Effects of TiB$_2$ Particles on the Microstructure Evolution and Mechanical Properties of B$_4$C/TiB$_2$ Ceramic Composite

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1. Introduction

Boron carbide (B$_4$C) ceramics are interesting structural ceramics in view of their outstanding physical and mechanical properties, especially the combination of low density and extremely high hardness which make them superior anti-ballistic materials over other armor ceramics (such as Al$_2$O$_3$, SiC) $^{[1–3]}$. However, the expensive costs of B$_4$C ceramics fabricated through the hot isostatic pressing (HIP) method severely limits its wide application in the armor protection field $^{[4–6]}$. In addition, its low self-diffusivity efficiency indicates that the sintered body could not achieve the goal of densification through the single solid-state sintering technique. Recently, numerous attempts have been made to overcome these disadvantages, such as the introduction of a second phase and sintering additives into the B$_4$C matrix to fabricate composites. Transition metal borides, such as TiB$_2$ $^{[7,8]}$, ZrB$_2$ $^{[9,10]}$, and HfB$_2$ $^{[11]}$, having high thermal expansion coefficients, and the residual stress fields between B$_4$C and borides rising during the cooling process possibly enhance the fracture toughness of the fabricated composites $^{[12,13]}$.

Recently, the B$_4$C/TiB$_2$ ceramic composites have been the object of numerous works $^{[14–17]}$. The additives of TiB$_2$ to B$_4$C phase can maintain the advantages of high Vickers hardness and low density of B$_4$C and, in addition, inhibit the grain growth $^{[16]}$. Additionally, the physical and mechanical properties of the B$_4$C/TiB$_2$ composites without...
additives prepared from the B₄C and TiB₂ powder are very low. The relative density of B₄C-30 wt.% TiB₂ composites without any additives prepared via pressureless sintering was lower than 90% [18,19]. The flexural strength of the B₄C/TiB₂ ceramic composite reached 717 MPa for the hot-pressed method, which was above two times higher than those (260–361 MPa) fabricated via pressureless sintering [16]. Many researchers have used the B₄C-TiO₂-C powder mixture to prepare the B₄C/TiB₂ composites in different ways, such as the reactive pressureless sintering, hot-pressing, and pulse electric-current sintering [20,21]. Since the introduction of fine TiB₂ grains by in-situ reaction, the B₄C and TiB₂ grain size retained submicron sizes, and the mechanical property tests indicated that the prepared B₄C/TiB₂ ceramic composites achieved the excellent Vickers hardness ~39.3 GPa and flexural strength ~865 MPa, respectively [7]. B₄C with various particle sizes was introduced to fabricate B₄C/TiB₂ ceramic composites under the condition of hot pressing, and both of the B₄C and TiB₂ grains were grown compared to the raw powders after hot pressing [22]. Many studies have shown that for B₄C ceramic composites, C and Si are good sintering aids [23–27]. Carbon removes oxides (such as B₂O₃) in the B₄C raw powder, and improves the interfacial tension by the way of solid solution of carbon atoms into the boron carbide lattice, which increases the sintering driving force [23,24]. A small amount of Si in the B₄C ceramics tends to form a silicide phase, which could improve the sintering ability of B₄C [25–27].

Although hot-pressing and pulse electric current sintering can obtain high-performance composites, the equipment and production costs are high, and the product size is small. The pressureless sintering is an efficient way to fabricate B₄C/TiB₂ composites with large sizes and low costs. At present, the research on improving the performance of the B₄C/TiB₂ ceramic composites prepared under pressureless sintering conditions is relatively scattered [18,28,29], and these reports indicate that the sintering temperature and TiB₂ content have a great influence on the microstructure and density of the composite. Additionally, the research regarding the TiB₂ particle size affecting the sintering behavior of B₄C/TiB₂ ceramic composites under pressureless sintering conditions is rarely reported. In our present work, the B₄C/TiB₂ ceramic composites with 30 wt.% TiB₂ were fabricated via the pressureless sintering method from commercial B₄C raw powder with the average size of 3 μm and TiB₂ raw powder with three different size scales (7 μm, 500 nm, and 50 nm), and mixed in variable mass ratio. In addition, carbon black and silicon particles were used as sintering auxiliary components. Furthermore, the effect of TiB₂ grains on the interfaces to optimize the microstructure of the B₄C/TiB₂ composites was thoroughly investigated. This research should be beneficial to fabricate the excellent performance of B₄C/TiB₂ ceramic composite.

2. Materials and Methods

Raw materials were B₄C powder (3 μm, purity: >99.5%; Zhengzhou Songshan Boron Technology Co., Ltd., Zhengzhou, China), silicon raw powder and carbon black raw powder (submicron, purity: >99.8%, Shanghai ST-NANO Co. Ltd., Shanghai, China), and TiB₂ powder (purity: >99%; Shanghai ST-NANO Co. Ltd., Shanghai, China). Figure 1a-c show the three type morphologies of the TiB₂ raw powders. Figure 1a depicts the microtopography of micro-TiB₂ powder with average size about 7 μm. Figure 1b,c show the microtopography of submicron TiB₂ powder with average size about 500 nm and nano-TiB₂ powder with average size about 50 nm, respectively. Table 1 lists the phase composition of the three mixtures. The mixed raw powders were ball-milled in ethyl alcohol absolute with ZrO₂ balls and then dried using a rotary evaporator (R205B, Shanghai Shensheng Technology Co. Ltd., Shanghai, China). The powder mixture was pressed in a graphite die and then cold isostatic pressed (CIP, LDJ100/320–300, Sichuan Aviation Industry Chuanxi Machine Factory, Sichuan, China) to form a green body with a 50 mm diameter. The samples were processed by pressureless sintering in a graphite crucible (FCT Systeme GmbH, Rauenstein, Germany) at 2100 °C for 60 min at a heating rate of 10 °C per minute under flowing Ar atmosphere.
The relative densities of the samples were determined through Archimedes’ principle in deionized water. The average grain size was estimated by intercept method and more than 200 grains on the surface after polishing and thermally etching were measured. The flexural strength of the prepared specimens which were cut into the bars of $3 \times 4 \times 35$ mm$^3$ was tested on an electromechanical universal testing machine (INSTRON-5566, Norwood, MA, USA) of which the crosshead speed was 0.5 mm per minute and the span was 30 mm. The fractural toughness of the composites tested on bars (the size of $3 \times 6 \times 35$ mm$^3$), and a notch depth of 3 mm, was measured by the single-edge notched beam (SENB) test of which the crosshead speed was 0.05 mm per minute and the span was 24 mm. Vickers hardness measurement applied a load of 1 kg for 15 s to the sample surfaces on a hardness testing device (AHVD-1000, Shanghai Jujing Precision Instrument Manufacturing Co., Ltd., Shanghai, China). The phases and components were characterized by X-ray diffraction (D8 Advance, Germany). The microstructure was analyzed by a scanning electron microscope (SEM, Hitachi-S3400N, Hitachi, Tokyo, Japan) and a transmission electron microscope (TEM, Oxford INCAX-ACT, Oxford Instruments, Oxford, UK). The TEM sample of a selected specimen was prepared through conventional mechanical thinning and finished with precision ion polishing system machine (PIPS, Gatan-691, Pleasanton, CA, USA).

### 3. Results and Discussion

The phase compositions of the sintered B$_4$C/TiB$_2$ ceramic composites with various raw powders are shown in Figure 2. All the samples contained B$_4$C, TiB$_2$, SiC, and graphite. The X-ray characteristic peak patterns of the BM30 and BM10S20 were the same. With the introduction of TiB$_2$ nanoparticle powders, the characteristic peaks of TiB$_2$ changed significantly. For the BS20N20, the $\theta = 68.206^\circ$ characteristic peak of the TiB$_2$ was higher than the characteristic peak intensity of the sample BM30 and BM10S20. The well-defined peaks in the as-prepared B$_4$C/TiB$_2$ composite suggests that the TiB$_2$ phase has a preferred orientation in (102) and (111).

Figures 3 and 4 show the SEM pictures of the fractured surface of the microstructure of the B$_4$C/TiB$_2$ ceramic composites. It could be clearly seen that due to the fact that the BM30 raw material powder particles are coarse and the sintering driving force is small, as shown in Figure 3a,b, there were a large number of interconnected open pores, and the coarsened particles were connected in an island chain. A large amount of sinter-necks with clear contours among the grains in the BM30 sample were still visible. With the size of TiB$_2$ powder decreasing, the pore content and pore size decreased, and the dense areas increased significantly, as shown in Figure 3c,f. In the BS20N10 sample containing both 500 nm and 50 nm particle sizes of TiB$_2$ powder, the shapes of the pores were relatively regular, tending to form regular polygon or nearly circular shapes, as shown in Figure 4a,b. Additionally, it can be inferred that these small particles belong to TiB$_2$.

| Grade     | B$_4$C (wt.%) | C (wt.%) | Si (wt.%) | Micron TiB$_2$ (wt.%) | Submicron TiB$_2$ (wt.%) | Nano TiB$_2$ (wt.%). |
|-----------|---------------|----------|-----------|-----------------------|--------------------------|----------------------|
| BM30      | 60            | 7        | 3         | 30                    | /                        | /                    |
| BM10S20   | 60            | 7        | 3         | 10                    | 20                       | /                    |
| BS20N10   | 60            | 7        | 3         | /                     | 20                       | 10                   |

Table 1. Starting composition of BM30, BM10S20, and BS20N10 ceramic composites.
coarsened particles were connected in an island chain. A large amount of sinter-necks with clear contours among the grains in the BM30 sample were still visible. With the size of TiB2 powder decreasing, the pore content and pore size decreased, and the dense areas increased significantly, as shown in Figure 3c, f. In the BS20N10 sample containing both 500 nm and 50 nm particle sizes of TiB2 powder, the shapes of the pores were relatively regular, tending to form regular polygon or nearly circular shapes, as shown in Figure 4a, b. Additionally, it can be inferred that these small particles belong to TiB2.

The TiB2 grains on the grain boundaries can pin the movement of the B4C grain boundaries and hinder the grain growth, thus increasing the content of grain boundaries and increasing the sintering rate [29]. In the BS20N10 sample, the interfaces between TiB2 and B4C phases are well distributed, indicating that TiB2 and other phases achieved good wetting during the sintering process as shown in Figure 5. The interface between B4C and TiB2 is jagged, which indicates that the interface feature helps to improve the ability to resist external loads.

Figure 2. XRD patterns of B4C/TiB2 ceramic composites obtained with different grades of TiB2 powders.

Figure 3. Fracture morphology SEM images of the B4C/TiB2 ceramic composites with various TiB2 raw powder mixtures. (a,b) BM30, (c,d) BM10S20 and (e,f) BS20N10.
The TiB₂ grains on the grain boundaries can pin the movement of the B₄C grain boundaries and hinder the grain growth, thus increasing the content of grain boundaries and increasing the sintering rate [29]. In the BS20N10 sample, the interfaces between TiB₂ and B₄C phases are well distributed, indicating that TiB₂ and other phases achieved good wetting during the sintering process as shown in Figure 5. The interface between B₄C and TiB₂ is jagged, which indicates that the interface feature helps to improve the ability to resist external loads.

Figure 4. Small TiB₂ grains in the B₄C/TiB₂ ceramic composite processed with a mixture of sub-micron and nano-sized TiB₂ particles. (a) SEM image and (b) corresponding BSE image.

The SEM pictures of the polished surfaces of the specimens sintered with various TiB₂ powders are shown in Figures 6 and 7. In Figure 6, SiC grains were dispersed and distributed on the B₄C substrate in sample BS20N10, which acts as a pinning to prevent the grain boundary and inhibit grain growth. Additionally, the compound reaction of Si and C generated SiC exotherm, which helps the sintering process. Figure 7 show that the average grain sizes of the TiB₂ in the prepared specimens with various raw TiB₂ particles obtained under pressureless sintering conditions at 2100 °C for 60 min dwell were similar. B₄C grains ranged from 2 μm to 10 μm, and comparing with the TiB₂ raw powder with an average grain size of 50 nm, the grain sizes of the ceramic composites increased by a maximum of 200 times. With the size of TiB₂ raw powder decreasing, the amount and size of the pores in the samples decreased significantly. The B₄C average grain size of the BM30 sample to which the 7 μm-sized TiB₂ powder was added was 3.01 μm, but many large pores were present in Figure 7a. B₄C average grain size of the BM10S20 sample, with the
TiB₂ addition of 7 µm and 500 nm, was consistent with BM30, but the amount of the pores decreased, and the densification area of the BM10S20 sample increased. B₄C average grain size of the BS20N10 sample with the TiB₂ addition of the 500 nm and 50 nm remained close to the starting raw powder, about 2.63 µm, and the amount and size of the pores in the BS20N10 sample was significantly reduced. The relative density of the BS20N10 sample was also increased to 98.6%, as shown in Table 2.

Figure 6. SEM images of the polished surfaces (a) and corresponding BSE images (b) in the sample.

Figure 7. (a–c) SEM images of the polished surfaces and (d) plot of the average grain sizes in the samples.

Table 2. Mechanical properties of the B₄C/TiB₂ ceramic composites.

| Sample    | Relative Density (%) | Flexural Strength (MPa) | Fracture Toughness (MPa·m¹/²) | Vickers Hardness (GPa) |
|-----------|----------------------|-------------------------|-------------------------------|-----------------------|
| BM30      | 90.1 ± 0.2           | 217 ± 13                | 3.70 ± 0.19                   | 8.3 ± 0.6             |
| BM10S20   | 92.6 ± 0.1           | 288 ± 12                | 4.46 ± 0.12                   | 12.5 ± 1.1            |
| BS20N10   | 98.6 ± 0.1           | 364 ± 9                 | 5.47 ± 0.12                   | 30.2 ± 2.6            |

Figure 8a–b are TEM images of the interface structure between B₄C and SiC in the BS20N10 sample. According to the selected area-electron diffraction (SAD) result in Figure 8b, the unit cell structure parameter of B₄C was a = b = 0.56 nm, c = 1.21 nm, α = β = 90°, γ = 120°, and the unit cell structure parameter of SiC was a = b = c = 0.44 nm, α = β = γ = 90°. The zone axis of the two phases of B₄C and SiC satisfies the relationship: [120]₀B₄C // [T12]₀SiC, and a group of
crystal planes satisfies the relationship: \((303)_{\text{B}_4\text{C}}/(311)_{\text{SiC}}\). Additionally the interface between crystal plane \((303)_{\text{B}_4\text{C}}\) and crystal plane \((311)_{\text{SiC}}\) satisfies:

\[
\delta = \frac{d_{(303)} - d_{(311)}}{d_{(303)}} = \frac{0.151 \text{nm} - 0.137 \text{nm}}{0.151 \text{nm}} = 9.27\% 
\]

(1)

![Figure 8](image)

**Figure 8.** Interface between B\(_4\)C and SiC. (a) Bright field TEM image, (b) SAED pattern.

According to the calculation Formula (1), the mismatch degree between the crystal plane \((303)_{\text{B}_4\text{C}}\) and crystal plane \((311)_{\text{SiC}}\) is 9.27%, which could form a semi-coherent interface, and it helps to reduce the interface energy and obtains a bonding strong interface [30].

Figures 9 and 10 are the bright field and high-resolution TEM images of the interfaces between TiB\(_2\) and B\(_4\)C, SiC, respectively. As can be seen in the bright field images of Figures 9a and 10a, the interfaces were clean and straight, and there were no other new phases. There were lattice distortion regions with a wide range of 2~3 nm at the interfaces, which were also the transition regions of the lattice structures between TiB\(_2\) and the other two phases, shown in Figures 9b and 10b. The main reason for the formation of these transition zones may be attributed to the unit cell structure parameters of TiB\(_2\): a = b = 0.30 nm, c = 0.32 nm, \(\alpha = \beta = 90^\circ\), \(\gamma = 120^\circ\). Additionally, the difference of the unit cell structure between B\(_4\)C, SiC, and TiB\(_2\) was huge. During the sintering process, the transition zones were created to coordinate the arrangement of atoms at the interfaces.

The mechanical and physical properties of the prepared ceramic composites with different TiB\(_2\) particle sizes are presented in Table 2. With the size of TiB\(_2\) raw powder decreasing, the relative density and mechanical properties of the prepared composites all showed a significantly increasing trend. The relative density of the prepared specimens increased, which helped to achieve the excellent mechanical properties of the prepared specimens. The relative density of the BS20N10 sample reached 98.6%, which is the first major requirement to obtain competitive B\(_4\)C/TiB\(_2\) ceramic composites. The optimized flexural strength, Vickers hardness, and fracture toughness of the BS20N10 sample reached 364 MPa, 30.2 GPa, and 5.47 MPa·m\(^{1/2}\), respectively.

The relative density of the BS20N10 sample was high (98.6%) and the grain sizes were fine (about 2.63 \(\mu\)m), which were mainly due to the following four aspects: (1) the 50 nm-sized TiB\(_2\) particles filled the pores of the green body and increased the density of the green body, being conducive to higher densification upon sintering; (2) with the size of the TiB\(_2\) powder decreasing, the specific surface energy of the green body was higher than in analogous compositions with coarser grain sizes, which provides a strong driving force for sintering; (3) with the size of TiB\(_2\) powder decreasing, the amount of the grain boundary increased, resulting in enhanced grain boundary diffusion during the sintering process;
(4) TiB₂ grains on the grain boundaries hindered the movement of the grain boundaries and helped to preserve a fine B₄C grain size.

![Interface structure between B₄C and TiB₂](image1)

**Figure 9.** Interface structure between B₄C and TiB₂. (a) Bright field TEM image, (b) HRTEM image.

![Interface structure between SiC and TiB₂](image2)

**Figure 10.** Interface structure between SiC and TiB₂. (a) Bright field TEM image, (b) HRTEM image.

The improvement of the relative density and reduction of the grain size of the samples both contributed to obtain high flexural strength. In addition, the shapes of the pores in the BS20N10 were regular polygons or near circles, as shown in Figure 4. According to the fracture mechanics of ceramic materials [31–33], these types of the pores could significantly increase the critical value of fracture failure caused by the stress concentration in the sample, and the sample could achieve a high flexural strength.

The thermal expansion coefficients of TiB₂ (8.1 × 10⁻⁶/°C), B₄C (4.5 × 10⁻⁶/°C), and SiC (4.7 × 10⁻⁶/°C) are quite different [34,35]. During the cooling process, the residual tensile stress fields rise at the interfaces between TiB₂ and another phase (such as B₄C or SiC). When the crack enters the residual stress field zone, the crack propagated proceeds in the direction perpendicular to the tensile stress as shown in Figure 11, so that the crack propagation directions can be deflected. The crack deflections and the crack propagation paths are extended, which increase the energy consumption and increase the fracture toughness of the prepared ceramic composite.
4. Conclusions

$B_4C/TiB_2$ ceramic composites containing different proportions of submicron and nano $TiB_2$ powders were prepared by pressureless sintering at 2100 °C. With the decrease of the particle size of $TiB_2$ raw powders, the surface energy of the powder increased significantly and the density of the sintered body increased. During the sintering process, nano-$TiB_2$ inhibited the grain growth, increased the number of the grain boundaries, and promoted the densification of the material to 98%. With the size of $TiB_2$ powders decreasing, the average grain sizes of the $B_4C/TiB_2$ ceramic composites decreased, and the interfaces between the different phases were strongly bonded, which helped to obtain good mechanical properties. As a result, the $B_4C/TiB_2$ ceramic composite with 20 wt.% submicron and 10 wt.% nano-$TiB_2$ addition had a significant improved in mechanical and physical properties. The optimized relative density, grain size, Vickers hardness, flexural strength, and fracture toughness of the sample were 98.6%, 2.63 μm, 30.2 GPa, 364 MPa, and 5.47 MPa·m$^{1/2}$, respectively. Finally, it was illustrated that the sub-fine $TiB_2$ powder could control the grain growth in the preparation of the $B_4C/TiB_2$ ceramic composite under the pressureless sintering condition, and was confirmed to be an effective approach to enhance the mechanical properties of $B_4C$ ceramics.

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References
1. Thevent, F. Boron Carbide—A Comprehensive Review. J. Eur. Ceram. Soc. 1990, 6, 205–225. [CrossRef]
2. Jiang, Z.G.; Zeng, S.Y.; Shen, Z.Q. Research progress on lightweight ceramic composite armor structure. Acta Armamentarii 2010, 31, 603–610. [CrossRef]
3. Karandikar, P.G.; Evans, G.; Wong, S.; Aghajanian, M.K.; Sennett, M. A review of ceramics for armor applications. Adv. Ceram. Armor IV 2009, 29, 163–175. [CrossRef]
4. Savio, S.G.; Ramanjaneyulu, K.; Madhu, V.; Bhat, T.B. An experimental study on ballistic performance of boron carbide tiles. Int. J. Impact Eng. 2011, 38, 535–541. [CrossRef]
5. Da Rocha, R.M.; de Melo, F.C.L. Pressureless Sintering of B₄C-SiC Composites for Armor Applications. *Ceram. Eng. Sci. Proc.* **2009**, *30*, 113. [CrossRef]

6. Wu, C.; Li, Y.K.; Wan, C.L. Reactive-sintering B₄C matrix composite for Armor Applications. *Rare Met.* **2020**, *39*, 529–544. [CrossRef]

7. Huang, S.G.; Vanmeensel, K.; van der Biest, O.; Vleugels, J. In situ synthesis and densification of submicrometer-grained B₄C-TiB₂ composites by pulsed electric current sintering. *J. Eur. Ceram. Soc.* **2011**, *31*, 637–644. [CrossRef]

8. Xu, C.M.; Cai, Y.B.; Flodström, K.; Li, Z.; Esmaeilzadeh, S.; Zhang, G.J. Spark plasma sintering of B₄C ceramics: The effects of milling medium and TiB₂ addition. *Int. Reactif. Met. Hard Mater.* **2012**, *30*, 139–144. [CrossRef]

9. Goldstein, A.; Geffen, Y.; Goldenberg, A. Boron Carbide–Zirconium Boride In-Situ Composites by the Reactive Pressureless Sintering of Boron Carbide–Zirconia Mixtures. *J. Am. Ceram. Soc.* **2001**, *84*, 642–644. [CrossRef]

10. Subramanian, C.; Roy, T.; Murthy, T.S.; Sengupta, P.; Kale, G.B.; Krishnaiah, M.V.; Suri, A.K. Effect of zirconia addition on pressureless sintering of boron carbide. *Ceram. Int.* **2008**, *34*, 1543–1549. [CrossRef]

11. Sairam, K.; Sonber, J.K.; Murthy, T.S.; Subramanian, C.; Hubli, R.C.; Suri, A.K. Development of B₄C–HfB₂ composites by reaction hot pressing. *Int. Reactif. Met. Hard Mater.* **2012**, *35*, 32–40. [CrossRef]

12. Tang, J.; Tan, S.H.; Chen, Z.M.; Jiang, D.L. Strengthening and Toughening of B₄C-TiB₂ Multiphase Ceramics. *J. Inorg. Mater.* **1997**, *12*, 169–174. [CrossRef]

13. Nils, C.; Bernhard, M.; Michael, V.S. Grain-Size dependence of fracture energy in ceramics. *J. Am. Ceram. Soc.* **1981**, *64*, 345–350. [CrossRef]

14. Liu, Z.; Wang, D.; Li, J.; Huang, Q.; Ran, S. Densification of high-strength B₄C–TiB₂ composites fabricated by pulsed electric current sintering of TiC–B mixture. *Scr. Mater.* **2017**, *135*, 15–18. [CrossRef]

15. Wang, D.; Ran, S.; Shen, L.; Sun, H.; Huang, Q. Fast synthesis of B₄C–TiB₂ composite powders by pulsed electric current heating TiC–B mixture. *J. Eur. Ceram. Soc.* **2015**, *35*, 1107–1112. [CrossRef]

16. Huang, S.G.; Vanmeensel, K.; Malek, O.J.A.; Van der Biest, O.; Vleugels, J. Microstructure and mechanical properties of pulsed electric current sintered B₄C–TiB₂ composites. *Mater. Sci. Eng. A* **2011**, *528*, 1302–1309. [CrossRef]

17. Wu, C.; Li, Y.K. AlN-induced reinforcement of nano-amorphous B-C-N compound for TiB₂–B₄C ceramic composite. *J. Alloys Compd.* **2020**, *831*, 154074. [CrossRef]

18. Mashhadi, M.; Taheri-Nassaj, E.; Mashhadi, M.; Sglavo, V.M. Pressureless sintering of B₄C–TiB₂ composites with al additions. *Ceram. Int.* **2011**, *37*, 3229–3235. [CrossRef]

19. Malek, O.; Vleugels, J.; Vanmeensel, K.; Huang, S.; Liu, J.; Van den Berge, S.; Datye, A.; Wu, K.H.; Lauwers, B. Electrical discharge machining of B₄C–TiB₂ composites. *J. Eur. Ceram. Soc.* **2011**, *31*, 2023–2030. [CrossRef]

20. Goldstein, A.; Yeshurun, Y.; Goldenberg, A. B₄C/metal boride composites derived from B₄C/metal oxide mixtures. *J. Eur. Ceram. Soc.* **2007**, *27*, 695–700. [CrossRef]

21. Yamada, S.; Hirao, K.; Yamauchi, Y.; Kanazaki, S. High strength B₄C–TiB₂ composites fabricated by reaction hot-pressing. *J. Eur. Ceram. Soc.* **2003**, *23*, 1123–1130. [CrossRef]

22. Liu, Z.T.; Deng, X.G.; Li, J.M.; Sun, Y.; Ran, S. Effects of B₄C particle size on the microstructures and mechanical properties of hot-pressed B₄C-TiB₂ composites. *Ceram. Int.* **2018**, *44*, 21415–21420. [CrossRef]

23. Li, P.; Yang, J.F. Microstructure and Mechanical Properties of B₄C-Ceramic. *Rare Met. Mater. Eng.* **1999**, *28*, 151–154.

24. Suri, A.K.; Subramanian, C.; Sonber, J.K.; Murthy, T.C. Synthesis and consolidation of boron carbide: A review. *Int. Mater. Rev.* **2010**, *55*, 4–40. [CrossRef]

25. Hayun, S.; Frage, N.; Dariel, M.P. The morphology of ceramic phases in B₄C-SiC-Si infiltrated composites. *Solid State Chem.* **2006**, *179*, 2875–2879. [CrossRef]

26. Feng, Y.; Hou, Z.; Zhang, H.; Liu, L. Densification and Mechanical Properties of Spark Plasma Sintered B₄C with Si as a Sintering Aid. *J. Am. Ceram. Soc.* **2010**, *93*, 2956–2959. [CrossRef]

27. Zhang, Z.; Du, X.; Li, Z.; Wang, W.; Zhang, J.; Fu, Z. Microstructures and mechanical properties of B₄C–SiC intergranular/intragranular nanocomposite ceramics fabricated from B₄C, Si, and graphite powders. *J. Eur. Ceram. Soc.* **2014**, *34*, 2153–2161. [CrossRef]

28. Skorokhod, V.V.; Vlajic, M.D.; Kristic, V.D. Pressureless Sintering of B₄C-TiB₂ Ceramic Composites. *Mater. Sci. Forum* **1998**, *282–283*, 219–224. [CrossRef]

29. Baharvandi, H.R.; Hadian, A.M. Pressureless Sintering of TiB₂-B₄C Ceramic Matrix Composite. *J. Mater. Eng. Perform.* **2008**, *17*, 838–841. [CrossRef]

30. Pan, J.S.; Tong, J.M.; Tian, M.B. **Fundamentals of Materials Science**; Tsinghua University Press: Beijing, China, 2011.

31. Mu, B.C. Strengthening and Toughening of Ceramic Materials; Metallurgical Industry Press Co., Ltd.: Beijing, China, 2002.

32. Choi, S.R.; Sanders, W.A.; Salem, J.A.; Tikare, V. Young’s modulus, strength and fracture toughness as a function of density of in situ toughened silicon nitride with 4 wt.% Scandia. *J. Mater. Sci. Lett.* **1995**, *14*, 276–278. [CrossRef]

33. Li, Z.N. *Applied Fracture Mechanics*; Bei Hang University Press: Beijing, China, 2012.

34. Wu, Q.R.; Wen, B.X. Study on temperature dependence of thermal conductivity and linear expansion for SiC material. *South China Univ. Technol. Nat. Sci. Ed.* **1996**, *24*, 11–15.

35. Einarsrud, M.A.; Hagen, E.; Pettersen, G.; Grande, T. Pressureless sintering of titanium diboride with nickel, nickel boride, and iron additives. *J. Am. Ceram. Soc.* **2005**, *88*, 3013–3020. [CrossRef]