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B_4C-CrB_2 composites with improved mechanical properties

Suzuya Yamada[a,*], Kiyoshi Hirao[b], Yukihiko Yamauchi[b], Shuzo Kanzaki[b]

[a]*Synergy Ceramics Laboratory, Fine Ceramics Research Association, 2268-1, Shimo-Shidani, Moryama-Ru, Nagoya, Aichi, 463-8687 Japan*
[b]*Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology Nagoya, Aichi, 463-8687 Japan*[1]

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Abstract

B_4C based ceramic composites with 0–25 mol% CrB_2 were fabricated by hot-pressing at 1900 °C, and their mechanical properties were examined. The B_4C-CrB_2 composites with both high strength of 630 MPa and modest fracture toughness of 3.5 MPa $m^{1/2}$ could be obtained by the addition of 20 mol% CrB_2. It seems that improvement in fracture toughness is due to the formation of microcracks and deflection of propagating cracks caused by the thermal expansion mismatch between CrB_2 and B_4C.

Keywords: B_4C; Composites; Strength; Toughness and toughening; CrB_2

1. Introduction

Due to their excellent properties such as high hardness, high elastic modulus, wear resistance, high melting point, low density and good chemical stability, boron carbide (B_4C) based ceramics have good potential for various industrial fields.[1–4] However, the major problems with B_4C based ceramics are their relatively low strength and fracture toughness as well as poor sinterability, caused by the low self-diffusion coefficient. Several additives have been examined to promote the densification of B_4C. The effect of carbon addition on the densification of B_4C has been reported.[5–9] A relative density of 96.4% was obtained by pressureless sintering of B_4C doped with carbon at 2150 °C. Full densification was achieved by means of post-HIP treatment of the specimens. The flexural strength and the fracture toughness of the post-HIP specimen were 579 MPa and 2.4 MPa $m^{1/2}$, respectively.[9] It was reported that Al and Al containing compounds such as AlF_3 are also effective additives for densification of B_4C. For example, high relative density of 95% was achieved for B_4C with the addition of 1 mass% Al by pressureless sintering at 2200 °C.[10] Kim et al. stated that the addition of a small amount of Al_2O_3 greatly improved the sinterability of B_4C, and that a flexural strength of 550 MPa was obtained for a B_4C based ceramic hot-pressed at 2000 °C with the addition of 2.5 vol.% Al_2O_3.[12] The effect of other additives such as SiC, TiC, WC and BN have also been investigated, with limited success.[11,13–15]

The purpose of these investigations was mainly to enhance the densification and, thereby, to increase the strength of B_4C ceramics. B_4C ceramics with dispersed TiB_2 particles have been investigated in order to increase both strength and toughness.[16–20] The improvement of fracture toughness was accomplished in terms of microcracking formation caused by the thermal expansion mismatch between dispersed particles and the matrix. Skorokhod and Krstic reported that a flexural strength of 621 MPa and a fracture toughness of 6.1 MPa $m^{1/2}$ were obtained for a B_4C–15 vol.% TiB_2 composite produced by reaction hot-pressing of B_4C with the addition of TiO_2 and C at 2000 °C.[20] The high strength of this material was attributed to the combination of high fracture toughness and fine microstructure.

The addition of CrB_2 is expected to be more effective for increasing the fracture toughness of B_4C ceramics because of the larger difference in thermal expansion between B_4C and CrB_2 than B_4C and TiB_2.[1] In addition, CrB_2 exhibits high hardness, high melting point and chemical stability.[21–22] B_4C and CrB_2 phases can coexist according to the phase diagram of the B_4C-CrB_2 system.[23] However, mechanical properties of B_4C-CrB_2 ceramics have not been investigated. In the present

* Corresponding author. Tel.: +81-52-739-0152; fax: +81-52-739-0051.
E-mail address: su-yamada@aist.go.jp (S. Yamada).
[1] Formerly, National Industrial Research Institute of Nagoya

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study, B_4C ceramics with dispersed CrB_2 particles were fabricated by hot-pressing a powder mixture of fine B_4C powder and CrB_2, and the microstructure and mechanical properties of the specimens were examined and compared with monolithic B_4C.

2. Experimental procedure

The B_4C starting powder (Grade No. 1500, Denki Kagaku Kogyo Co., Tokyo, Japan) has an average particle size of 0.40 μm and a specific surface area of 22.4 m^2/g. The powder contains oxygen (3.6 mass%), Fe (4000 ppm), and Al (1100 ppm) as impurities. The B_4C powder was mixed with CrB_2 powder with an average particle size of 3.5 μm (Japan New Metals Co., Osaka, Japan) using a planetary ball mill with a SiC pot and SiC balls in methanol for 30 min. The chromium diboride content was varied from 5 to 25 mol%. The slurry was dried in a rotary vacuum evaporator for 1 h, followed by oven drying at 115 °C for 24 h. The powder mixture was passed through a 60 mesh sieve. Hot-pressing was performed using a carbon resistance furnace in a rectangular graphite die (47×42 mm) at 1900 °C for 1 h with an applied load of 50 MPa under 0.1 MPa argon pressure. The temperature was monitored by an optical pyrometer which was calibrated in advance using a thermocouple. The heating rates were 40 °C/min from room temperature to 1200 °C, 20 °C/min to 1500 °C and 10 °C/min to 1900 °C. For the sake of comparison, B_4C specimen without CrB_2 was also fabricated by the same procedure.

For measuring mechanical properties, test pieces were cut from the hot-pressed specimens and ground with a 400-grit diamond wheel to dimensions of 42×4×3 mm. The flexural strength was measured by a four-point bending test with inner and outer spans of 10 and 30 mm, respectively. The fracture toughness, K_{IC}, was measured by the SEPB method.[24] The densities of test pieces were determined by the Archimedes' method. Phase identification was performed by X-ray diffractometry (XRD: RINT 2500, Rigaku Co, Tokyo, Japan) with CuK_α radiation. In order to observe the microstructure, specimens were polished with 1 μm diamond slurry. Some specimens were etched with Murakami's reagent (10 g of NaOH and 10 g of $K_3Fe(CN)_6$ in 100 mL H_2O at 110 °C). Microstructural analysis was carried out using scanning electron microscopy (SEM: JSM5600, Jeol Ltd., Tokyo, Japan). The mean grain size of B_4C was measured using image analysis (Scion Image, Scion Co., Maryland, USA).

Table 1
Starting compositions and densities of B_4C based specimens

	CrB_2 content		Theoretical density (g/cm^3)	Measured density (g/cm^3)	Relative density (%)
	(mol%)	(vol.%)			
(1)	0	0	2.52	2.50	99.0
(2)	5	3.1	2.61	2.60	99.6
(3)	10	6.2	2.71	2.70	99.7
(4)	15	9.6	2.82	2.79	99.0
(5)	20	13.0	2.92	2.89	99.0
(6)	25	16.7	3.03	2.99	98.6

3. Results and discussion

Table 1 shows the starting compositions and densities of the hot-pressed specimens. High relative density of 99.0% was achieved even in the specimen without CrB_2. Although relative densities of the specimens with up to 20 mol% the addition of CrB_2 were higher than 99% of theoretical densities, B_4C with 25 mol% CrB_2 was slightly lower than 99%.

The specimen without CrB_2 was composed of fine equiaxed grains as shown in the etched surface of the specimen (Fig. 1). The grain size of B_4C is 0.93 μm (σ: 0.28) in diameter. The development of such a fine microstructure is ascribed to the use of fine B_4C powder with an average particle size of 0.40 μm and the relatively low sintering temperature of 1900 °C preventing substantial grain growth. Fig. 2 shows microstructures of B_4C-5 mol% CrB_2, B_4C-20 mol% CrB_2, and B_4C-25 mol% CrB_2 specimens observed in the polished surfaces of the specimens. The CrB_2 particles appear as areas of high contrast in the darker B_4C matrix. It can be seen that CrB_2 particles of a few micron size are dispersed in the B_4C matrix. It is apparent that the average interparticle spacing between CrB_2 particles decreases as the CrB_2 volume fraction increases as shown in Fig. 2. In order to clarify the grain morphology of the B_4C matrix in the composites, chemical etching was conducted. Fig. 3 shows a polished and chemically etched

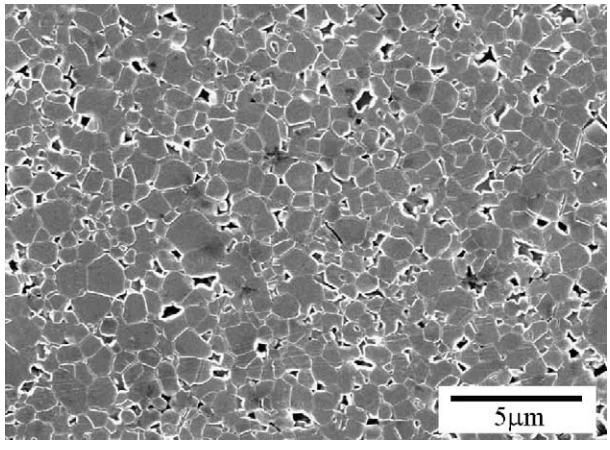

Fig. 1. Microstructure of specimen without CrB_2.

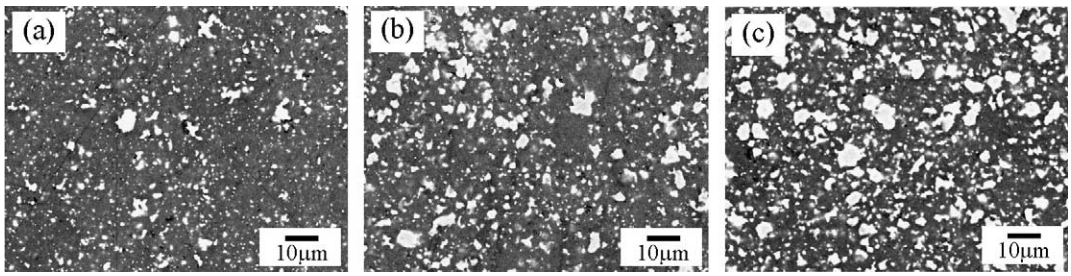

Fig. 2. Microstructures of B_4C-CrB_2 specimens: (a) B_4C-5 mol% CrB_2, (b) B_4C-20 mol% CrB_2 and (c) B_4C-25 mol% CrB_2.

surface of the B_4C-20 mol% CrB_2 specimen. Large pores were formed by dissolution of CrB_2 during etching. The grain size of the B_4C matrix is 1.0 μm (σ: 0.32) in diameter which is similar to that of the specimen without CrB_2.

Fig. 4 shows X-ray diffraction spectra of the specimens. For the specimen without CrB_2, only the B_4C phase was identified except for a small peak at 35.7° which corresponds to diffraction from 6H-SiC (102). This SiC contamination is thought to originate from the SiC pot and balls during mixing. XRD analysis of the B_4C-5 mol% CrB_2 and B_4C-20 mol% CrB_2 specimens revealed that they were composed of B_4C and CrB_2 phase with trace of SiC. No other phase was identified.

The flexural strength and fracture toughness of the specimens as a function of CrB_2 content are shown in Fig. 5. The fracture toughness of the specimen without CrB_2 was as low as 2.5 MPa $m^{1/2}$. The fracture toughness increased to 3.5 MPa $m^{1/2}$ with increasing the CrB_2 content up to 20 mol% (13 vol.%), and thereafter decreased slightly (Fig. 5b). Fig. 6 shows fractured surfaces of the specimen without CrB_2 and the B_4C-20 mol% CrB_2 specimen. The fracture surface of the specimen without CrB_2 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 of the specimen. On the contrary, the fracture surface of the B_4C-20 mol% CrB_2 specimen was relatively rough. It is clearly seen that CrB_2 particles are dispersed in the fine grained B_4C matrix. The B_4C matrix fractured transgranularly, whereas intergranular fracture occurred partially at the interfaces between the CrB_2 particles and the B_4C matrix. It appears that this change of fracture mode by the addition of CrB_2 gives rise to the improvement of the fracture toughness.

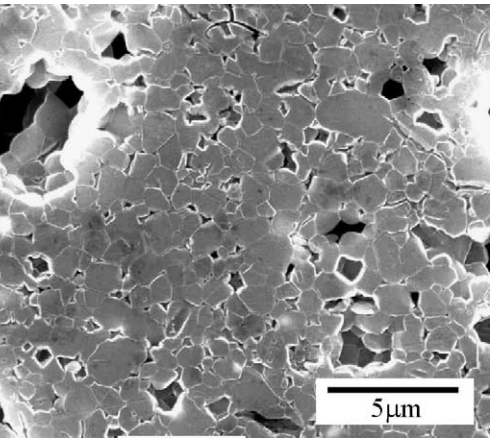

Fig. 3. Microstructure of B_4C-20 mol% CrB_2 specimen.

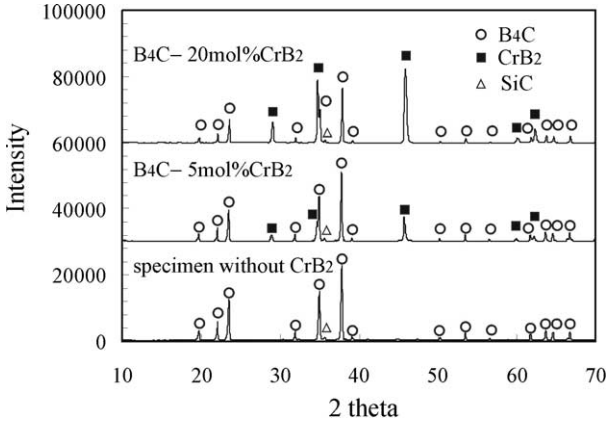

Fig. 4. X-ray diffraction spectra of specimen without CrB_2 and B_4C-CrB_2 specimens.

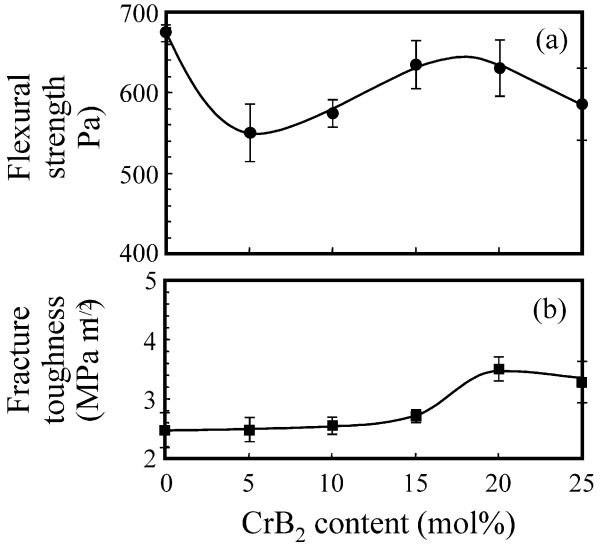

Fig. 5. Mechanical properties of specimens as a function of CrB_2 content: (a) flexural strength and (b) fracture toughness.

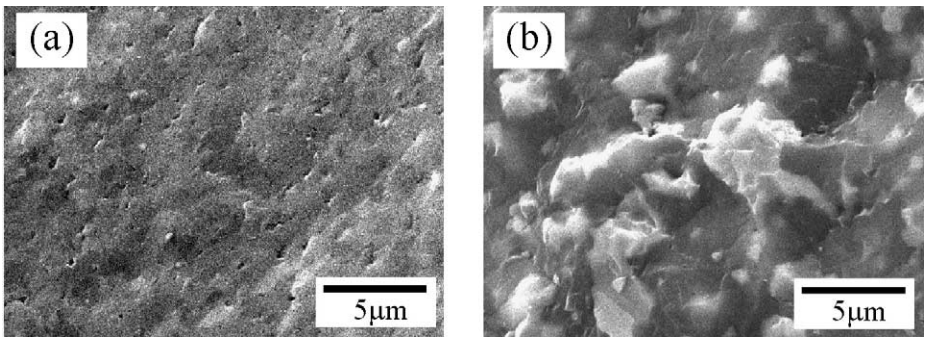

Fig. 6. Fractured surfaces of specimens: (a) specimen without CrB_2 and (b) B_4C-20 mol% CrB_2.

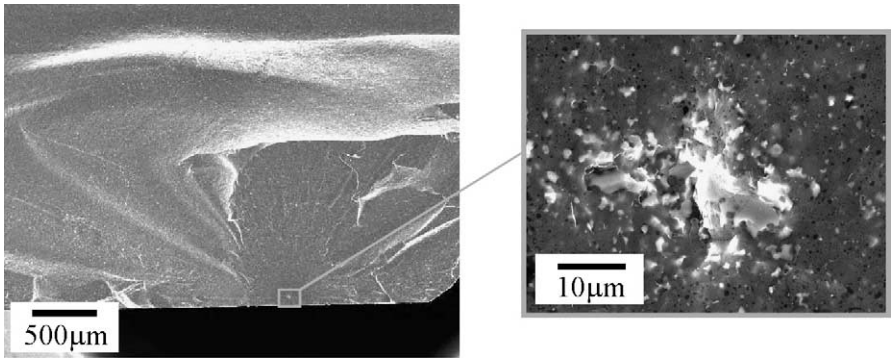

Fig. 7. Fractured surface after bending test for B_4C-5 mol% CrB_2 specimen.

The thermal expansion coefficient of CrB_2 is larger than that of B_4C,[1] such that residual stress is generated around the CrB_2 particles during cooling. It seems that this residual stress results in the formation of microcracks and, to some degree, deflection of propagating cracks, and leads to improved fracture toughness of the composite materials.[17–20,25]

As shown in Fig. 5a, the specimen without CrB_2 exhibited the highest strength of 675 MPa. This value is higher than the strength of monolithic B_4C ceramics reported in previous works.[8,9,11] It seems that the high flexural strength obtained in the present work is attributed to the very fine grained microstructure shown in Fig. 1. The variation of strength with CrB_2 content was complicated. The flexural strength decreased initially to 551 MPa with the addition of 5 mol% CrB_2, then increased with CrB_2 content in the range between 5 and 15 mol%. However, CrB_2 contents greater than 20 mol% led to reduction in strength. High strength of over 630 MPa was obtained for CrB_2 contents of 15 and 20 mol%. In particular, both high strength of 630 MPa and modest fracture toughness of 3.5 MPa $m^{1/2}$ could be achieved in the specimen with 20 mol% CrB_2. The fractured surface of the B_4C-5 mol% CrB_2 specimen after bending test is shown in Fig. 7. It can be seen that the fracture origin was an aggregation of CrB_2 particles. The decrease in the flexural strength by the addition of 5 mol% CrB_2 may be caused by the increase in flaw size due to the aggregated CrB_2 particles. The flexural strength increases with further addition of CrB_2 owing to the improvement of the fracture toughness. It was assumed that the reduction of flexural strength with the addition of 25 mol% CrB_2 was attributed to the shortening of the average of interparticle spacing which leads a large flaw size by the connecting of microcracks.[25]

In this study, the CrB_2 particle size was relatively larger than the B_4C grain size. It has been reported that the size of the dispersed particles remarkably influences the flexural strength and the fracture toughness for two phase composites.[25] Future studies will therefore concentrate on optimizing the CrB_2 particle size.

4. Conclusions

B_4C-CrB_2 ceramic composites were fabricated by hot-pressing powder mixtures of fine B_4C powder and $0-25$ mol% CrB_2 particulate. The hot-pressed specimens exhibited a composite microstructure where CrB_2 particles of a few micron were dispersed in a fine grained B_4C matrix. The fracture toughness increased as the CrB_2 content increased. Both high strength of 630 MPa and modest fracture toughness of 3.5 MPa $m^{1/2}$ could be achieved in the specimen with 20 mol% CrB_2 (13 vol.%). Residual stress is generated around the CrB_2 particles due to the thermal expansion mismatch. It

seems that this residual stress leads to the formation of microcracks and some deflection of propagating cracks, consequently improving the fracture toughness.

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