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Effect of additives introduced by ball milling on sintering behavior and mechanical properties of hot-pressed B_4C ceramics

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Abstract

The ball-milling process is a usual route employed to break up agglomerates in the powder or mix the powder with additives when preparing ceramics. Although it is well known that a powder can be ''contaminated'' by the wear particles from the milling balls, the study dealing with how the preparation and properties of a hard material would be affected by additives just introduced by scrape of milling balls has been scarce. In the present work, sintering behavior and mechanical properties of hot-pressed B_4C with additives derived from milling balls were investigated. Polyoxymethylene, ZrO_2, Al_2O_3 and Si_3N_4 were selected as different ball materials. The results show that the sinterability of B_4C could be significantly enhanced because of the incorporation of one of these additives, i.e. ZrO_2, Al_2O_3 and Si_3N_4 (approximately 3–6 vol%). As a result of improvement in density, excellent mechanical properties of B_4C ceramics were obtained. Among them a flexural strength of B_4C added by ZrO_2 reached 630 MPa.

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1. Introduction

Boron carbide (B_4C) is known as a brilliant material due to its performances such as low density, high melting point, good wear resistance, high hardness and elastic modulus, and good chemical stability as well as high neutron absorption cross-section [1]. Therefore the components made of B_4C can be used in nuclear industry as control bar and shield [1,2], also in wear resistant applications, like blast nozzles. On the other hand, sintering of pure boron carbide parts is very difficult because of its low self-diffusion coefficient, which results from the strong covalent bonding between atoms [3]. Moreover, the presence of B_2O_3 that is coated on the surface of B_4C particles deteriorates the sinterability [4]. Some additives, such as Al_2O_3, ZrO_2 and Si_3N_4, have been tested to improve the sinterability and to increase the densification [5–8].

Basically, in order to obtain homogeneously mixed powders, which consist of B_4C and additives, the ball-milling process is a usual route to be employed whether at lab or in industry. It is noticed however that the balls would be slightly worn away by B_4C powders during the ball-milling process. As a result, a weight loss of milling balls would occur and the scraped ball material would be mixed with B_4C as an extra additive. Although it is well known that a powder can be ''contaminated'' by the wear particles from the milling balls, the study dealing with how the preparation and properties of a hard material would be affected by additives just introduced by the scrape of milling balls has been scarce. Since this kind of phenomenon is mostly inevitable during preparation of starting powders for sintering of ceramic material, the study on effect of additives resulted from the milling process on sinterability and mechanical properties becomes important. In the present work, four kinds of balls (polyoxymethylene, zirconia, alumina and silicon nitride) with different hardness, were selected as ball materials to deal with B_4C powders in the ball-milling process, and the influences of additives scraped off from the balls during ball-milling process on phase assemblages, sintering behavior and mechanical properties of the resulted B_4C ceramics were investigated.

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2. Experimental procedure

Boron carbide powder (Jingangzuan Boron Carbide Company Ltd., Mudanjiang, China) with an average particle size of 1.5 μm was used as starting material. Four kinds of balls, polyoxymethylene (Shanghai Xingxing Steel Ball Factory, Shanghai, China), ZrO_2 (Dongguan CSG Ceramic Technology Co. Ltd., 3 mol% Y_2O_3 stabilized ZrO_2), Al_2O_3 (Nikkato Corporation, Osaka, Japan, SSA-995 Al_2O_3, 99.6%) and Si_3N_4 (Huasheng Fine Ceramics Co. Ltd., Jingtan, Jiangsu Province, China) were selected as milling media in ball-milling process and the corresponding samples were nominated as BCC, BCZ, BCA and BCS respectively. Because of light molecular weight of polyoxymethylene (density is around 1.4 g/cm^3), the weight ratio of balls to B_4C powders being 1:1 was taken during ball-milling process and ethanol was used as milling medium, while the weight ratio of 2:1 was fixed for the remaining three kinds of balls, as listed in Table 1. The ball-milling process lasted for 5 h, and was performed in a planet milling machine at a speed of 500 rpm, in which the container is made from nylon. The weight loss of the balls after milling was measured. Before and after the milling process, the balls were carefully washed several times by water and cleaned with ultrasonic for 20 min in order to collect all the wear particles into the powder to be sintered. The dried powders were obtained by sequential rotating vaporization and desiccation at 90 °C for 2 h followed by sieving with a nylon sieve (200 mesh).

Powder compacts with a dimension of 32 mm × 36 mm were hot-pressed (30 MPa) in a graphite furnace (ZT-60-22Y, Chenghua Electric Furnace Co. Ltd., Shanghai, China) at 2000 °C for 1 h under flowing Ar. In order to promote the volatilization of boron oxide, the compacts were first heated under vacuum from room temperature to 1500 °C at a heating speed of 15 °C/min and dwelled at 1500 °C for 30 min. Then the temperature was continuously increased up to 2000 °C at a speed of 5 °C/min under flowing Ar. The pressure of 30 MPa was given on the sample when the temperature reached 2000 °C. After sintering, the thickness of the samples was around 5 mm. For the sake of comparison, the boron carbide specimen derived from the starting powder without milling was also fabricated with the same process, in which the sample was nominated as BC.

Density of the sintered samples was measured by Archimedes principle. Phase assemblages were determined by X-ray diffraction (XRD) (D/max 2550V, Rigaku Co., Tokyo, Japan). Microstructures of fractured and polished surface of the samples were observed by a scanning electron microscopy (S-570 SEM, Hitachi, Tokyo, Japan) and an electron probe microanalyzer (JXA-8100F, Jeol, Tokyo, Japan) respectively.

The Vickers' hardness and fracture toughness were determined by using a Vickers diamond indenter and a load of 20 N for 10 s (Wilson-Wolpert Tukon2100B, Instron, Boston, America). The flexural strength was determined via three-point bending at a cross-head speed of 0.5 mm/min on bars with dimensions of 3 mm × 4 mm × 35 mm, in which the span was 30 mm and the tensile surface was polished to 1 μm polishing paste and chamfered edges according to ASTM Standard Method C-1161. The data of average strength and standard deviation for each material (BCZ, BCA and BCS) were obtained based on the determination of five samples.

3. Results and discussion

The weight loss of the balls after the milling process was determined and it can be considered as additives for B_4C. The weight ratios of the additives, which were caused by ball milling, to B_4C powders are calculated and listed in Table 1. The corresponding volume percentages of the ball materials to B_4C are 3.35: 96.65, 5.69: 94.31 and 3.03: 96.97 respectively for samples BCZ, BCA and BCS, as listed in Table 1. The results confirmed the considerable abrasion of the balls during the ball-milling process of B_4C powders.

The XRD patterns of BC, BCC, BCZ, BCA and BCS samples hot-pressed at 2000 °C for 1 h are shown in Fig. 1 and the corresponding phase assemblages are listed in Table 1. It can be seen that there is no existence of other phase in BC and BCC samples but only boron carbide (B_4C) is detected, which accords with the JCPDS card, No. 35-0798. For BCZ, BCA and BCS samples, B_4C phase is still a common major phase. Besides, second phase, ZrB_2 is found in BCZ, while Al_2O_3, $AlB_{12}C_2$ and AlB_2 are detected in BCA, and SiC and trace amount of BN exist in BCS, as shown in Fig. 1. It could be understood that the formation of ZrB_2 in BCZ results from the reaction between B_4C and ZrO_2 during sintering. The possible reaction to form ZrB_2 could be described [9] as

$$4B_4C + 5ZrO_2 \rightarrow 5ZrB_2 + 4CO\,(g) + 6BO\,(g) \quad (1)$$

The similar situation occurs in BCS sample, by reaction of B_4C and Si_3N_4 as follows, in which the carbon is resulted from

Table 1
Phase assemblages and bulk densities of B_4C samples with and without additives.

Sample	Materials of balls	Ratio of additive to B_4C		Phase assemblage[a] (wt%)	Measured density (g/cm^3)	Relative density (%)
		(wt%)	(vol%)			
BC	Without ball milling	0: 100		B_4C/s	2.29	91
BCC	Polyoxymethylene	2.37: 97.63	4.12: 95.88	B_4C/s	2.31	92
BCZ	Zirconia	7.12: 92.88	3.35: 96.65	B_4C/s, ZrB_2/w	2.53	97
BCA	Alumina	8.68: 91.32	5.69: 94.31	B_4C/s $AlB_{12}C_2$/vw Al_2O_3/vw AlB_2/vw	2.57	99
BCS	Silicon nitride	3.80: 96.20	3.03: 96.97	B_4C/s, SiC/w BN/tr	2.51	98

[a] s = strong, w = weak, vw = very weak, tr = trace.

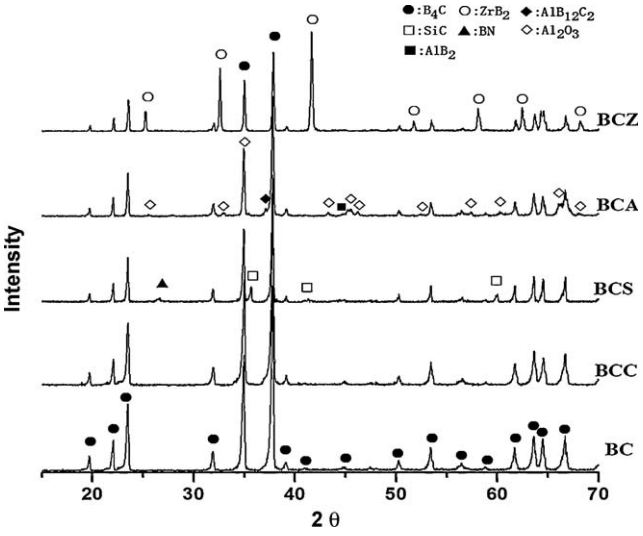

Fig. 1. XRD patterns of boron carbide samples hot-pressed at 2000 °C for 1 h.

the atmosphere in the graphite furnace:

$$B_4C + Si_3N_4 + 2C \rightarrow 3SiC + 4BN \quad (2)$$

The formation of a small amount of SiC together with BN is in accordance with the results reported in the literature [10]. As to the BCA sample, the XRD peaks for Al_2O_3, $AlB_{12}C_2$ and AlB_2 are affirmed, although the amount of these phases is very limited, in which Al_2O_3 is considered as the un-reacted additive. There are several binary and ternary phases in the B–C–Al system [11,12]. In B_4C–Al cermet systems [13], the reaction products detected by XRD include Al_3BC, AlB_2, Al_4C_3, $AlB_{12}C_2$ and $AlB_{24}C_4$. However, in the present case only $AlB_{12}C_2$ and AlB_2 phases are detected in BCA, except for B_4C and very small amount of un-reacted Al_2O_3. The possible reactions between boron carbide and alumina are as follows:

$$B_4C + Al_2O_3 + 2C \rightarrow 2AlB_2 + 3CO\,(g) \quad (3)$$

$$6B_4C + Al_2O_3 + C \rightarrow 2AlB_{12}C_2 + 3CO\,(g) \quad (4)$$

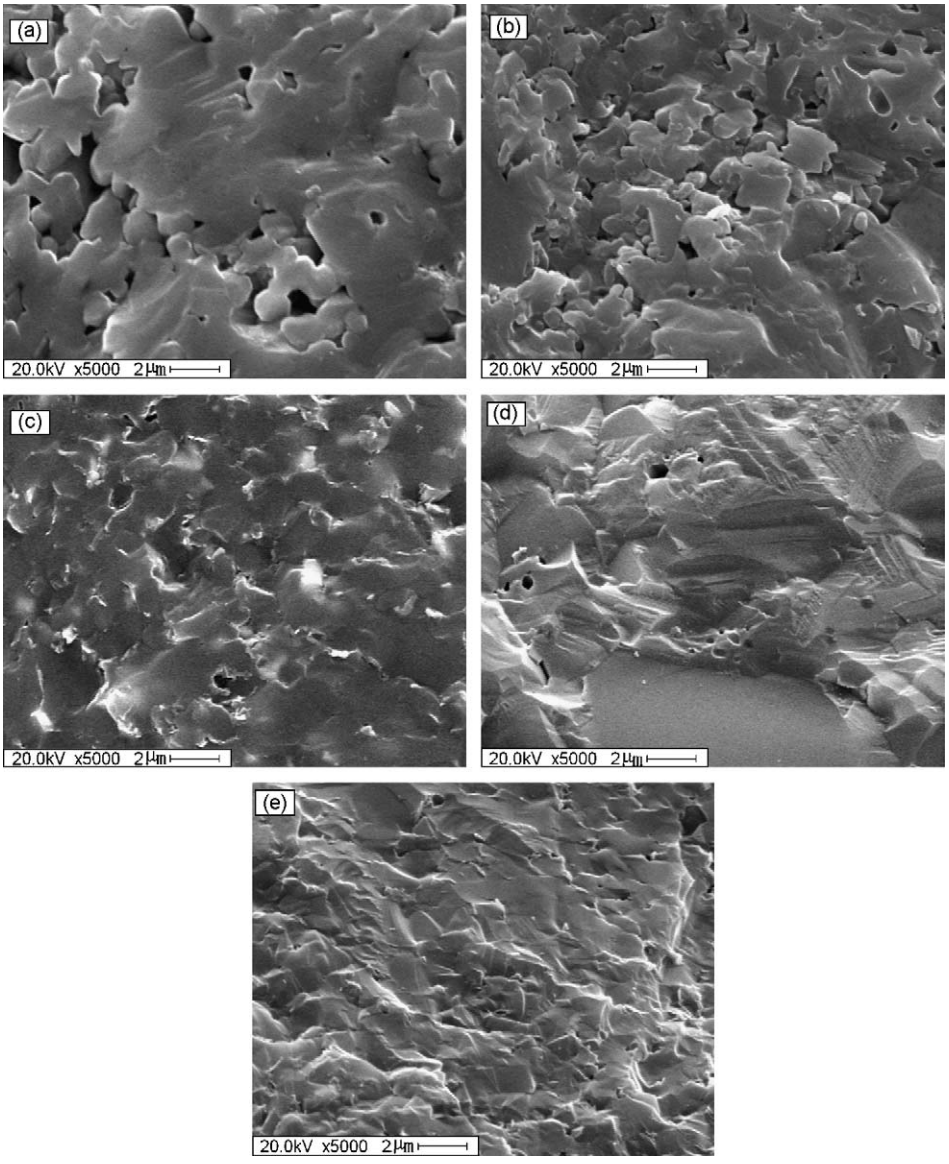

Fig. 2. SEM micrographs of fracture surfaces of (a) BC, (b) BCC, (c) BCZ, (d) BCA and (e) BCS from samples after strength tests.

It was noted that the intensity of the strongest X-ray diffraction peak of ZrB_2 was even higher than that of B_4C in BCZ by the addition of ZrO_2 with amount of 3.35 vol%, as shown in Fig. 1. Therefore, a calibration curve of weight percents of ZrB_2 to (ZrB_2 + B_4C) *vs* ratio of the strongest XRD peaks of ZrB_2 ($h\,k\,l$ = 1 0 1) to (ZrB_2 ($h\,k\,l$ = 1 0 1) + B_4C ($h\,k\,l$ = 0 2 1)) was established by the intensity determination of XRD patterns of several samples with known weight ratios between the two phases. It was found that the amount of ZrB_2 and B_4C was 7 wt% and 93 wt% respectively in BCZ sample based on the calibration curve.

The measured bulk densities of the samples are listed in Table 1. It is obviously seen that without the additives, like in the case of BC, the sample is not dense as the relative density of BC is around 91%. It was reported in the literature [14,15] that the addition of carbon into boron carbide increased the densification indeed. In the present case, some free carbon introduced by the decomposition of polyoxymethylene would be included during sintering of BCC. However, the amount of additive is small as the scraped polyoxymethylene is only 2.37 wt%, thus the relative density of BCC is not increased. The relative densities of BCZ, BCA and BCS are all higher than 96%, revealing that the densification is significantly improved by the addition of small amount of inorganic additives, like ZrO_2, Al_2O_3 and Si_3N_4. The densification behavior is also in accordance with the results reported in the literature [9,5], in which sinterability was greatly improved by the addition of a small amount of Al_2O_3 or ZrO_2 (approximately 2.5 vol%).

SEM micrographs of fracture surfaces of BC, BCC, BCZ, BCA and BCS from samples after strength tests are shown in Fig. 2(a)–(e) respectively, while the back-scattered electron images of polished surfaces of BCZ, BCA and BCS samples are illustrated in Fig. 3. The improvement of sinterability in the samples with additives ZrO_2, Al_2O_3 and Si_3N_4 can also be confirmed by SEM micrographs since no evident pores are observed in Fig. 2(c)–(e), whereas a lot of pores are found in BC and BCC (Fig. 2(a) and (b)). It can be understood that the matrix phase in grey shown in Fig. 3(a)–(c) corresponds to B_4C, while the white particles result from the second phases, whose average atomic numbers in these samples are more or less higher than B_4C. The main feature of the microstructure of BCZ, BCA and BCS consists of B_4C matrix and uniformly distributed second phase particles, as shown in Fig. 3.

As a result of improvement in densification, hardness and strength of BCZ, BCA and BCS ceramics are enhanced remarkably, as listed in Table 2. The hardness values of BCZ, BCA and BCS are within the values of 28–30 GPa, in which higher hardness of 30 GPa of BCS than that (28 GPa) of BCZ may be attributed to appearance of second phase SiC that was harder than ZrB_2, whereas hardness of BC and BCC (∼16 GPa) is obviously lower owing to the high porosity. On the other hand, the fracture toughness of less hard samples of BC and BCC (∼4.4 MPa $m^{1/2}$) is a little higher than that of BCZ, BCA and BCS (3.1–3.5 MPa $m^{1/2}$). Compared with the flexural strength of 336 MPa of BC and 341 MPa of BCC, the addition of ZrO_2, Al_2O_3 and Si_3N_4 remarkably increases the strength of the ceramics, in which the BCZ reaches the highest strength of 630 MPa, which is much higher than that of the pure B_4C, while it is 537 MPa and 570 MPa for BCA and BCS respectively. The enhancement in strength of BCZ, BCA and BCS is apparently

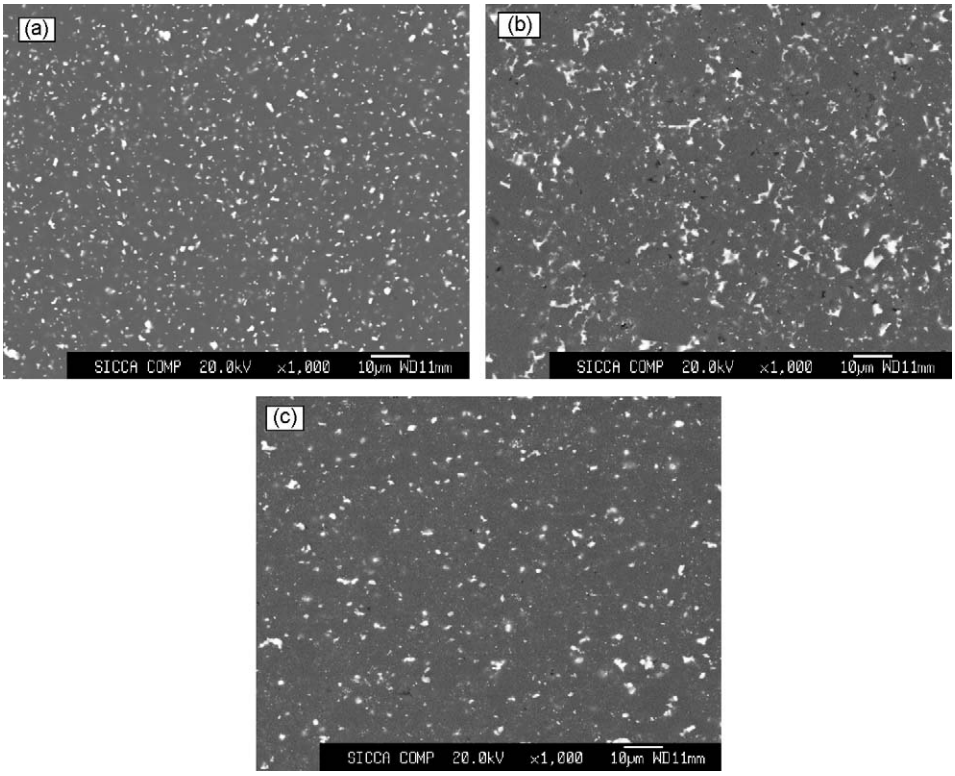

Fig. 3. Back-scattered electron images of polished surfaces of (a) BCZ, (b) BCA and (c) BCS samples hot-pressed at 2000 °C for 1 h.

Table 2
Mechanical properties of B_4C samples hot-pressed at 2000 °C for 1 h.

Samples	BC	BCC	BCZ	BCA	BCS
Hardness (GPa)	15.6 ± 1.1	16.0 ± 1.1	28.2 ± 0.3	29.3 ± 0.4	30.0 ± 0.3
Toughness (MPa $m^{1/2}$)	4.4 ± 0.2	4.4 ± 0.1	3.5 ± 0.1	3.5 ± 0.2	3.1 ± 0.1
Strength (MPa)	336 ± 20	341 ± 16	630 ± 33	537 ± 67	570 ± 23

due to the increased relative density and the second phase strengthening in comparison to BC and BCC. Similar to reaction sintering, the formation of the second phases in the present case results from the reactions between additives and the B_4C matrix. The advantage of the reaction sintering in the B_4C system is that it allows densification to occur at lower temperatures. Accordingly, the grain growth will be still small and the anisotropic stresses of the hexagonal B_4C grains are not sufficiently high to cause transgranular cracking and reduction in strength [16].

Based on the above results, it could be concluded that the effect of additives caused by ball-milling process on sinterability and mechanical properties of hard materials could not be ignored. On the other hand, the additives introduced by this way could also be an effective approach, if the ball materials and milling time are carefully controlled.

4. Conclusion

The additives were introduced into B_4C starting powders by using different ball materials, including polyoxymethylene, ZrO_2, Al_2O_3 and Si_3N_4, during balls milling process. With the same weight ratio of milling balls to B_4C powders the amount of additives ZrO_2, Al_2O_3 and Si_3N_4 resulted from grinding were different, i.e. 3.35, 5.69 and 3.03 vol% for BCZ, BCA and BCZ respectively. The second phases were formed by a reaction sintering, i.e. ZrB_2 for BCZ sample, Al_2O_3, $AlB_{12}C_2$ and AlB_2 for BCA sample, SiC and BN for BCS sample. The sinterability was significantly enhanced by the incorporation of ZrO_2, Al_2O_3 and Si_3N_4. As a consequence, hardness and strength of the samples were remarkably improved. Compared with the flexural strength of 336 MPa for BC and 340 MPa for BCC, it was 630 MPa for BCZ, 537 MPa and 570 MPa for BCA and BCS respectively. Accordingly, the effect of additives caused by ball-milling process on sinterability and mechanical properties could not be ignored especially for hard materials, such as B_4C.

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