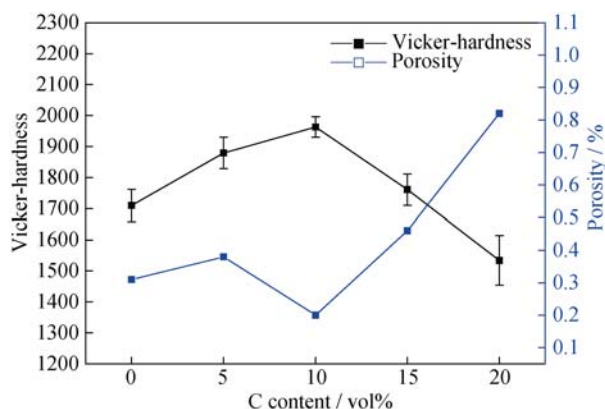


Fig. 3 Effect of carbon content on hardness and porosity

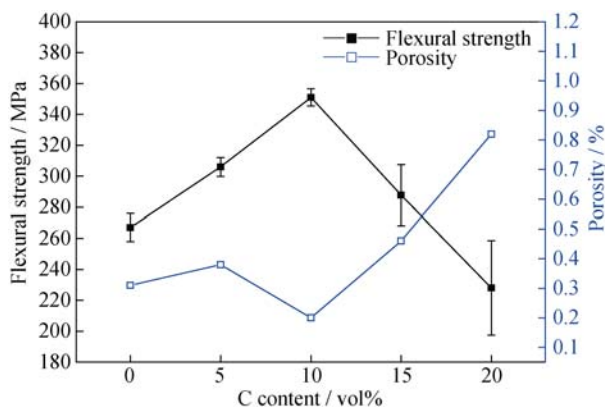


Fig. 4 Effect of carbon content on flexural strength and porosity

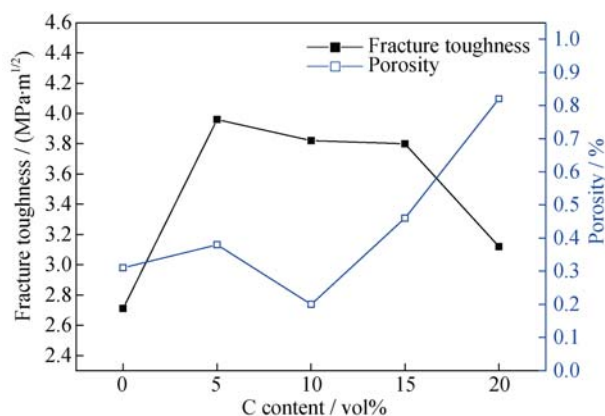


Fig. 5 Effect of carbon content on fracture toughness and porosity

2.4 Mechanisms of improvement mechanical properties

Figure 6 shows the SEM images of the composite with different carbon contents. In Fig. 6(a) and 6(b), the fracture mode of the composite is a combination of intergranular and transgranular fractures. On the other hand, there are a small amount of holes within the material shown in Fig. 6(b).

Such defects within the composite are because of the difficulty of B₄C sintering without the addition of carbon powder. The compactness of the resulting composite is low, which lead to lower strength.

According to Fig. 6(e) and 6(f), as the addition of carbon ranges from 0 to 10vol%, the fracture mode transforms from a combination of intergranular and transgranular to transgranular only, which contributes to the development of toughness. This is because of the different coefficients of thermal expansion between different phases (B₄C, Si and SiC), which leads to the phenomenon of crack deflection. In addition, defects such as holes within the material gradually disappear because of the addition of carbon used as a sintering aid. On the other hand, the formation of SiC may fill the pores and improve compactness, whereas the decrease in defects leads to increase in strength.

By continually increasing the amount of carbon powder, especially above 10vol%, the fracture mode of the composite remains transgranular (Fig. 6(g)). However, larger-sized individual grains were observed, and this abnormal grain growth may lead to the poor mechanical properties of the composite. In addition, some holes could be observed, which may resulting in poor mechanical properties (Fig. 6(h)). Two factors contribute to this phenomenon. On one hand, because the pre-sintering is controlled by the accelerated reaction, the SiC formed during the reaction promotes aggregate formation and partially blocks the

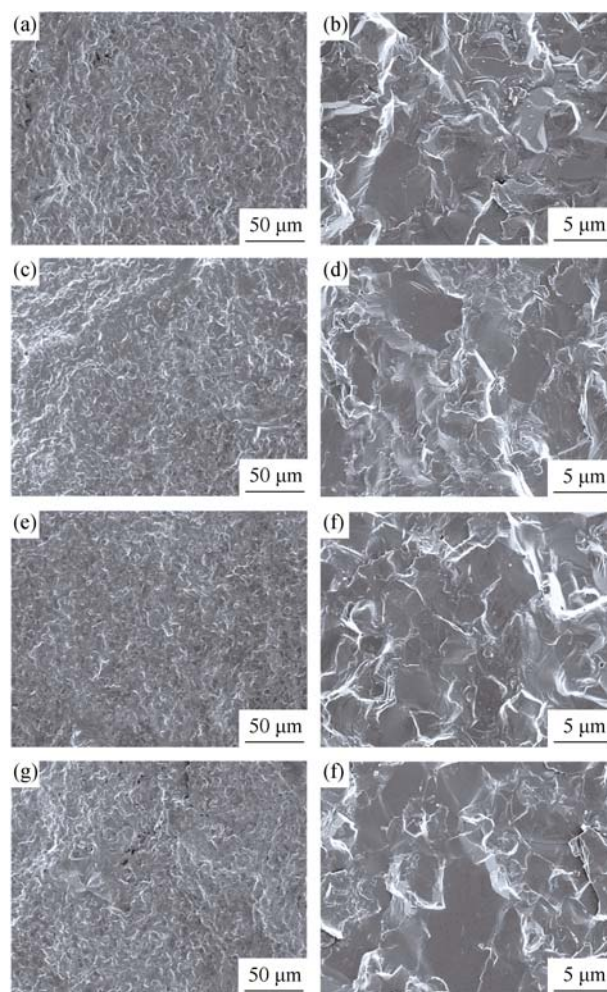


Fig. 6 SEM images of the SiC/B₄C composite with different carbon contents

(a, b) 0; (c, d) 5vol%; (e, f) 10vol%; (g, h) 15vol%

channels from silicon infiltration, creating pores within the composite. On the other hand, the later stages of sintering are controlled by diffusion, and the pores are barely filled. Therefore, some holes appear in the SiC/B₄C composite. The infiltration process of Si is the same as that of Al in the report of Arslan^[11].

Therefore, strength and toughness increased firstly and then dropped as carbon content increased, according to the mechanical properties data.

3 Conclusions

1) The mechanical properties of the SiC/B₄C composite improved firstly and then worsened as the carbon content increased. With the addition of 10vol% carbon, the optimum hardness, bending strength and fracture toughness of the composite were 19.63 GPa, 358 MPa, and 3.96 MPa·m^{1/2}, respectively.

2) When carbon content was less than 10vol%, the

microstructure became more uniform as the carbon content increased. At carbon content more than 10vol%, there was an opposite tendency, which led to a change in strength.

3) The addition of carbon led to fracture mode transforming from a combination of intergranular and transgranular to transgranular only, which contributed to a change in toughness.

4) When the carbon content was more than 10vol%, defects such as holes within the composite led to a decrease in the mechanical properties.

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碳含量对反应烧结 SiC/B₄C 力学性能的影响

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摘要: 采用渗硅反应烧结工艺制备了 SiC/B₄C 复合材料, 并研究了碳含量对复合材料的力学性能及微观结构的影响。结果表明, SiC/B₄C 复合材料的力学性能(硬度、抗弯强度、韧性)随着碳含量的增加呈先增强后减弱的趋势。在碳含量为 10vol% 的条件下, 复合材料的综合性能最佳, 其硬度、抗弯强度和韧性分别为 19.63 GPa、358 MPa 和 3.96 MPa·m^{1/2}。此外, 当碳含量不足 10vol%, 复合材料的组织随碳含量增加均匀性提高; 当碳含量超过 10vol%, 显微组织均匀性变差, 并且添加碳粉后, 复合材料由沿晶、穿晶混合断裂向穿晶断裂转变, 最终导致 SiC/B₄C 复合材料力学性能的改变。

关键词: SiC/B₄C 复合材料; 反应烧结; 渗硅; 断裂模式

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