Effect of graphene nano-platelet reinforcement on the mechanical properties of pressureless-sintered boron carbide

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Abstract. Boron carbide (B₄C) doped with graphene nano-platelet (GNP) as reinforcement has been prepared by pressureless sintering. Effect of GNP addition on mechanical properties of the composite, such as fracture toughness, hardness, flexural strength was investigated. Phase evolution and microstructure was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results demonstrated that addition of GNP improved the fracture toughness (KIC) of B₄C with the decrease of hardness, flexural strength. The fracture toughness (KIC) can reach 4.45 MPam¹⁄² with 1wt% addition of GNP, which was 49.3% higher than that of the composite without graphene platelets. It was found that the toughening mechanism can be contributed to pulling-out of graphene platelets, crack deflection, bridging and branching.

1. Introduction

Boron carbide (B₄C) ceramics has been considered as one of the best candidate material for light-weight ballistic armour due to the outstanding performance, such as extremely high hardness (Vickers hardness: 3770 kg mm⁻²), low density (2.52 g cm⁻³), high elastic modulus(450 GPa) [1-3]. B₄C has been used as front panel in armor for eroding and rupturing the projectile [4]. In addition, B₄C ceramics has been widely used as high temperature thermocouples, neutron absorber, reactor control rods in nuclear power engineering, polishing media for hard materials, abrasive media for lapping and grinding, and wear resistant components (blasting nozzles, die tips and grinding wheels) because of the high melting point(2427°C), high thermoelctromotive force, high chemical resistance, high neutron absorption cross section, high impact and excellent wear resistance [1-5].

However, the relatively low fracture toughness caused by the intrinsic brittleness of covalent bonding ceramics significantly reduced the stability and reliability of B₄C ceramics products. When B₄C was used as armour materials, the low fracture toughness degraded the multi-hit performance and field durability. So, it has attracted considerable research interest to enhance the toughness of B₄C ceramics by addition of reinforcements to form the matrix. Generally, carbides, oxides, borides (eg: like CrB₂, SiC, Al₂O₃, ZrO₂, TiB₂ etc) and several other additives have been used as the reinforcements [1,6]. For example, ZrO₂ and CrB₂ were effective sintering aids and enabled the material to achieve high density even in pressureless sintering, which have become some of the commonly used reinforcement used by researchers to enhance the mechanical properties [7,8]. But B₄C ceramics only can be toughed to a certain degree through adding these reinforcements, and the hardness of B₄C ceramics will be reduced significantly. Recently, carbon nanomaterials, like carbon nanotube (CNT)
and graphene nano-platelet (GNP), have been extensively studied as reinforcements in ceramics for obtaining superior fracture toughness without the significant decrease of hardness [9]. Among which, GNP was considered superior because of its better dispersibility in the ceramic matrix and higher resistance to structural damage at elevated temperatures [10]. It has been reported that GNP can effectively enhance the toughness of ceramics like Si₃N₄, ZrO₂, Al₂O₃, and ZrB₂ [11-14]. The effects of GNP addition on the mechanical, thermal and electrical properties of B₄C ceramics were also discussed in the hot pressing, pressureless sintering and spark plasma sintering [15-17].

Pressureless sintering is a cheaper and simpler process which is benefit for the large-scale production and the preparation of complex components [1, 18]. Due to the very strong covalent bonds, densification of B₄C ceramics is extremely difficult. Especially, it was indicated that the addition of GNP will reduce the density (< 97%) of B₄C ceramics according to many reports. Therefore, it is valuable for practical application to enhance the fracture toughness of B₄C ceramics with the high density and strength maintaining. In this work, we investigated the effect of GNP contents on the mechanical properties of B₄C ceramics by the pressureless sintering process. Through the mechanical tests and microstructural characterization of the composites, the optimum content of GNP was determined, and the toughened mechanism was analyzed.

2. Experimental Section

2.1. Materials

The starting materials in the present study including commercial pure powders of B₄C (Mudanjiang Jingangzuan Boron Carbide Co. Ltd., D50 approx. 2.1 μm, purity greater than 93.0%) and GNP (Angellead Nanotechnology Co. Ltd., average layer thickness less than 3.0 nm, special surface area approx. 600 m² g⁻¹) were used without any purity. The ZrB₂ (ShangHai Shuitian Materials Technology Co. Ltd., D50 approx. 2.1 μm) was employed as the sintering aids which can increase the density of B₄C ceramics. Phenolic resin was used as the organic adhesive in the spray drying process and later was coked to amorphous carbon while heating the body to the sintering temperature.

2.2. Synthesis

Different amounts of GNP, from 0.5% to 2.0 wt% were added in the B₄C materials. In a typical procedure, raw materials containing 94 wt% of B₄C powder, 20 wt% phenolic resin (equal to 4 wt% C), 1.0 wt% ZrB₂ and 1 wt% GNP were mixed and milled in a ball-mill using SiC as grind bodies in the deionized water container for 12 h. The mixtures were dried by spray drying process at 110°C and then sieved through a 60 mesh sieve to form granules. The powder mixtures were uniaxially cold pressed under 120 MPa into 50 mm×50 mm×8 mm samples in stainless steel mold. Samples were then heated for 1 h at 800°C in order to burn out phenolic resin. Green samples were then sintered under Ar atmosphere at 2150°C using a heating rate of 5°C/min and dwell time equal to 0.5 h.

2.3. Characterization and measurement

The sintered bodies were surface ground and polished with diamond paste. The density of the sintered samples was measured by water immersion technique on the basis of Archimedes principle. The phase composition of the sintered sample was checked by XRD on a Bruker D8 advanced X-ray diffractometer equipped. The microstructure of samples was observed using the scanning electron microscopy Hitachi S4800 on fractured surface. The sizes of strip-sample used to obtain the fracture toughness and bending strength were 2mm×4mm×40mm with an incision of 2mm depth and 3mm×4mm×40mm, respectively. Four items of each sample were measured to get a relativity precise value. Hardness was measured by a Vickers hardness instrument (HBVS-30C, Laizhou Huayin Test Instrument Co. Ltd.) with a load of 4.90 N and loading time of 15 s. Four samples of the every composition were also tested.
3. Results and discussion

3.1. Phase analysis

![Figure 1](image.png)

**Figure 1.** XRD pattern of sintered B₄C ceramics with different amounts of GNP.

The XRD pattern of pressureless sintered B₄C ceramics without GNP addition and with different amounts of GNP is given in the figure 1. All samples are showing the presence of B₄C peaks. The peak of ZrB₂ added in B₄C ceramics as the sintering aids also can be seen. The characteristic peaks of GNP in all the samples are observed with the addition amounts of GNP from 0.5% to 2.0 wt%. By contrast, the B₄C ceramics without GNP addition are not showing the peak of graphite. The XRD analysis indicates the presence of GNP in the B₄C ceramics after sintering. XRD shows that the sintering of B₄C ceramics was achieved without oxide formation because of vacuum and carbon inform phenolic resin and GNP which could reduce the oxide in the B₄C powder.

![Figure 2](image.png)

**Figure 2.** (a) The SEM micrograph of polished surface of B₄C/0.5wt% GNP and (b) the EDS of the sample from part 1.
The SEM micrograph of polished surface of B<sub>4</sub>C/0.5wt% GNP and the EDS spectrum of the point 1 of the sample are shown in figure 2a and b to further determine the phase evolution after sintering with respect to the raw materials. It can be seen that elements of B, C and Zr are checked in the sample, which meaning no impurity substance in the sintered B<sub>4</sub>C and GNP ceramics.

3.2. Density and Microstructure

![Figure 3](image.png)

Figure 3. Variation of relative density of B<sub>4</sub>C ceramics with GNP contents.

The relative density of B<sub>4</sub>C ceramics with addition of GNP is measured to investigate the effect of addition of GNP on the sintered density of B<sub>4</sub>C ceramics. The relative density values of B<sub>4</sub>C ceramics samples with different wt% of GNP are given in figure 3. The relative density of B<sub>4</sub>C ceramics without GNP addition was measured as 95.6% of the theoretical density. Under similar pressureless sintering conditions, the relative density of sintered samples increased with the increase of GNP contents. When 1 wt% GNP was added to B<sub>4</sub>C the relative density improved to 97.5%. On further increase of GNP to 1.5 and 2.0 wt%, lower relative density of 96.9% and 95.3% of the theoretical density was measured. Initially, the addition of GNP in B<sub>4</sub>C ceramics enhanced the relative density because the GNP acted as sintering aid [19]. Carbon reduced the oxide layer (B<sub>2</sub>O<sub>3</sub>) existing on the surface of B<sub>4</sub>C particles, which induced the sintering of B<sub>4</sub>C ceramics. According to the previous report, GNP also accelerated the initial stages of sintering through enhancing the particle rearrangement due to its lubricating effect [14].

The reason why relative density of B<sub>4</sub>C was lowered by higher amounts of GNP might come from two points. On the one hand, the diffusion between B<sub>4</sub>C particles was prevented by the interconnected network forming by high proportion of GNP. On the other hand, the coefficient of thermal expansion of GNP (30×10<sup>-6</sup> C<sup>-1</sup>) in the lateral direction is much higher than that of B<sub>4</sub>C (5×10<sup>-6</sup> C<sup>-1</sup>) making the GNP contract more during cooling period of sintering in the lateral direction than B<sub>4</sub>C (matrix). In lateral direction GNP is only held by weak Van Der Waal's force resulting in the GNP to separate out from B<sub>4</sub>C matrix, which produces pores at the interface [15].

The microscopic images of the B<sub>4</sub>C ceramics with different amounts of GNP from 0.5 wt% to 2.0 wt% are shown in figure 4, in which the GNP are clearly marked. Transgranular mode of fracture in the four samples with different GNP contents can be observed from the fractured surfaces. The B<sub>4</sub>C ceramics exhibited more porosity when the GNP content was lower with 0.5 wt% addition. The porosity decreased with the content of GNP increasing to 1.0 wt%. Then, the porosity increased with
the content of GNP further increasing. Furthermore, few isolated GNP could be observed in the interstice of interstitial grain site when the GNP content was from 0.5% to 1.5 wt%. The surface morphology of 1.0 wt% addition of GNP appears that the B₄C matrix and GNP are more closely linked at the level of 1.0 wt%, implying the sintering aid function of GNP. From figure 4d, it can be seen that agglomeration of GNP occurred in the B₄C ceramics when 2.0 wt% GNP was added. The difference of porosity and distribution of GNP in the B₄C ceramics between the samples consists with the result of relative density given in figure 3. The detailed microstructural views of samples with different GNP contents are shown in figure 5, in which isolated GNP could not be observed. The phenomenon of agglomeration of GNP got worse when the contents of GNP were 1.5 wt% and 2.0 wt%, which affected greatly the diffusion of B₄C particles and the final relative density. It is revealed that close combination exists between B₄C matrix and GNP resulting in the superior properties of composite ceramics.

**Figure 4.** SEM images of fracture surface of B₄C samples with different amounts of GNP: (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt%, (d) 2.0 wt%.

**Figure 5.** Detailed microstructural images of B₄C samples with different amounts of GNP: (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt%, (d) 2.0 wt%.
3.3. Mechanical properties
The mechanical properties including flexural strength, hardness and fracture toughness of B₄C samples with different amounts of GNP were tested to investigate the effect of GNP addition on the mechanical properties.

3.3.1. Flexural strength

![Graph showing variation of flexural strength with GNP content.](image)

**Figure 6.** Variation of flexural strength in the B₄C ceramics with GNP content.

Figure 6 shows the variation of flexural strength with GNP content. Flexural strength of B₄C ceramics without GNP addition was measured as 340±11.2MPa. With the addition of GNP 0.5 wt%, 1 wt%, 1.5 wt% and 2.0 wt% flexural strength values are 365±15.6 MPa, 382±14.9 MPa, 357±11.8 MPa, 336±16.3 MPa, respectively. The variation of flexural strength with GNP addition reflected the relative density and porosity. The B₄C ceramics with GNP of 1 wt% addition displayed the highest flexural strength because GNP as the sintering aids improved the density of B₄C and there was no agglomeration to prevent the diffusion between B₄C particles.

3.3.2. Hardness

![Graph showing influence of GNP addition on hardness.](image)

**Figure 7.** Influence of the GNP addition on hardness.
Figure 7 presents the variation trend of hardness values of B₄C ceramics with varying the amount of GNP. Hardness value of B₄C without GNP addition was 25.8±0.52 GPa. Moreover, the hardness increased immediately as the content of GNP rose to 0.5 wt%. The peak of the highest hardness reached 27.1±0.6 GPa with 1 wt% content of GNP. And then the hardness of B₄C showed a downward trend to its bottom at 24.2±0.52 GPa when the content of GNP was 2.0 wt%. The hardness of B₄C ceramics with 2.0 wt% content of GNP was much lower than that of the B₄C without GNP addition, implying that excessive addition of GNP will greatly reduce the hardness of B₄C due to the agglomeration of GNP.

3.3.3. Fracture toughness

Figure 8. Variation of fracture toughness in B₄C with GNP contents.

The relationship between fracture toughness of B₄C samples and different GNP contents is demonstrated in figure 8. As similar to the variation trend of flexural strength and hardness, the fracture toughness of B₄C ceramics increased with the addition of GNP and then decreased. Value of 2.98 MPa·m⁰.⁵ was measured when the B₄C was added without GNP. Highest fracture toughness of 4.45 MPa·m⁰.⁵ for 2.0 wt% content was obtained, which is 49.3% higher than that of the B₄C without GNP addition. It should be noted that the fracture toughness with 2.0 wt% GNP addition was higher than the value of B₄C without GNP, which differed from the hardness variation under the GNP addition. The result revealed that addition of GNP in B₄C ceramic under pressureless sintering method is more efficient for improving fracture toughness compared with hardness and bending strength even in the high GNP contents level.

Figure 9. Crack propagation in B₄C composites with 1 wt% GNP content.
The crack propagation patterns were obtained for B₄C composites with 1 wt% GNP addition in order to understand the fracture toughness mechanism and presented in figure 9. The crack propagation in B₄C-GNP composite shows crack deflection, branching and bridging mechanisms. These mechanisms are responsible for the increase in the fracture toughness of composite. These crack propagation patterns are supporting the obtained values of fracture toughness. Besides, the enhanced toughness probably results from the pullout of GNP shown in figure 5, which has been reported by other literatures [19-21]. It is considered that two mechanisms are responsible for the pullout of GNP, which is not completely same to that of the pure single graphene or other fibres. In one mechanism, the whole GNP is pulled out when the fracture happens, displaying a similar pullout mechanism of the carbon fibre [22]. In another mechanism, the fracture process consists of two steps. Firstly, fracture occurs at the outermost graphene layers and then the pullout of GNP takes place between intimal slices of GNP, leaving a hole in the matrix. In the latter mechanism, the resistance from graphene layers and bonding force between graphene and the B₄C grains should be overcome, which can absorb more rupture energy to prevent the continuing expanding of cracks.

From the result of relative density and mechanical properties of samples prepared in this work, it was found that the mechanical properties of B₄C ceramics doped with GNP highly depended on the relative density. The monolithic B₄C ceramics had low relative density resulting in the poor mechanical properties. When 0.5 wt% content of GNP was added, the density of composites increased resulting in the improvement of mechanical properties compared with monolithic B₄C ceramics. But the aids-functional GNP was not sufficient for B₄C sintering; the relative density and mechanical properties were improved limitedly. Excessive addition of GNP (2.0 wt%) resulted in formation of the interconnected network, agglomerates and interfacial porosity, which could not contribute to the enhancement of density and mechanical properties. The investigation on the role of GNP has revealed that optimum content of GNP was 1 wt%. Under this condition, the densification of B₄C ceramics can reach 97.5%. The fracture toughness of B₄C can be greatly improved which was accompanied with the high flexural strength and hardness. The outstanding mechanical properties make the GNP reinforced B₄C ceramics be useful for armour application.

4. Conclusions
In summary, high densification of B₄C ceramics were prepared by the pressureless sintering method with different GNP amounts. Effect of GNP contents on the properties of sintered samples including relative density, flexural strength, hardness and fracture toughness has been investigated. All the properties displayed the similar tendency with addition of 1 wt% GNP, which had the highest relative density of 97.5%, flexural strength of 382 MPa, hardness of 27.1 GPa and fracture toughness of 4.45 MPa·m⁰. Fifty, respectively. The microstructural analysis of samples revealed that appropriate content of GNP both acted as sintering aids to induce the sintering of B₄C and improve the mechanical properties. Excessive addition of GNP will reduce the relative density and mechanical properties due to the agglomeration of GNP and the increased porosity.

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References
[1] Zhang W, Yamashita S and Kita 2019 Adv. in App. Ceram 118 222-39
[2] Thevenot F 1990 J. Eur. Ceram. Soc 6 205–25
[3] Rosa M, Francisco C L 2010 Ceram. Eng. Sci. Pro 30 113-9
[4] Shokrieh M M and 2008 Compos. Struct 82 269–76
[5] Reinmuth K, Lipp A and Knoch H 1984 J. Nucl. Mater 124 175-84
[6] Suri A K, Subramanian,C, SonberJ K and Murthy T 2010 Inter. Mater. Rev 55 4-40
[7] Subramanian C, Roy TK, Murthy T, Sengupta P, Kale GB,Krishnaiah MV and Suri AK 2008
Ceram. Int. 34 1543–9

[8] Yamada S, Hirao K, Yamauchi Y and Kanzaki S 2002 J. Mater. Sci 37 5007–12
[9] Tan Y, Zhang H and Peng S 2016 Scr. Mater 114 98–102
[10] Walker LS, Marotto VR, Rafiee MA, Koratkar N and Corral EL 2011 ACS Nano 53 182–90
[11] Dusza J, Morgiel J, Duszová A, Kvetková L, Nosko M, Kun P and Balážsi C, 2012 J.Eur. Ceram. Soc 32 3389–97
[12] Ramirez C and Osendi MI 2014 Ceram. Int 40 187–92
[13] Liu J, Yan H, Reece MJ and Jiang K 2012 J. Eur. Ceram. Soc 32 4185–93
[14] Yadhumalakrishnan GB, Karumuri S, Rahman A, Singh RP, Kalkan AK, Harimkar SP, Kalkan AK and Harimkar SP 2013 Ceram.Int. 39 6637–46
[15] Alexander R, Murthy T S R, Ravikanth K V, Prakash J, Mahata T, Bakshi S R, Krishnan M and Dasgupta K 2018 Ceram. Inter. 44 9830-8
[16] Gao D, Jing J, Yu J, Guo X, Zhang Y, Gong H and Zhang Y 2018 R. Soc. Open Sci 51 718-37
[17] Chen M, Yin Z, Yuan J, Xu W, Ye J and Yan S 2018 Ceram.Int.4415 370-7
[18] Roy TK, Subramanian C and Suri AK 2006 Ceram. Int. 32 227-33
[19] Kovalcikova A, Sedlak R, Rutkowski P and Dusza J, 2016 Ceram. Int. 42 2094–8
[20] Li Q, Zhang Y, Gong H, Sun H, Li W, Ma L and Zhang Y 2016 J. Mater. Sci. Technol.32 633–8
[21] Liu L, Wang Y, Li X, Xu L, Cao X, Wang Y, Wang Z, Meng C, Zhu W and Ouyang X 2016 J. A. Ceram. Soc 99 257-64
[22] Han B, Zhang L, Zhang C, Wang Y, Yu X and Ou J 2016 Constr. Build.Mater 125 479–89