

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF B₄C-GNP COMPOSITES PREPARED BY SPARK PLASMA SINTERING

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This study investigates the effect of graphene nanoplatelet (GNP) reinforcement on the densification, microstructure, and mechanical properties of boron carbide (B₄C) ceramics. B₄C-xGNP (x = 0.5, 1, 2, and 3 vol.%) composites were fabricated by spark plasma sintering (SPS) at 1600 °C under 40 MPa for 5 min. The highest relative density (94.40%), hardness (38.4 GPa), and fracture toughness (6.83 MPa·m^{1/2}) were obtained for the BG2 sample, which exhibited a homogeneous GNP distribution. Overall, GNP reinforcement effectively improved the mechanical performance of B₄C ceramics, making the developed composites promising candidates for advanced lightweight engineering applications.

Keywords: Boron carbide (B₄C); Graphene nanoplatelets (GNPs); Spark plasma sintering (SPS); Microstructure; Mechanical properties; Fracture toughness

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1. Introduction

Boron carbide (B₄C) has low density (2.52 g/cm³), high chemical stability, high hardness (>30 GPa), high elastic modulus (448 GPa), high neutron absorption, and high-temperature resistance. It is a non-oxidizing ceramic material widely used in defense industry applications, including armor technologies, fuel tank technologies for air combat vehicles, and cabin interior components [1-3]. Nevertheless, its low fracture toughness and low sinterability limit the engineering applications in which B₄C can be used. The strong covalent bonding in B₄C hinders densification to the theoretical density during sintering. Although methods such as

hot pressing (HP) and hot isostatic pressing (HIP) achieve high densities, they degrade mechanical properties by promoting grain growth [4-5]. Compared to traditional methods, spark plasma sintering (SPS) enables densification at lower temperatures and shorter holding times [6-8]. Numerous studies have investigated the incorporation of reinforcements into B₄C to mitigate these limitations [9,10]. As reported in the literature, the addition of appropriate additives increases fracture toughness and densification, thereby improving mechanical properties [9,11,12].

Table 1. Comparison of previous studies on carbon-reinforced B₄C composites and the present study.

Study	Material System	Production Method	Main Focus	Limitation
Alexander <i>et al.</i> [12]	B ₄ C-GNP	HP	High densification achieved Reduction in toughness and hardness observed	SPS processing and systematic GNP content evaluation are not considered
Yavas <i>et al.</i> [13]	B ₄ C-CNT	SPS	Improved fracture toughness and sinterability	GNP reinforcement is not considered
Balci <i>et al.</i> [14]	B ₄ C-CNT-GNP	SPS	Hybrid reinforcement improved selected properties	The effect of GNP alone is not isolated
Tan <i>et al.</i> [15]	B ₄ C-GNP	HP	Improved hardness, toughness, and electrical conductivity	Conventional sintering route; limited GNP
Mokhtari <i>et al.</i> [16]	B ₄ C-ZrB ₂ -GNP	SPS	Combined effects of ZrB ₂ and GNP investigated	The influence of GNP content has not been systematically studied
Present study	B ₄ C-GNP	SPS	Densification, hardness, and fracture toughness evaluated at different GNP contents	-

This study aims to enhance the sinterability and fracture toughness of B₄C composites by reinforcing with GNPs. As summarized in Table 1, previous studies on B₄C-based composites have primarily focused on traditional sintering methods, such as hot pressing, or on hybrid reinforcement systems containing multiple additives. The literature includes studies on GNP reinforcement in various ceramic matrices [17, 18]. Although reports on GNP-reinforced B₄C composites exist in the literature, the effects of varying GNP content on the densification behavior, microstructure, and mechanical properties of SPS-processed B₄C composites have not been systematically evaluated. Therefore, the present study investigates B₄C–GNP composites with varying GNP contents fabricated by SPS, leveraging the rapid densification capability of this technique. The study aims to provide a comprehensive understanding of the relationship between GNP content, microstructural evolution, densification behavior, hardness and fracture toughness, thereby contributing to the development of high-performance B₄C-based composites.

2. Materials and Methods

B₄C (H.C Starck, Grade HS, AB 134566, >98% purity) and graphene nanoplatelets (GNPs; Nanografi, NG01GNP0108, thickness: ~3 nm, specific surface area: 530 m²/g, lateral size: ~1.5 μ m, 99% purity) were used as raw materials. To minimize agglomeration of GNP and B₄C powders, they were dispersed in ethanol and homogenized for 3 minutes using a Hielscher UP 200 HT ultrasonic handheld homogenizer. The separately prepared B₄C powders and GNP suspensions were combined and ultrasonically mixed for 5 minutes. Then, ethanol was removed by magnetic stirring, and the powder mixture was dried in an oven at 90 °C. The dried powders were subsequently ground in a mortar to break up possible agglomerates.

Prior to SPS, the inner surface of the graphite die and punch interfaces were lined with graphite paper to facilitate sample removal and minimize friction during sintering. The powder mixtures were loaded into the die and pre-compacted at 10 MPa using a hand press to reduce internal voids. To minimize heat loss during sintering, the die assembly was wrapped with a graphite blanket before being placed in the SPS chamber. The powder mixtures were consolidated using a spark plasma sintering (SPS) system with a maximum current capacity of 20,000 A (Model 7.40 MK VII, SPS Syntex Inc.), producing disk-shaped specimens with a diameter of 50 mm and a thickness of 4 mm. Sintering was performed under a uniaxial pressure of 40 MPa at a heating rate of 100 °C/min, reaching a sintering temperature of 1600 °C with a dwell time of 5 minutes under dynamic vacuum conditions maintained by the SPS system throughout the process. During the SPS process, while the mold temperature was monitored using an optical pyrometer (Chino, IR-AH), the current, voltage, draw rate and draw amount were checked every minute, and the sample's shrinkage behavior was evaluated. After sintering, the samples were cooled naturally to room temperature inside the SPS chamber while maintaining the vacuum atmosphere.

The B₄C-GNP composites produced were designated by their GNP content, and the corresponding sample codes and powder contents are listed in Table 2.

Table 2. Nominal composition of the samples (vol.%).

Sample Codes	Compound (Volume %)	
	B ₄ C	GNP
Monolithic	100	0
BG05	99.5	0.5
BG1	99	1
BG2	98	2
BG3	97	3

In this notation, B₄C is represented by the letter B, while GNP is represented by the letter G. The additive content in composites is indicated by numerical values.

The bulk densities of the samples were measured using Archimedes' principle and the corresponding relative densities were calculated. Phase identification was performed using X-ray diffraction (XRD) with Cu K α radiation using Rigaku Geigerflex and Rigaku Miniflex diffractometers. The diffractometers were operated at a scanning speed of 2°/min in the 5°–85° 2 θ range. Raman analyses were performed using a Renishaw inVia Raman Microscope to investigate the structural evolution of GNP-reinforced B₄C composites. Microstructural characterization was performed using a field-emission scanning electron microscope (FESEM; JSM-7000F, JEOL Ltd.).

The Vickers hardness (HV) and fracture toughness (K_{1C}) values were determined using a Vickers microhardness tester (Leica VH-MOT) under a load of 9.8 N. Ten measurements were performed for each sample, and the averages were calculated in accordance with ASTM C1327-08. Fracture toughness was calculated using the Palmqvist approach based on cracks formed during the indentation test [19].

3. Results and Discussion

3.1 Densification behavior

The sintering behavior of the produced GNP-reinforced B₄C composite samples was first examined, and the end of shrinkage was observed at a temperature of ~1600 °C for all samples. When the values in Figure 1 are examined, a correlation between shrinkage and sample density is observed. Increasing the GNP content up to 2 vol.% enhanced shrinkage, whereas higher GNP contents reduced it.

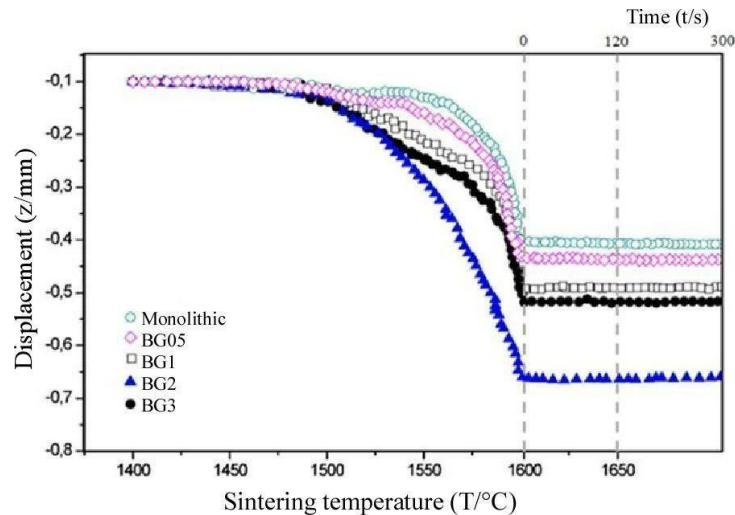


Figure 1. Shrinkage curves of monolithic, BG05, BG1, BG2, and BG3 samples.

Since the shrinkage differences are minimal and the sintering temperatures are nearly identical, GNP reinforcement does not significantly affect the sintering kinetics of B₄C. The maximum relative density for sample BG2 is 94.40%, which is below full densification, indicating approximately 5.6–7.0% residual porosity. Such residual pores can act as local stress intensifiers and potential sites of crack initiation under mechanical loading.

Therefore, it is thought that the existing porosity has an effect on the hardness and fracture toughness values of the composites [20]. In successive studies conducted by Yavas *et al.* [13] and Balci *et al.* [14], the effect of GNP addition at varying ratios on the sintering behavior of B₄C–CNT composites was investigated. It was found that the sintering temperature decreased with increasing CNT content but was not affected by the addition of GNP. These findings are consistent with the results obtained in this study.

Density measurements were performed using Archimedes' principle, yielding a relative density of 93.02% for the monolithic sample. This value increased to 94.40% in the BG2 sample. However, the relative density slightly decreased to 94.12% for the BG3 sample. The results indicate a relationship between shrinkage and relative density. This behavior can be attributed to the lubricating effect of carbon, which promotes particle rearrangement at low GNP content, whereas at higher GNP content, graphene agglomeration hinders the diffusion of B₄C particles. In the study conducted by Wang *et al.* [9], the relative density values increased with the addition of GNP reinforcement up to 2 vol.%, but decreased after 5 vol.%, consistent with the literature.

As seen in the current experimental data and in the study of Tan *et al.* [21], GNP reinforcement up to 2 vol.% has been shown to increase the relative density of the B₄C structure. If the reinforcement amount exceeds this value, a small decrease in relative density occurs. The study conducted by Balci *et al.* [14] also indicates that GNP reinforcement does not significantly affect the relative density of the B₄C–CNT structure. Given that the density differences are very small and consistent with the literature, GNP reinforcement does not cause a significant change in density.

3.2 Phase analysis

Phase analyses of the sintered samples were performed, and the results are shown in Figure 2.

There is no significant change observed in the XRD peaks after GNP reinforcement. All samples mainly exhibited characteristic diffraction peaks corresponding to B₄C [JCPDS 00-006-0555], indicating that the B₄C phase was retained after SPS. No additional reaction products or secondary crystalline phases were clearly detected within the resolution limit of the XRD analysis. This suggests

that the incorporation of GNPs did not cause a detectable phase transformation during SPS.

A weak diffraction peak at approximately $2\theta = 27.4^\circ$ became more pronounced as GNP content increased, particularly in the BG2 and BG3 samples. This peak can be attributed to the graphitic carbon structure of GNPs [JCPDS 00-041-1487]. However, the intensity of this peak remained relatively low compared with the dominant B_4C peaks.

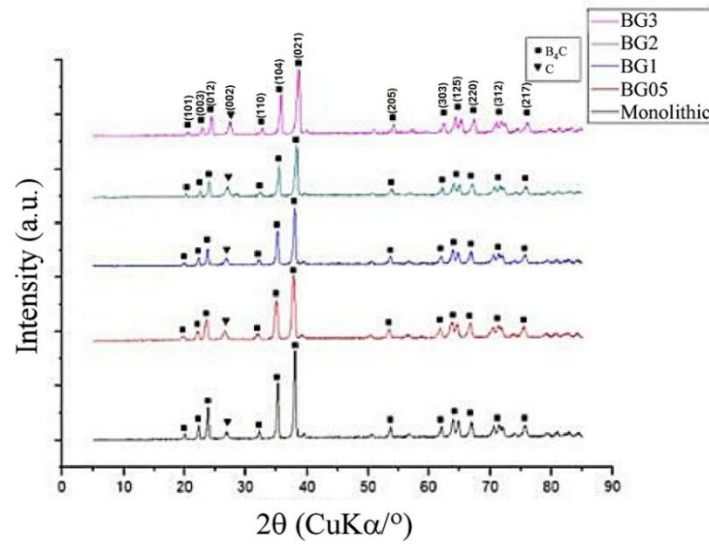


Figure 2. XRD patterns of monolithic, BG05, BG1, BG2, and BG3 samples.

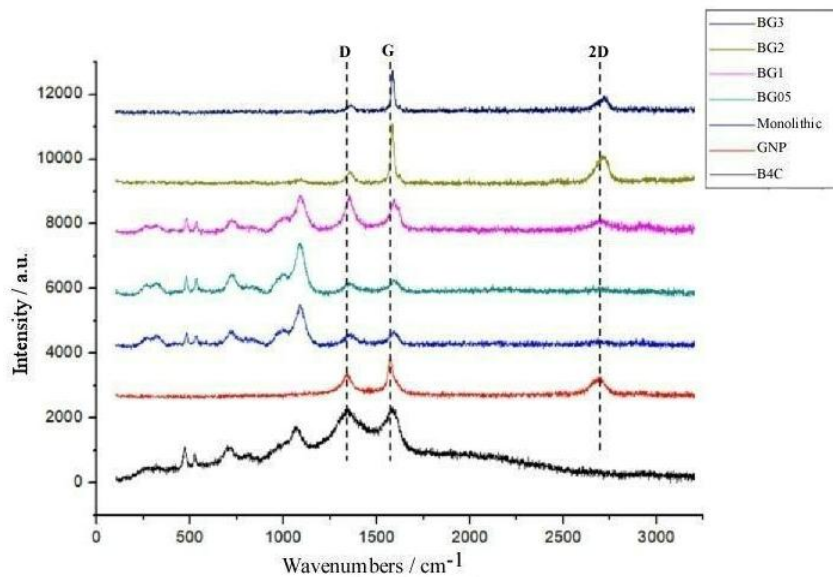


Figure 3. Raman spectra of monolithic and GNP-reinforced B_4C samples.

This may be associated with the low amount of GNPs, their nanoscale thickness, limited crystallite size and possible overlap with the background or neighboring B₄C reflections. Similar observations have been reported in previous studies, in which graphene-related diffraction peaks were weak or difficult to detect in ceramic matrix composites with low graphene content [12]. Therefore, the XRD results indicate that B₄C remained the dominant crystalline phase, while the gradual increase in the carbon-related peak at 27.4° supports the presence of GNPs in the composites.

B₄C, GNP powders and samples were analyzed by Raman spectroscopy, and as shown in Figure 3, the G and D bands were observed in each sample. In GNP powder, the G band, representing the first-order characteristic spectrum resulting from the bond stretching of sp² carbon atoms in linear and ring structures, was observed at 1574 cm⁻¹. This spectrum, associated with sp²-hybridized planar structures, is commonly observed in materials such as carbon nanotubes and nanoplatelets. The 2D band observed at 2693 cm⁻¹ in the GNP powder indicates the presence of graphene, and its shape can be used to determine the number of graphene layers [22-24]. The D band, representing irregularities and defects in the carbon structure, is found at 1341 cm⁻¹. The presence of this band in the spectrum indicates certain structural defects, such as amorphous carbon types and voids in graphite [25].

For the monolithic, BG05, and BG1 samples, the Raman spectra were mainly dominated by the characteristic bands of boron carbide, and the carbon-related bands were relatively weak due to the low GNP content. In contrast, the D, G and 2D bands became more distinguishable in the BG2 and BG3 samples, confirming the presence of GNPs after SPS. The preservation of the G and 2D bands indicates that the graphitic structure of GNPs was largely maintained during SPS. The calculated ID/IG ratios were 0.61 for the starting GNP powder, 0.23 for BG2, and 0.27 for BG3. The lower ID/IG values of the sintered composites compared with the initial GNP powder suggest that the degree of structural disorder in the detectable graphitic phase did not increase after SPS. However, the slight increase in ID/IG from BG2 to BG3 indicates that higher GNP content may promote local agglomeration or defect formation. Overall, the Raman results confirm that GNPs were retained in the B₄C matrix after SPS and that their graphitic structure remained relatively stable under the applied sintering conditions.

3.3 Microstructural analysis

Figure 4 shows SEM micrographs of the fracture surfaces of monolithic and GNP-reinforced B₄C composites. Microstructural investigations reveal that, up to 2% by volume of GNP addition (Figure 4(b-d)), the GNPs are homogeneously distributed along the grain boundaries.

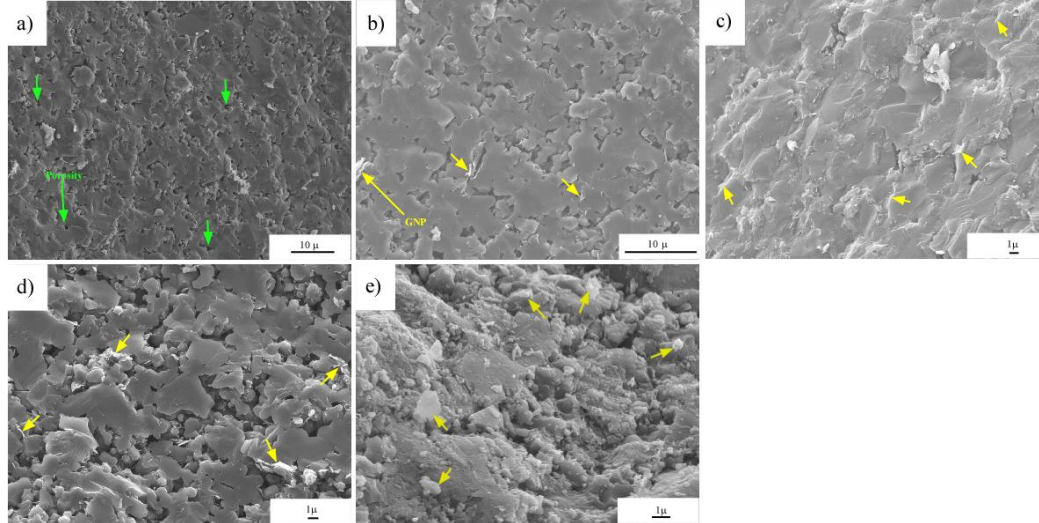


Figure 4. SEM images of the fracture surfaces of (a) monolithic, (b) BG05, (c) BG1, (d) BG2, and (e) BG3 samples.

This uniform distribution effectively filled the microvoids; indeed, this is in complete agreement with the density data, which show that the relative density increased from 93.02% in the monolithic sample to a maximum of 94.40% in the BG2 sample. On the other hand, when the reinforcement ratio reached 3% by volume (BG3), the GNPs exhibited significant agglomeration (indicated by yellow arrows in Figure 4(e)) and disrupted structural homogeneity. These agglomerations acted as stress concentrators within the matrix, creating local defects and reducing the relative density to 94.12%. Tan *et al.* [21] reported that GNPs were homogeneously distributed along grain boundaries and enveloped grains within the B₄C structure, creating a hybrid effect; however, agglomeration occurred as reinforcement content increased.

3.4 Mechanical properties

As shown in Figure 5, the hardness value of monolithic B₄C is 29.66 ± 0.5 GPa, while the highest hardness value of 38.44 ± 0.4 GPa was obtained in sample BG2.

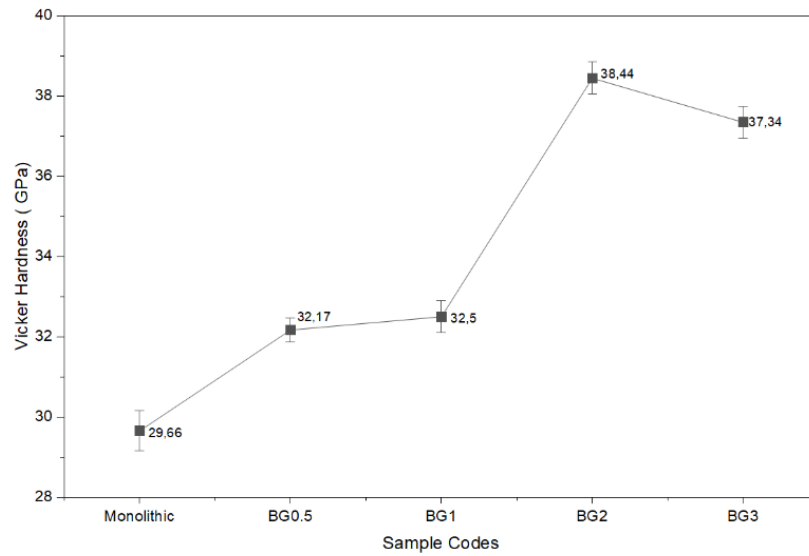


Figure 5. Vickers hardness of monolithic B₄C and GNP-reinforced B₄C composites as a function of GNP content.

It was observed that hardness decreased when the reinforcement ratio exceeded 2% by volume. As clearly seen in Figure 4(e), the agglomeration of GNPs stands out as the main reason for this decrease. In the literature, Nieto *et al.* [26] also reported that reinforcement amounts above a certain threshold lead to graphene agglomeration, which reduces hardness in both metal and ceramic matrix composites. As stated in Section 3.1, there is piecemeal residual porosity in all samples due to insufficient densification; this value is approximately 5.60% (94.40% relative density) for BG2 and approximately 6.98% (93.02% relative density) for the monolithic sample.

Porosity negatively impacts mechanical performance by acting as stress concentration centers; therefore, the measured hardness and fracture toughness values reflect the combined effect of GNP strengthening mechanisms and residual pore content. The fact that sample BG2 has lower porosity (higher relative density) compared to BG3 also supports its better mechanical performance. In a similar study, Alexander *et al.* [12] investigated the effects of graphene concentration on the properties (hardness, fracture toughness and flexural strength) of hot-pressed boron carbide. Adding 2% GNP by volume to the B₄C matrix increased the hardness from 31.1 ± 2.4 GPa to 36.4 ± 3.3 GPa, which was attributed to an increase in density. Increasing the GNP content to 5% and 10% by volume resulted in hardness values of 34.2 ± 4.1 GPa and 23.3 ± 5.1 GPa, respectively.

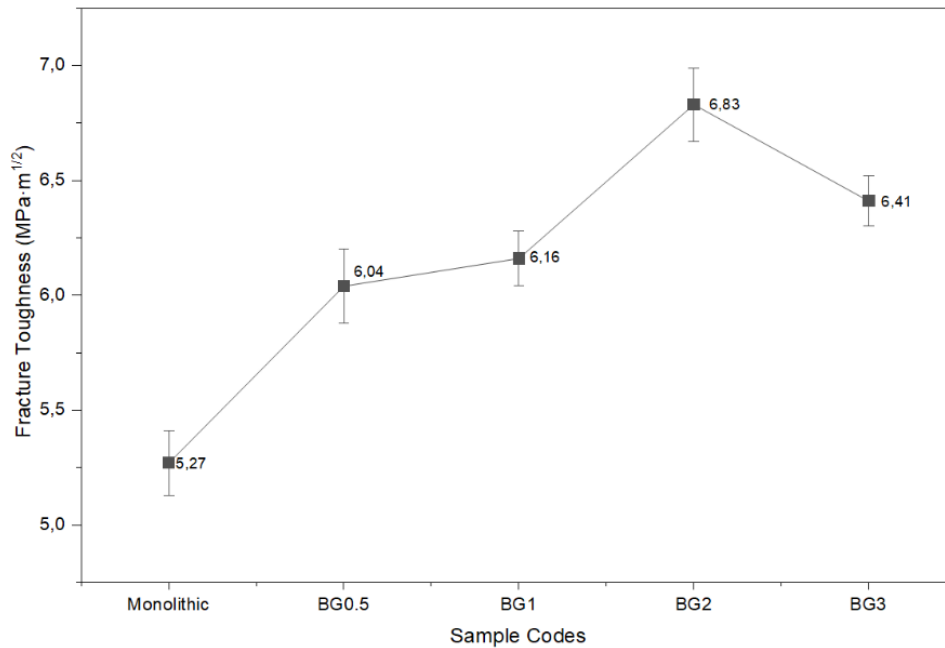


Figure 6. Fracture toughness of monolithic B₄C and GNP-reinforced B₄C composites.

This decrease in hardness was again attributed to GNP agglomeration, because the agglomeration of GNPs, which are inherently softer than the B₄C matrix, compromises the overall structural integrity. Furthermore, it was noted that the decrease in density observed upon adding 5% and 10% GNP by volume also contributed to the decrease in hardness. Additionally, it has been emphasized that GNPs can act as a lubricant within the matrix, triggering grain boundary slippage, increasing composite deformation, and consequently reducing stiffness.

As presented in Figure 6, the fracture toughness of monolithic B₄C was measured as $5.27 \pm 0.14 \text{ MPa}\cdot\text{m}^{1/2}$. In sample BG2, this value increased by 29.6% to $6.83 \pm 0.16 \text{ MPa}\cdot\text{m}^{1/2}$.

However, increasing the reinforcement content to 3% by volume caused the fracture toughness of sample BG3 to decrease to $6.41 \pm 0.11 \text{ MPa}\cdot\text{m}^{1/2}$. To investigate the increase in fracture toughness and the underlying reinforcement mechanisms, the fracture surfaces of the samples were examined by SEM. As shown in Figure 7(b, c), propagating cracks interact with the GNP, resulting in crack deflection. When the crack tip encounters a nanoplatelet, it deviates from its initial planar trajectory. This deviation increases the length of the effective crack propagation path and likely introduces additional energy-consuming mechanisms such as crack bridging and nanoplatelet pull-out. Collectively, these interactions reduce the crack tip propagation force and directly contribute to the measured increases in fracture toughness [27].

As shown in Figure 7(a), the fracture surface also reveals a notable level of residual porosity within the matrix.

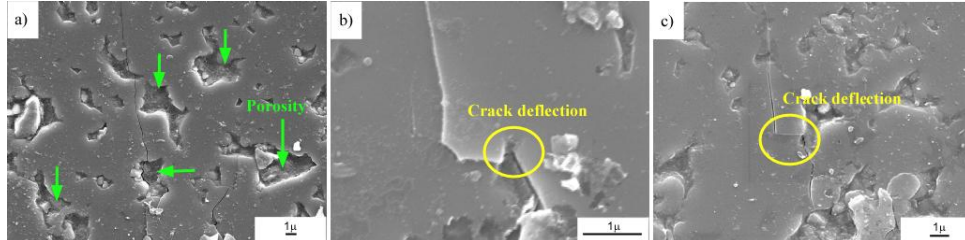


Figure 7. SEM images of the polished surfaces of (a) BG1, (b) BG2, and (c) BG3 samples.

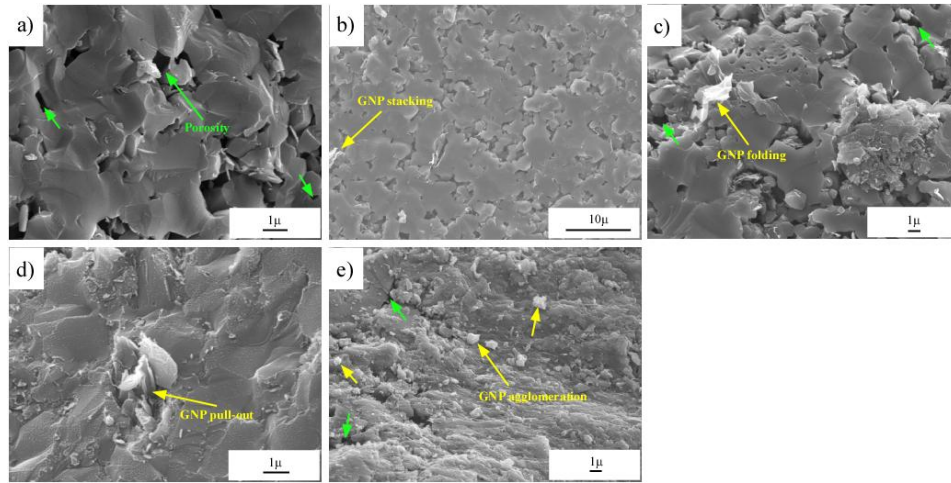


Figure 8. SEM images of the fracture surfaces of (a) monolithic, (b) BG05, (c) BG1, (d) BG2, and (e) BG3 samples.

Pores act as pre-existing stress concentrators, providing preferential nucleation sites for crack initiation and potentially offsetting the toughening contribution of the GNPs [28]. Consequently, the improvement in fracture toughness results from the balance between the toughening effect of GNPs and the detrimental effect of porosity.

This balance strongly depends on the reinforcement content and the resulting microstructural density. In the study conducted by Ocak *et al.* [29] on the mechanical properties of ZrC-TiC-GNP composites, the fracture toughness values increased from 3.76 MPa·m^{1/2} to 5.17 MPa·m^{1/2} at a 3 vol.% reinforcement ratio, while the 5 vol.% reinforcement resulted in a decrease to 5.12 MPa·m^{1/2}. It was concluded that graphene's ability to inhibit crack propagation and alter crack direction was responsible for the increase in fracture toughness. In another study, Walker *et al.* [30] investigated the changing properties of silicon nitride (Si₃Ni₄) ceramic materials with GNP reinforcement, and Si₃Ni₄ showed a 135%

improvement in fracture toughness with only 1.5 vol.% GNP reinforcement. Similarly, Liu *et al.* [31] reported changes in mechanical properties with graphene reinforcement in zirconia-toughened alumina (ZTA) composites, and the toughness value of pure ZTA increased from $6.46 \text{ MPa}\cdot\text{m}^{1/2}$ to $9.05 \text{ MPa}\cdot\text{m}^{1/2}$. This increase has been attributed to GNP pull-out, crack bridging, crack deflection and chipping mechanisms.

The fracture surface images in Figure 8 reveal distinct GNP-related features across the sample series that may be linked to different operative toughening mechanisms. In BG05 (Figure 8(b)), GNP stacking is observed. This morphology suggests limited interfacial interaction between the platelets and the matrix, which is consistent with a reduced capacity for energy dissipation. This may partly explain the modest improvement in toughness at this composition. In BG1 (Figure 8(c)), GNP folding is evident. This potentially indicates platelet flexibility under crack-tip stress fields. Such behavior could be associated with crack bridging or localized energy absorption, though confirmation would require more detailed fractographic analysis. In BG2 (Figure 8(d)), GNP pull-out features are clearly visible. This observation is consistent with a pull-out toughening mechanism, in which frictional sliding along the platelet–matrix interface dissipates crack propagation energy. The prevalence of this mechanism in BG2 likely contributes to its superior fracture toughness compared with other compositions. In BG3 (Figure 8(e)), GNP agglomeration disrupts the homogeneous platelet distribution. This is expected to diminish the effectiveness of crack deflection and pull-out mechanisms. Furthermore, platelet clustering introduces interfacial voids. The combination of reduced toughening activity and higher residual porosity compared to BG2 (5.88% vs. 5.60%) is suggested as the primary cause of the toughness reduction observed in this sample. Furthermore, the slightly higher residual porosity in BG3 may additionally contribute to the observed decrease in fracture toughness. In a study conducted by Das *et al.* [32] on SPSed magnesium composites, it was reported that GNP reinforcement enhances both density and mechanical properties up to an optimal concentration. However, increasing the reinforcement beyond this threshold leads to GNP agglomeration, which subsequently causes a decline in density and a deterioration of mechanical performance. In this case, the obtained density and fracture toughness analysis results are consistent with the microstructure.

4. Conclusions

In this study, GNP-reinforced B₄C composites were successfully produced using the SPS method at different volumetric ratios (0.5, 1, 2, 3 vol.%). The results showed that GNP addition did not significantly alter the densification behavior, but the relative density reached a maximum of 94.40% with 2 vol.% GNP addition and

decreased due to agglomeration at higher GNP contents. XRD and Raman analyses revealed that the graphitic structure was preserved up to 2 vol.% GNP addition, whereas structural disorder increased at 3 vol.% GNP. SEM examinations showed that GNPs were homogeneously distributed at grain boundaries up to 2 vol.%, whereas agglomeration occurred with 3 vol.% GNP addition. These microstructural changes are consistent with the observed trends in relative density and mechanical properties. The highest hardness (38.4 GPa) and fracture toughness (6.83 MPa·m^{1/2}) values were obtained in sample BG2, and this improvement is thought to be due to crack deflection and GNP pull-out mechanisms that may be related to the homogeneous GNP distribution. In conclusion, it was determined that 2 vol.% GNP reinforcement is the optimum content for improving the microstructure and mechanical performance of B₄C ceramics, and the developed composites showed promise for advanced lightweight engineering applications.

Author Contributions

Conceptualization, G.G. and Y.O.A.; methodology, G.G. and Y.O.A.; investigation, Y.O.A.; validation, G.G. and Y.O.A.; formal analysis, G.K., O.B., and I.C.; data curation, G.K.; visualization, G.K.; writing—original draft preparation, G.K., O.B., and I.C.; writing—review and editing, G.G., I.A., G.K., O.B., I.C., and Y.O.A.; supervision, G.G.; project administration, G.G.; funding acquisition, G.G. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement

Data supporting the findings of this study are available upon reasonable request from the corresponding author.

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Conflicts of Interest

The authors declare no conflict of interest.

Artificial Intelligence Disclosure

Artificial intelligence-based tools were used solely for language editing, grammar checking, and stylistic refinement of the manuscript. The tool used was ChatGPT (OpenAI, GPT-5.5). The authors remain fully responsible for the content of this work.

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