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Citation: Chin. Phys. B . 2019, 28(6): 066201. **doi:** 10.1088/1674-1056/28/6/066201
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Nanosheet-structured B_4C with high hardness up to 42 GPa*

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(Received 1 February 2019; revised manuscript received 24 March 2019; published online 8 May 2019)

High-quality bulk boron carbide (B_4C) is successfully prepared at high pressure and high temperature (HPHT) by using B_4C powder as a precursor. The as-synthesized B_4C possesses a nanosheet structure with a thickness value of 15 nm and a length of several dozen micrometers. Its Vickers hardness value and fracture toughness value are 42.4 GPa and 4.51 MPa·$m^{1/2}$, respectively, which are superior to those of B_4C obtained from spark plasma sintering due to its high densification and nanosheet structure. Additionally, it shows good property of oxidation resistance. In air, its oxidation resistance temperature is 1100 °C which is higher than that of diamond under the same test condition.

Keywords: boron carbide, hardness, fracture toughness, oxidation resistance

PACS: 62.23.–c ,61.46.Hk, 61.66.Fn, 62.20.–x **DOI:** 10.1088/1674-1056/28/6/066201

1. Introduction

Boron carbide (B_4C) has been widely used in cutting tools, wear resistant parts, ball mills, neutron absorber and shielding material in nuclear industry due to its high melting point, outstanding hardness, low specific weight, high modulus, high chemical stability, good wear resistance, high neutron absorption cross-section, and so forth.[1–6] However, two problems still need to be solved urgently to synthesize high-quality B_4C. (i) The hardness of B_4C is usually lower than the threshold of superhard materials (40 GPa) resulting from a low densification.[7–9] Synthesis of high-densification of B_4C is extremely difficult and costly due to its very strong covalent bonds and the low self-diffusivity. (ii) Phase-pure B_4C has a low fracture toughness (generally lower than 4 MPa·$m^{1/2}$),[10] which restricts its wider applications in structural materials. Hence, it is imperative to fabricate B_4C with both high hardness and high fracture toughness to satisfy the requirement of practical application. To date, many approaches to increasing the densification of B_4C, such as via increasing sintering temperature, introducing sinter additives and using pressure-assisted sintering have been utilized. Pressureless sintering of pure B_4C is extremely difficult and only obtains a relative density of 93% even at 2375 °C.[8,10,11] The addition of additives to raw material has proven to be an effective way to improve the densification as well as mechanical properties by hindering grain growth and forming second phase at the grain boundaries. Metallic sintering aids such as Al, Ti, Ni, and Fe are frequently added to provide a medium for liquid-phase sintering.[12–14] However, metallic phases at the grain boundaries generally deteriorate the unique properties of hard ceramics. Pressure-assisted sintering is a useful strategy to enhance the densification of sintered products. Pure B_4C can be densified by pressure-assisted sintering at 1600 °C for 10 min–20 min under 300 MPa.[15] Compared with the sample prepared by pressureless sintering (19 GPa–32 GPa),[3] the sample obtained by pressure-assisted sintering shows an improved hardness value, reaching up to 35 GPa. Nevertheless, the hardness of B_4C prepared by both pressureless sintering and pressure-assisted sintering are always lower than the threshold of superhard materials (40 GPa). The nano-structured ceramic has higher hardness and fracture toughness due to the effect of Hall–Petch than the micro-structured ceramic.[16,17] Unfortunately, the nano-structured B_4C cannot be prepared via the above mentioned method due to the grain growth at a very slow rate of densification. Although higher densification can be achieved at higher temperatures, it is difficult to prevent the grains from growing. The hardness of B_4C with high densification and nano-structure should be greatly improved.

In this work, we successfully synthesize the nanosheet-structured B_4C by using HPHT apparatus. The synthesized B_4C is demonstrated to reach a hardness value of 42.4 GPa and a fracture toughness value of 4.51 MPa·$m^{1/2}$. To the best of our knowledge, this hardness value is the highest for B_4C to date, even higher than that of B_4C single crystal. Consequently, it displays excellent application prospects in the mechanical field.

2. Experiment

In this study, high-purity B_4C (97% purity, Mudanjiang Diamond Boron Carbide Co., Ltd., China) powders were used as starting material. The average grain size of B_4C power was about 50 μm. The powder of B_4C was pressed into a rod shape

*Project supported by the Scientific Research Fund of Jilin Provincial Education Department, China (Grant No. JJKH20190826KJ)
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of 4 mm in diameter and 3 mm in thickness, which was enclosed in a hexagonal BN capsule. The hexagonal BN capsule was surrounded by a graphite sleeve, which was used as a heater. An SPD6 × 600 T-type hexahedral anvil press was used, and all experiments were performed under HPHT conditions of 5.2 GPa and 1800 °C–2200 °C. The temperature was measured by a chromel–alumeltype thermocouple placed in the center of the BN capsule. The pressure was given by a calibration curve that was established by determining the applied loads corresponding to the phase transformation pressures of bismuth, thallium and barium. The samples were kept at target pressures and temperatures for 15 min. The crystal structures and morphologies of the final powders were characterized using an x-ray diffractometer (XRD) with Cu Ka radiation (Siemens D5000, Germany), a field-emission scanning electron microscope (JEOL JSM-6700 F, Japan). The density was measured by the Archimedes method with distilled water as an immersion medium. The Vickers hardness was measured by a Vickers hardness tester (HV-1000ZDT) with an applied load of 9.8 N for a dwell time of 15 s. The fracture toughness (K_{1C}) of the ceramic was calculated after the indentation from the following equation:[18]

$$K_{1C} = 0.203 H_v a^{1/2} (c/a)^{-2/3}. \quad (1)$$

Here, H_v is the hardness, a is the impression radius, and c is the radial/median crack length.

3. Results and discussion

The typical XRD patterns of bulk B_4C synthesized under 5.2 GPa for 15 min at a temperature ranging between 1800 °C and 2200 °C are shown in Fig. 1. The x-ray diffraction patterns of the prepared samples match very well with the standard diffraction data of B_4C, which demonstrates that no reaction product is observed. Figure 2 displays the SEM images taken at low magnification from pure B_4C prepared under 5.2 GPa for 15 min at temperatures of 1800 °C, 2000 °C, and 2200 °C, respectively. It can be seen that the number of pores decreases as the temperature increases. Nearly no obvious residual porosity can be seen in B_4C synthesized at 2200 °C. Thus, it may possess the highest densification. High-magnification SEM images of B_4C synthesized at 1800 °C, 2000 °C, and 2200 °C are shown in Figs. 2(d), 2(e), and 2(f), respectively. As revealed in the SEM images, the crystal morphologies of B_4C are very fine nanosheets with thickness of about 10 nm–60 nm. The average thickness of B_4C synthesized at 1800 °C, 2000 °C, and 2200 °C are 52.3 nm, 34.7 nm, and 15.2 nm, respectively. It is reported that the B_4C nanosheet can act as a metal-free catalyst for high-performance electrochemical nitrogen-to-ammonia fixation under ambient conditions.[19] The catalyst can achieve a high ammonia yield of 26.57 $\mu g \cdot h^{-1} \cdot mg_{cat}^{-1}$, and a fairly high Faradaic efficiency of 15.95% at −0.75 V with respect to reversible hydrogen electrode, and is placed in the most active aqueous-based nitrogen reduction reaction electrocatalysts. The fine as-synthesized nanosheet B_4C suggests that it is a promising candidate for use as an electrocatalyst. It is worth nothing that the grain size apparently decreases as the synthesis temperature is raised at a certain pressure. It is known that increasing synthesis temperature can accelerate the grain growth. However, in our method, grain size decreases with temperature increasing at a certain pressure. The melting point of B_4C is 2350 °C. The highest synthesis temperature in our method is only 2200 °C, which is lower than the melting point of B_4C. The higher the temperature, the easier the deformation is. Consequently, grain change may happen in the process of modification and recrystallization.

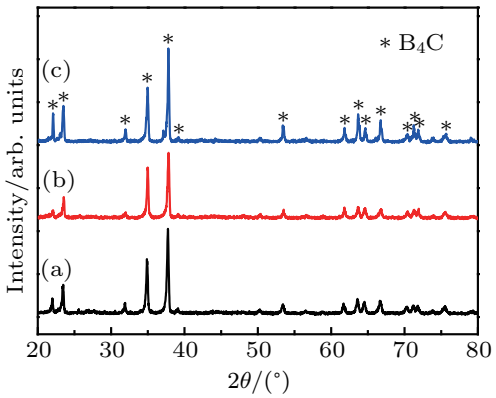


Fig. 1. X-ray diffraction patterns of bulk B_4C synthesized under 5.2 GPa for 15 min at different temperatures of 1800 °C (a), 2000 °C (b), 2200 °C (c), respectively.

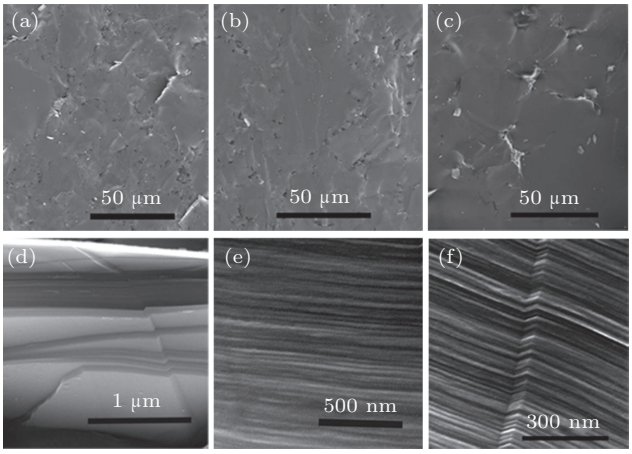


Fig. 2. SEM results of as-synthesized sample, showing (a)–(c) SEM results of B_4C prepared at 5.2 GPa for 15 min, with different temperatures of 1800 °C, 2000 °C, 2200 °C, respectively, and (d)–(f) magnified parts of panels (a)–(c), respectively.

All samples are then polished and examined by Vickers hardness (H_v) measurement, which are characterized by the Vickers indentation method with a pyramidal diamond indenter. The fracture toughness (K_{1C}) of B_4C is calculated after

being indented. The Vickers hardness data measured at difference loading pressure for B_4C are shown in the inset of Fig. 3. The hardness decreases with loading pressure increasing. In recent studies, researchers suggest that hardness for hard and brittle materials should be reported in the asymptotic-hardness region under the prerequisite of a well-controlled indentation process.[20,21] The hardness value of B_4C is converged at an applied load of 9.8 N. So, we measure the hardness value of B_4C synthesized at difference temperature with an applied load of 9.8 N and the Vickers hardness data are shown in Fig. 3. It is obvious that the hardness is enhanced with the increase of density at a higher temperature. The highest hardness value is 42.4 GPa measured at 9.8 N for B_4C synthesized at 2200 °C, which is much superior to all the reported values (26 GPa–37 GPa) and also higher than the values of single-crystal B_4C in Refs. [3], [15], [22], and [23]. The fracture toughness is 4.51 MPa·$m^{1/2}$, which is superior to that of phase-pure B_4C (2.5 MPa·$m^{1/2}$–3.0 MPa·$m^{1/2}$) synthesized by the conventional method, corresponding to a growth rate ranging between 50% and 80%.[3] The relatively high hardness and fracture toughness for B_4C may be caused by the fine nanosheets with thickness in a range of about 10 nm–20 nm. Reducing the particle size is found to be an efficient method to improve the mechanical properties. The compacting of smaller grain sizes leads to a greater concentration of grain boundaries. Thus, there is a greater frequency at which moving dislocations encounter grain boundaries. The resulting dislocation pileups at grain boundaries require a larger stress for further deformation, resulting in a greater measured hardness value. Two-dimensional nanostructures are a promising platform for producing hybrid structures and improving structural and mechanical properties of metal matrix composites.[24] The combination of sheet-like B_4C with the addition of additives to form a hybrid structure should improve the hardness and fracture toughness. Consequently, using the HPHT method to fabricate B_4C with the addition of additives may be an effect way to increase hardness and fracture toughness.

Oxidation resistance is a very important property for B_4C. Here, we study the oxidation resistance of B_4C prepared at 2200 °C. It has been reported that the B_4C has a good oxidation resistance beyond 1000 °C.[3] So, the oxidation tests are conducted in a muffle furnace and samples are heated to temperatures 700 °C, 1100 °C, and 1300 °C, respectively, with the dwelling times 5 h and 10 h in stagnant air. The furnace is then cooled naturally. The sample vanishes after being heated at a temperature of 1300 °C, due to B_2O_3 volatilizing when temperature approaches to 1300 °C. The thickness values of oxidation layer are ∼ 3 μm and ∼ 21 μm for 700 °C and 1100 °C, respectively. The thickness of oxidation layer does not change apparently as heating time increases. Surface morphologies of the oxidized specimens are shown in Fig. 4. The B_4C and B_2O_3 are connected through the grain boundaries. Therefore, the oxidized B_4C generates the oxidation layer on the surface in oxidation process which acts as O_2 barrier layer to resist oxygen corrosion in the interior of the sample. These results indicate that the B_4C has a good property of oxidation resistance.

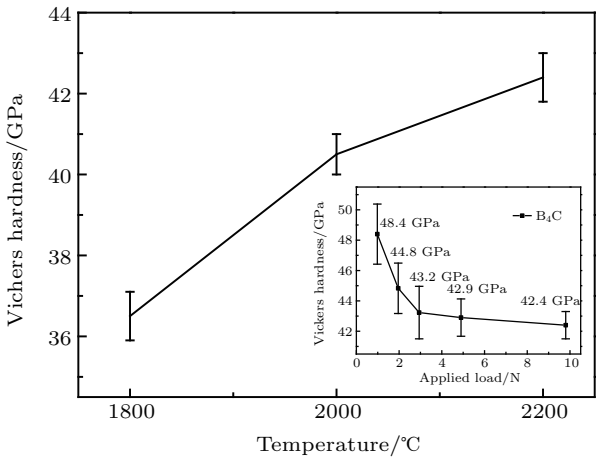


Fig. 3. Variation of hardness with temperature for B_4C synthesized at 5.2 GPa and temperatures 1800 °C, 2000 °C, and 2200 °C for 15 min. Inset shows measured Vickers hardness of B_4C synthesized at 5.2 GPa and temperatures of 2200 °C for 15 min at different applied loads.

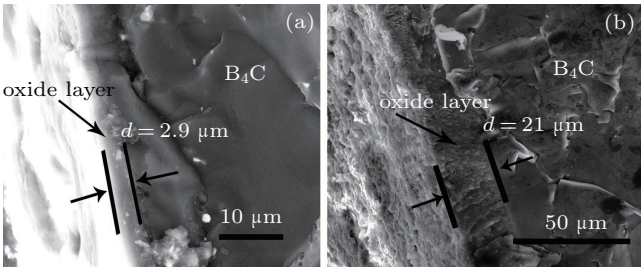


Fig. 4. Surface morphology of the oxidized B_4C heated in the air at temperatures (a) 700 °C and (b) 1100 °C.

4. Conclusions and perspectives

In summary, this study presents a novel process for manufacturing high-quality dense B_4C with a two-dimensional nanosheet structure. The pressure assisted sintering methods are useful in restraining crystal grain from growing up in the recrystallizing process. The sheet-like B_4C particles show excellent mechanical properties, including a Vickers hardness value of 42.4 GPa and fracture toughness value of 4.51 MPa·$m^{1/2}$. The B_4C shows a good property of oxidation resistance even under temperature up to 1100 °C by generating the oxidation layer on the surface to provide effective protection against oxidation.

References

[1] Domnich V, Reynaud S, Haber R A and Chhowalla M 2011 *J. Am. Ceram. Soc.* **94** 3605

[2] Sarithadevi H V, Swapna M S, Ambadas G and Sankararaman S 2018 *Chin. Phys. B* **27** 107702
[3] Suri A K, Subramanian C, Sonber J K and Murthy T S R C 2010 *Metall. Rev.* **55** 4
[4] Thévenot F 1990 *J. Eur. Ceram. Soc.* **6** 205
[5] Bao L H, Li C, Tian Y, Tian J F, Hui C, Wang X J, Shen C M and Gao H J 2008 *Chin. Phys. B* **17** 4247
[6] Li L W 2016 *Chin. Phys. B* **25** 037502
[7] Cho N, Bao Z and Speyer R F 2005 *J. Mater. Res.* **20** 2110
[8] Lee H and Speyer R F 2003 *J. Am. Ceram. Soc.* **86** 1468
[9] Rehman S S, Wei J, Fu Z, Wang W, Hao W, Asif M and Zhang J 2015 *J. Eur. Ceram. Soc.* **35** 1139
[10] Lee H and Speyer R F 2004 *J. Am. Ceram. Soc.* **85** 1291
[11] Roy T K, Subramanian C and Suri A K 2006 *Ceram. Int.* **32** 227
[12] Bhattacharya A K and Petrovic J J 1992 *J. Mater. Sci.* **27** 2205
[13] Ji W, Todd R I, Wang W, Wang H, Zhang J and Fu Z 2016 *J. Eur. Ceram. Soc.* **36** 2419
[14] Moradkhani A, Baharvandi H and Samani M M M 2016 *Mater. Sci. & Eng. A* **665** 141
[15] Badica P, Borodianska H, Xie S, Zhao T, Demirskyi D, Li P, Tok A I Y, Sakka Y and Vasylkiv O 2014 *Ceram. Int.* **40** 3053
[16] Gan W M, Zheng M Y, Chang H, Wang X J, Qiao X G, Wu K, Schwebke B and Brokmeier H G 2009 *J. Alloys & Compd.* **470** 256
[17] Tian Y, Bo X, Yu D, Ma Y, Wang Y, Jiang Y, Hu W, Tang C, Gao Y and Luo K 2013 *Nature* **493** 385
[18] Niihara K, Nakahira A and Hirai T *Journal of the American Ceramic Society* **67** c-13
[19] Qiu W, Xie X Y, Qiu J, Fang W H, Liang R, Ren X, Ji X, Cui G, Asiri A M, Cui G, Tang B and Sun X 2018 *Nat. Commun.* **9** 3485
[20] Brazhkin V, Dubrovinskaia N, Nicol M, Novikov N, Riedel R, Solozhenko V and Zhao Y 2004 *Nat. Mater.* **3** 576
[21] Qin J, He D, Wang J, Fang L, Lei L, Li Y, Hu J, Kou Z and Bi Y 2008 *Adv. Mater.* **20** 4780
[22] Domnich V, Gogotsi Y, Trenary M and Tanaka T 2002 *Appl. Phys. Lett.* **81** 3783
[23] Hayun S, Paris V, Dariel M P, Frage N and Zaretzky E 2009 *J. Eur. Ceram. Soc.* **29** 3395
[24] Alizadeh M, Alizadeh M and Amini R 2013 *J. Mater. Sci. & Technol.* **29** 725