I O U R N A L O F

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Effect of silicon additions on the hot pressing of B₄C

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In the present study, the effect of silicon additions on the hot pressing of boron carbide was investigated. B₄C-based ceramic composites with the addition of silicon powder up to 12 wt.% were prepared by hot pressing at 1850 °C under a vacuum and 60 MPa pressure. The results show that addition of silicon powder affected the sintering behavior of B₄C significantly. Silicon powder reacted with free-carbon originating in the B₄C phase and formed a solid solution in the B₄C structure. For the B₄C-8 wt.%Si specimen, a high fracture toughness of 5.04 MPa m^{1/2} and modest flexural strength of 354 MPa were obtained. It seems that the improvement in fracture toughness is attributed to the high relative density and the change of fracture mode by the formation of the SiC phase.

Key words: Boron carbide, Silicon, Microstructure, Mechanical properties, Hot pressing.

Introduction

Boron carbide is an extremely promising material for a variety of applications due to its excellent properties such as high hardness, wear resistance, high melting point, low density and good chemical stability. However, the widespread use of boron carbide is limited due to the relatively low strength and fracture toughness as well as poor sinterability caused by the low self-diffusion coefficient [1, 2]. Fully densified B₄C ceramics without additives are usually fabricated by means of hot pressing above 2100 °C with an applied load of more than 30 MPa [3]. Numerous additives have been used as sintering aids to increase the sinterability of B₄C. The effect of carbon additions on the densification of B_4C has been reported [4-6]. The maximum values for flexural strength and Young's modulus, 579 MPa and 444 GPa, respectively, were obtained for moldings sintered at temperatures from 2150 to 2175 °C [6]. The sinterability of B₄C was remarkably improved by the addition of Al₂O₃. For B₄C specimen with 2.5 vol.% Al₂O₃ sintered at 2000 °C, a flexural strength of 550 MPa was obtained [7]. Yamada et al. [8] fabricated B₄C-CrB₂ composites with both a high strength of 630 MPa and fracture toughness of 3.5 MPa·m^{1/2} by hot pressing at 1900 °C. Deng et al. reported that additions of (W,Ti)C affected the densification rates of B₄C-based ceramic composites markedly. The sintering temperature was lowered from 2150 °C for monolithic B₄C to 1850 °C for $B_4C/(W,Ti)C$ composites [9].

In this paper, B₄C-based ceramic composites with different

contents of silicon powder were fabricated using a hotpressing technique. The mechanical properties, phase composition and the microstructure of the specimens were studied.

Experimental Procedures

A boron carbide powder with an average particle diameter powder was utilized as a sintering aid. Boron carbide and silicon powders were milled in an alumina ball mill. Samples were hot pressed at 1850 °C for 30 minutes in a furnace equipped with a graphite resistant heater under a pressure of 60 MPa and a vacuum. The heating rate was 20 K/minute.

After sintering, samples were finely ground using diamond powder on a polishing wheel, and then cut into $30 \times 4 \times$ 3 mm and $30 \times 4 \times 2$ mm pieces for the purpose of measuring three-point flexural strength and fracture toughness. The fracture toughness, K_{IC} , was measured using a single etched notched beam containing scratches, which were about 2 mm in depth and 0.2 mm in width. The bridging distance was 25 mm and the loading velocities for the flexural strength tests and fracture toughness tests were 0.5 mm/minute and 0.05 mm/minute, respectively. The densities of hot-pressed samples were determined by the Archimedes' method. Phase compositions were determined by a Rigaku D/MAX- γ A diffractometer. Microstructural analysis was carried out using scanning electron microscopy (SEM: S-2500, Hitachi)

Results and Discussion

Table 1 shows the starting compositions, densities and mechanical properties of the specimens hot pressed at

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Table 1. Starting compositions, densities and mechanical properties of B_4C based specimens hot pressed at 1850 °C for 30 minutes under a pressure of 60 MPa and a vacuum

	Si content (wt.%)	Measured density (g/cm ³)	Flexural strength (MPa)	Fracture toughness (MPa·m ^{1/2})
Pure B ₄ C	0	2.29	175	4.25
B ₄ C-4wt.%Si	4	2.50	283	4.37
B ₄ C-8wt.%Si	8	2.57	354	5.04
B ₄ C-12wt.%Si	12	2.59	302	4.76

1850 °C in a vacuum and under a pressure of 60 MPa (each value is the average of three samples). The results show that the addition of silicon evidently improves the sinterability of B_4C ceramic. The silicon powder melted above 1400 °C, and the existence of the liquid phase facilitated the sintering process. The liquid phase was not enough to achieve a full density until the Si content was up to 8 wt.%. The fracture toughness increased with an increase in the Si content up to 8 wt.%, and thereafter decreased slightly. Yamada *et al.* [8] reported that the fractured surface of pure boron carbide was quite smooth owing to the transgranular mode of fracture. It is considered that the transgranular mode of fracture resulted in the low fracture toughness.

Fig. 1 shows the microstructures of the etched fractured surfaces of B_4C based specimens sintered at 1850 °C under a 60 MPa pressure. Visible pores existed in the pure B_4C and B_4C -4 wt.%Si specimens as shown in Fig. 1(a and b) indicating low densities. The fractured surfaces of B_4C -8 wt.%Si and B_4C -12 wt.%Si specimens were compact and relatively rough. It is clearly seen that SiC (lighter in color) particles are dispersed in the B_4C matrix (Fig. 1(a)), and intergranular fracture occurred partially at the interfaces



Fig. 1. Micrographs of B_4C specimens sintered at 1850 °C under a pressure of 60 MPa : (a) Pure B_4C ; (b) B_4C -4 wt.%Si; (c) B_4C -8 wt.%Si; (d) B_4C -12 wt.%Si.

between the SiC particles and the B_4C matrix. It appears that this change of fracture mode by the existence of SiC and the increase of the relative density improve the fracture toughness. However, the SiC particles of the B_4C-12 wt.%Si specimen were bonded together, resulting in a much bigger grain size than that of the B_4C-8 wt.%Si specimen. It was assumed that the reduction of fracture toughness for the B_4C-12 wt.%Si specimen was probably attributed to the aggregated SiC particles. The addition of Si also increased the flexural strength, as shown in Table 1. A flexural strength of 354 MPa was obtained for the B_4C-8 wt.%Si sample. The improvement in strength by the addition of Si was apparently due to the densification, which led to a reduction in the number and size of the pores acting as the origins of fracture [10].

The phase compositions of B₄C based specimens sintered at 1850 °C under a 60 MPa pressure are shown in Fig. 2. For the pure B₄C specimen, the diffraction peak at 26.6° can be assigned to the graphite lattice plane (002). This diffraction peak disappeared for the specimens with Si, indicating that all the free carbon reacted with liquid silicon and synthesized the SiC phase. The XRD patterns of pure B₄C and B₄C-8 wt.%Si are shown in detail from 30°-45° $2 \le$ (Fig. 3). It is obvious that some shift of the B₄C peaks of the B₄C-8 wt.%Si specimen occured as compared to those of pure B₄C. Telle [11] studied the B₄C-B-Si system using a pressureless sintering technique. He found that the solid solubility of Si in B₄C at 2250 °C is about 2.5 at.%. In this experiment, the residual Si after reaction with the free carbon was fully solid soluted into B₄C, as our samples were hot pressed under a high pressure of 60 MPa. The lattice parameters a and c for pure B₄C are 0.5599 nm, 1.2080 nm, and increased to 0.5610 nm, 1.2180 nm for the B₄C-8 wt.%Si sample. The significantly larger increase in particular of the c lattice parameter is attributed to the presence of silicon dissolved in the boron carbide lattice [11, 12].



Fig. 2. XRD patterns of B_4C specimens sintered at 1850 °C under a pressure of 60 MPa.







Fig. 4. XRD patterns of B_4C-8 wt.%Si sintered at various temperatures.

Fig. 4 shows X-ray diffractograms of the B_4C-8 wt.%Si specimens sintered at various temperatures under a 60 MPa pressure. The XRD pattern of the B_4C-8 wt.%Si sample before sintering is also presented. The diffraction peak of Si could still be found at 1400 °C and disappeared with a

higher sintering temperature. This means that the silicon powder reacted with free carbon and solid soluted into the B_4C above 1400 °C.

Conclusions

SiC/B₄C composites were prepared by hot pressing. The Si powder reacted with free carbon and subsequently solid soluted into B₄C. Silicon powder improved the mechanical properties of boron carbide ceramic substantially. The optimal silicon content is 8 wt.%. The maximum value of the flexural strength and fracture toughness of the composite are 354 MPa and 5.04 MPa \cdot m^{1/2}.

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