

Fabrication and Mechanical Properties of Boron Nitride Nanotube Reinforced Boron Carbide Ceramics

Bingsai Liu

Guilin University of Technology

Yuanping Gu

Guilin Medical University Affiliated Hospital

Yuchun Ji

Guilin University of Technology

Guoyuan Zheng

Guilin University of Technology

Feiwen Ma

Guilin University of Technology

Jilin Wang (✉ jilinwang@glut.edu.cn)

Guilin University of Technology

Yi Wu

Guilin University of Technology

Fei Long

Guilin University of Technology

Bing Zhou

Guilin University of Technology

Research Article

Keywords: Boron carbide, Boron nitride nanotubes, Spark plasma sintering, Mechanical property

Posted Date: August 31st, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-67675/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Journal of the Ceramic Society of Japan on March 1st, 2021. See the published version at <https://doi.org/10.2109/jcersj2.20211>.

Abstract

A series of BNNTs/B₄C composite ceramic were prepared by the spark plasma sintering (SPS) technology using boron carbide (B₄C) powders as the matrix and boron nitride nanotubes (BNNTs) as the toughening phase. The XRD, SEM, TEM and HR-TEM were used to characterize the B₄C samples. The influence of sintering temperature, BNNTs content and matrix particle size on the microstructures and mechanical properties of B₄C composite ceramics, as well the toughening mechanism were investigated in detail. The experimental results showed that changing the particle size of the powder, increasing the sintering temperature and adding BNNTs could significantly improve the mechanical properties of the material. The ceramic samples obtained by adding 5wt.% BNNTs content sintered at 1750°C displayed the best mechanical properties. Its relative density, microhardness and fracture toughness respectively were 99.41%, 32.68 GPa and 6.87 Mpa·m^{1/2}, respectively. In particular, the fracture toughness value of the BNNTs/B₄C composite ceramic was 54.59% higher than that of B₄C ceramics without BNNTs.

1. Introduction

Boron carbide (B₁₂C₃ or B₄C) is a kind of oxide light solid material, its single hexahedron diamond crystal cell contains 15 atoms (composition B₁₁C icosahedron and a linear C-B-C three atomic chain, both by covalent bond connection, form a stable structure) [1, 2]. The highly stable covalent bond between B and C atoms in B₄C and its special crystal structure make B₄C have many excellent physical and chemical properties. For example, low density (2.52 g·cm⁻³), high hardness (> 30 Gpa, second only to diamond and cubic boron nitride), high melting point (2450°C), high temperature wear resistance (1400°C to 0.05), low thermal expansion coefficient (about 5.73 × 10⁻⁶/°C) and the thermoelectric performance, thermal neutron absorption ability, etc [3–6]. These properties make B₄C have broad application prospects in high-performance engineering ceramics, cutting tools, composite armor, body armor and other national defense and military industries. It is an important strategic material material in today's national economy and national defense construction [7, 8]. However, the high covalent bonds of B₄C content(> 90%) and high melting point, resulting in B₄C ceramic sintering difficulties and poor toughness(2–4 Mpa·m^{1/2}),these make the mechanical properties unable to be further improved, and greatly limits the application range of B₄C ceramics as structural ceramics [9].

At present, particle toughening and whisker (fiber) toughening are effective methods to improve fracture toughness of ceramics. Baris Yavas et al used SPS technology to prepare CNTs/B₄C ceramic composites with carbon nanotubes (CNTs) as toughening phase [10]. The results showed that adding CNTs or increasing the heating rate can improve the fracture toughness of B₄C ceramics. Recent years studies have found that BNNTs have better comprehensive mechanical properties, chemical stability and oxidation resistance than CNTs, making them an ideal toughening material [11, 12]. In 2018, Li used hot-pressing sintering technology to study silicon nitride (Si₃N₄) ceramics added with and without boron nitride nanotubes (BNNTs) were fabricated. The results showed that BNNTs can enhance the fracture

toughness of Si_3N_4 dramatically, which increases from $7.2 \text{ Mpa}\cdot\text{m}^{1/2}$ (no BNNTs) to $10.4 \text{ Mpa}\cdot\text{m}^{1/2}$ (0.8 wt.% BNNTs) [13]. Zeng Xiaojun et al studied the microstructure and mechanical properties of BNNTs/ B_4C composite ceramics by hot-pressing sintering process, and the results showed that the bending strength and fracture toughness of the composite with 1.5wt.% BNNTs increased by 28% and 31.5%, respectively [14, 15].

In this paper, the high-activity B_4C micro-nano powders was used as the matrix and the BNNTs/ B_4C composite ceramics were prepared by SPS low-temperature rapid sintering technology. The influence of the sintering temperature, BNNTs content and matrix particle size on the microstructures and mechanical properties of B_4C composite ceramics, as well the toughening mechanism were also investigated in detail.

Experimental section

1.1. Experimental Reagents

The commercially available micron-sized B_4C powders were purchased from Mudanjiang Boron Carbide Co., PR China (Particle size of about $3.5 \mu\text{m}$, purity > 98%, Fig. 1(a)), homemade B_4C nano-powders (Fig. 1(b)) [16], homemade BNNTs (Figs. 1(a) and (b)) [17, 18].

1.2. Preparation of BNNTs/ B_4C composite ceramics

Raw materials and pre-heat treatment: using homemade B_4C (H- B_4C) nano-powders and commercial B_4C (C- B_4C) micro-powders (Figs. 1(a) and 7(b)) as the experimental matrix materials. First, mixing B_4C -BNNTs according to a certain ratio; Then, putting the mixture into the mixing tank and grind for 6 h; Finally, the obtained mixture was subjected to pickling (removal of impurities) water washing, ethanol washing, suction filtration and vacuum drying and storage.

SPS sintering of the mixture: taking the mixture out of the vacuum drying oven, weighing an appropriate amount of the mixture and grinding for 15 min, putting the ground mixture into a graphite mold with a diameter of 15 mm for SPS sintering. The sintering temperature was $1700 \text{ }^\circ\text{C}$, the heating rate was $200 \text{ }^\circ\text{C}/\text{min}$, the sintering pressure was 30 MPa, and the holding time was 5 min. After the sintering, the graphite layer on the surface of the sintered sample was removed, then polished, ultrasonically cleaned and dried to perform related test and characterization. The experimental technical parameters of the samples are shown in Table 1

Table 1
Experimental technical parameters of the sample

Formulation	B ₄ C types	B ₄ C content /wt.%	BNNTs content /wt.%	Sintering temperature/°C	Sintering method
S1	C-B ₄ C	100	0	1700	SPS
S2	C-B ₄ C	95	5	1700	SPS
S3	C-B ₄ C	90	10	1700	SPS
S4	H-B ₄ C	100	0	1700	SPS
S5	H-B ₄ C	95	5	1700	SPS
S6	H-B ₄ C	90	10	1700	SPS
S7	H-B ₄ C	95	5	1600	SPS
S8	H-B ₄ C	95	5	1750	SPS
S9	H-B ₄ C	95	5	1800	SPS

1.3. Characterization

The relative density of the sintered sample was measured by the Archimedes method. The microstructure of the cross-section of the ceramic bulk sample was characterized by scanning electron microscope (SEM, FEI Quanta FEG 250 and Hitachi S-3400), transmission electron microscopy (TEM, JEOL JEM-2100F and Philip CM12). Vickers hardness tester and indentation method were used to test the microhardness and fracture toughness of the samples (the 430 Vickers Hardness Tester, Walbert, USA). The extrinsic load and dwell time of hardness test were respectively 5 N and 10 s. The extrinsic load and dwell time of fracture toughness test were 15 N and 15 s. And five positions on top and bottom surfaces were respectively tested to determine the average value of microhardness and fracture toughness test.

2. Results And Discussion

2.1. The influence of BNNTs content

Figure 2 is the XRD pattern of B₄C samples fabricated by sintering at 1700 °C with different adding amounts of BNNTs. It can be seen from the Fig. 2 that there were obvious XRD characteristic diffraction peaks of B₄C and h-BN in the samples of S-B₄C-5wt.% BNNT and S-B₄C-10wt.% BNNTs, and no other impurity peaks were found. This shown that the content of amorphous carbon in commercial boron carbide powder was relatively low. For samples Z-B₄C-5wt.% BNNTs and Z-B₄C-10wt.% BNNTs, there were obvious graphitic carbon peaks in the corresponding XRD spectra. This showed that part of the

amorphous carbon contained in the home-made boron carbide powder was completely transformed into crystalline carbon (graphite) under high temperature conditions.

The fracture morphology of ceramic samples with different ceramic matrix and different contents of BNNTs is shown in Fig. 3. It could be seen from Fig. 3 that all the sample sections showed low porosity and high density. It could be seen from Fig. 3(e) that there were some pores of about 0.5 μm and a small amount of white impurity particles (shown in the white wire frame) on the cross-section of C-B₄C ceramic. It was also found that the section of the C-B₄C sample was flat, and it was speculated that the main fracture mode was transgranular fracture. When adding 5wt.% BNNTs, the C-B₄C-5wt.% BNNTs sample appeared some intergranular fractures (Fig. 3(g)), indicating that the addition of a certain amount of BNNTs changed the fracture mode of B₄C ceramics. When the content of BNNTs was further increased to 10 wt%, there were basically no pores in the cross section of C-B₄C-10wt.% BNNTs, which was basically close to the theoretical density. It was worth noting that the cross-sections of H-B₄C and H-B₄C-5wt.% BNNTs ceramics showed some grooves formed after the B₄C grains were pulled out during the fracture process of the sample (shown in the square wire frame in Figs. 3(a) and 3(b). When the content of BNNTs was too high, the agglomeration between nanotubes was significant (Figs. 3(d) and 3(h)). This kind of agglomeration was equivalent to micron-sized defects, and this loose agglomerate will also produce more void defects at the junction of the nanotube and the matrix, which will hinder the densification of the matrix [14, 19].

It can be seen from Fig. 4(a) that when the content of BNNTs was the same, the B₄C-based ceramic composite material with H-B₄C nano-powders as the matrix had a higher relative density than the B₄C-based ceramic composite material with C-B₄C powders as the matrix. The reason may be that the particles of H-B₄C nano-powders are much smaller than micron-sized C-B₄C powders particles, under the same conditions, the smaller the particle size of the raw material, the more conducive to obtaining high-density ceramic samples. When C-B₄C was used as the matrix, the relative density of the B₄C-BNNTs ceramic composite material increased accordingly with the increase of BNNTs content. The reason is that because BNNTs have a relatively small particle size, in the ceramic sintering process, BNNTs are easy to fill the gaps between B₄C micron grains. However, when H-B₄C was used as the matrix, the relative density of B₄C-BNNTs ceramic composite material decreased slightly with the increase of BNNTs content [20], and the relative density of the four was close to the theoretical density.

It can be seen from Figs. 4(b) that under the same conditions, H-B₄C as a matrix had a higher hardness than C-B₄C. The reason may be that the particle size of H-B₄C powders are nanometer, while the particle size of C-B₄C powders are micrometer. Under the same conditions, the smaller the particle size of the raw material, the more conducive it is to obtain ceramic samples with high density and high hardness. When the matrix was the same, with the increase of BNNTs content, the hardness of the ceramic composite material gradually decreased. The reason may be as the content of BNNTs continued to increase, the possibility of nanotube agglomeration became higher, and the defects and matrix pores introduced by

agglomerations will increase, which will reduce the continuity and density of the ceramic matrix, which will eventually lead to the hardness of the ceramic material decreases [21].

It can be seen from Fig. 4(c) that whether the ceramic matrix is C-B₄C or H-B₄C, as the content of BNNTs increased, the fracture toughness of the composite ceramics first increased and then decreased. When the content of BNNTs was 5wt.%, the fracture toughness of C-B₄C-5wt.%BNNTs and H-B₄C-5wt.%BNNTs ceramics were both the best, respectively 4.31 Mpa·m^{1/2} and 5.92 Mpa·m^{1/2}. The results showed that adding an appropriate amount of BNNTs could effectively improve the fracture toughness of B₄C ceramics. The reason is that BNNTs are uniformly distributed on the grain boundaries and grains of the B₄C matrix. During the crack propagation process, the excellent mechanical properties of the nanotubes can effectively prevent the further propagation of the crack, thereby improving the fracture toughness of the ceramic [14, 22–24]. However, with the further increase of the BNNTs content, the agglomeration of the nanotubes continued to increase, which caused the pores around the nanotubes to increase, which easily induced crack propagation and reduced the toughness of the composite material. Thus, the optimum BNNTs content for B₄C composite ceramics in our study is determined to be 5wt.%. In addition, it was found that H-B₄C has better mechanical properties than C-B₄C under the same conditions.

2.2. The influence of sintering temperature

The mechanical properties of superhard structure ceramics are directly determined by its microstructure, which is affected by the sintering temperature. Figure 5 illustrates the SEM patterns of H-B₄C-5wt.% BNNTs samples section at different temperatures. It can be seen from Fig. 5(a) that at low temperatures, there existed more pores and pits in sintered samples, and the powder particles failed to combine with each other to form obvious grain boundaries. With the increase of the sintering temperature, the sample grains tended to fuse, and the grain size increased gradually, the pores reduced and closed, and the density increased. When the sintering temperature reached 1750 °C, the sample was almost completely sintered. The main reason is as the sintering temperature increases, the process of surface diffusion and interface diffusion mass transfer speeds up, the density increases, and the pores are continuously eliminated. When the sintering temperature was 1800°C, the sample section was uneven, which may be due to the high temperature, the grain boundary migration rate was greater than the pore migration rate, the grain size increased significantly, and small closed pores were formed inside the grains [15].

It can be seen from Fig. 6 that with the increase of the sintering temperature, the change trend of the microhardness of the H-B₄C-5 wt% BNNTs ceramic sample was the same as the change trend of the relative density of the B₄C ceramic, indicating that the particle rearrangement of the B₄C ceramic mixed with BNNTs was enhanced in the sintering process. With the increase of the sintering temperature, the driving force of B₄C sintering continued to increase, and the continuous growth of crystal grains increased the sintering densification of ceramics, which made the microhardness increase, gradually. When the sintering temperature was 1750°C, the microhardness and relative density of the sintered sample were the largest, which are 99.14% and 32.68 GPa, respectively. As the temperature continued to

rise, the particle size grew rapidly, and more pore defects were produced, which caused a decrease in the density and hardness of the composite material.

It can be seen from Fig. 6(b) that the trend of the fracture toughness of the composite material with the sintering temperature was similar to that of the microhardness. When the temperature was lower than 1750°C, the fracture toughness of the ceramic continued to increase as the temperature rose. When temperature reached 1750 °C, the fracture toughness was the largest at 6.87 Mpa·m^{1/2}. Thus, the optimum sintering temperature for H-B₄C-5wt.% ceramics in our study is determined to be 1750°C.

The reason is that when the sintering temperature increases, the bonding strength of the heterogeneous interface between BNNTs and the B₄C ceramic matrix increases. When the crack extends to the surface of the nanotube, the crack propagation path or crack growth energy is increased through crack deflection, bridging and pull-out effects. As the temperature continued to rise, the fracture toughness of ceramic materials decreased significantly. The reason is the B₄C grains grow rapidly, and the toughening effect of BNNTs is difficult to offset the abnormal growth of B₄C grains and the abnormal interface strength reduction, which leads to a significant reduction in the fracture toughness of the composite material [20].

2.3. Toughening mechanism

Figure 7 shows the microstructure of the BNNTs/B₄C composites. From Fig. 7(a), we can find that there is a relatively long groove (marked by the frame) formed between the crystal planes due to the pulling out of the nanotube. In addition, the nanotubes marked by the arrows in the Figure shown a clear hollow structure and the phenomenon of cracking occur, which was caused by the force during the cracking process. It could be inferred from this phenomenon that the mode of strengthening and toughening the B₄C ceramic was the fiber pull-out effect. In Fig. 7(c), BNNTs was connected between the two grain boundaries. It was speculated that the mechanism of strengthening and toughening the ceramic was the fiber bridging mechanism.

3. Conclusions

B₄C ceramics with and without BNNTs are fabricated by spark plasma sintering method. Regardless of whether the B₄C ceramic matrix is micron-powders or nano-powders, adding of BNNTs enhances the fracture toughness greatly. The optimum BNNTs content is 5wt.%. Moreover, adding a certain amount of BNNTs has little effect on the microhardness and density of B₄C-based ceramics. The relative density, microhardness and fracture toughness of H-B₄C-5wt.% BNNTs ceramics increased with the increase of sintering temperature, reaching 99.41%, 32.68 GPa and 6.87 Mpa·m^{1/2} (maximum value) at 1750°C. However, too much BNNTs can degrade the fracture toughness of the ceramics instead. The toughening mechanism may be pull-out of BNNTs, bridging of BNNTs and crack deflection. It is hoped that the research in this work can provide certain experimental and theoretical reference for the research on the strengthening and toughening of boron carbide-based ceramics.

Declarations

Acknowledgments

The authors acknowledge the financial support from National Natural Science Foundation of China (No.51972071), Guangxi Natural Science Foundation (2018GXNSFAA050032), Non-Ferrous Metals and Materials Processing New Technology Ministry of Education Key Laboratory Open Fund Project (No. 19KF-5 and No.19AA-14), Guilin Scientific Research and Technology Development Program (No.20190204-2).

References

1. Lazzari R, Vast N, Besson J, *et al.* Atomic structure and vibrational properties of icosahedral B₄C boron carbide. *Phys Rev Lett* 1999, **83**: 3230-3233.
2. Mauri F, Vast N, Pickard C J. Atomic structure of icosahedral B₄C boron carbide from a first principles analysis of NMR spectra. *Phys Rev Lett* 2001, **87**: 085506.
3. Mori T. Thermoelectric and magnetic properties of rare earth borides: Boron cluster and layered compounds. *J Solid State Chem* 2019, **275**: 70-82.
4. Werheit H, Leithejasper A, Tanaka T, *et al.* Some properties of single-crystal boron carbide. *J Solid State Chem* 2004, **177**: 575-579.
5. Watts JL, Spratt HJ, Talbot PC, *et al.* Precision structural and phase analysis of boron carbide. *Ceramics International* 2020, **46**: 11033-11040.
6. Suri AK, Subramanian C, Sonber JK, Murthy TS. Synthesis and consolidation of boron carbide: a review. *Int Mater Rev* 2020, **55**: 4-40.
7. Thevenot F. Boron carbide a comprehensive review. *J Eur Ceram Soc* 1990, **6**: 205-225.
8. Domnich V, Reynaud S, Haber RA, *et al.* Boron carbide: Structure, properties, and stability under stress. *J Am Ceram Soc* 2011, **94**: 3605-3628.
9. Xie KY, Toksoy MF, Kuwelkar K, *et al.* Effect of alumina on the structure and mechanical properties of spark plasma sintered boron carbide. *J Am Ceram Soc* 2014, **97**: 3710-3718.
10. Yavas B, Sahin F, Yucel O, *et al.* Effect of particle size, heating rate and CNT addition on densification, microstructure and mechanical properties of B₄C ceramics. *Ceramics International* 2015, **41**: 8936-8944.
11. Chen Y, Bi J, Wang W, *et al.* Toughening in boron nitride nanotubes/silicon nitride composites. *Mater Sci Eng A* 2014, **590**: 16-20.
12. Wang W, Bi J, Sun K, *et al.* Fabrication of alumina ceramic reinforced with boron nitride nanotubes with improved mechanical properties. *J Am Ceram Soc* 2011, **94**: 3636-3640.
13. Li TF, Chen, YJ, Li, W, *et al.* Fabrication and mechanical properties of boron nitride nanotube reinforced silicon nitride ceramics. *Ceramics International* 2018, **44**: 6456-6460.

14. Zeng XJ, Liu WL, Feng ZQ, *et al.* Microstructure and mechanical properties of BNNTs/B₄C ceramic composites. *J Ceram* 2013, **34**: 438-442.
15. Zeng XJ, Liu WL, Feng ZQ, *et al.* Effect of sintering temperature on microstructure and mechanical properties of BNNTs/B₄C ceramic composites. *China Ceramics* 2014, **41**: 7021-7027.
16. Wang JL, Long F, Wang WM, *et al.* Reaction coupling preparation of high sintering activity boron carbide nano-powders. *Ceramics International* 2016, **42**: 6969-6977.
17. Wang JL, Li Z, Gu YP, *et al.* Synthesis of boron nitride nanotubes using glass fabrics as catalyst growth framework. *Ceramics International* 2015, **41**: 1891-1896.
18. Wang JL, Peng D, Long F, *et al.* Glass fabrics self-cracking catalytic growth of boron nitride nanotubes. *Solid State Sci* 2017, **64**: 23-28.
19. Li X, Gao Y, Pan W, *et al.* Fabrication and characterization of B₄C-based ceramic composites with different mass fractions of hexagonal boron nitride. *Ceramics International*, 2015, **41**: 27-36.
20. Jiang T, Jin Z, Yang J, *et al.* Investigation on the preparation and machinability of the B₄C/BN nanocomposites by hot-pressing process. *J Mater Process Technol* 2009, **209**: 561-571.
21. Alexander R, Murthy TSRC, Ravikanth KV, *et al.* Effect of graphene nano-platelet reinforcement on the mechanical properties of hot pressed boron carbide based composite. *Ceramics International* 2018, **44**: 9830-9838.
22. Chen M, Yin Z, Yuan J, *et al.* Microstructure and properties of a graphene platelets toughened boron carbide composite ceramic by spark plasma sintering. *Ceramics International* 2018, **44**: 15370-15377.
23. Wang WL , Bi JQ , Wang SR , *et al.* Microstructure and mechanical properties of alumina ceramics reinforced by boron nitride nanotubes. *J Eur Ceram Soc* 2011, **31**: 2277-2284.
24. Xu JJ, Bai YJ , Wang WL, *et al.* Toughening and reinforcing zirconia ceramics by introducing boron nitride nanotubes. *Materials ence & Engineering A* 2012, **546**: 301-306.

Figures

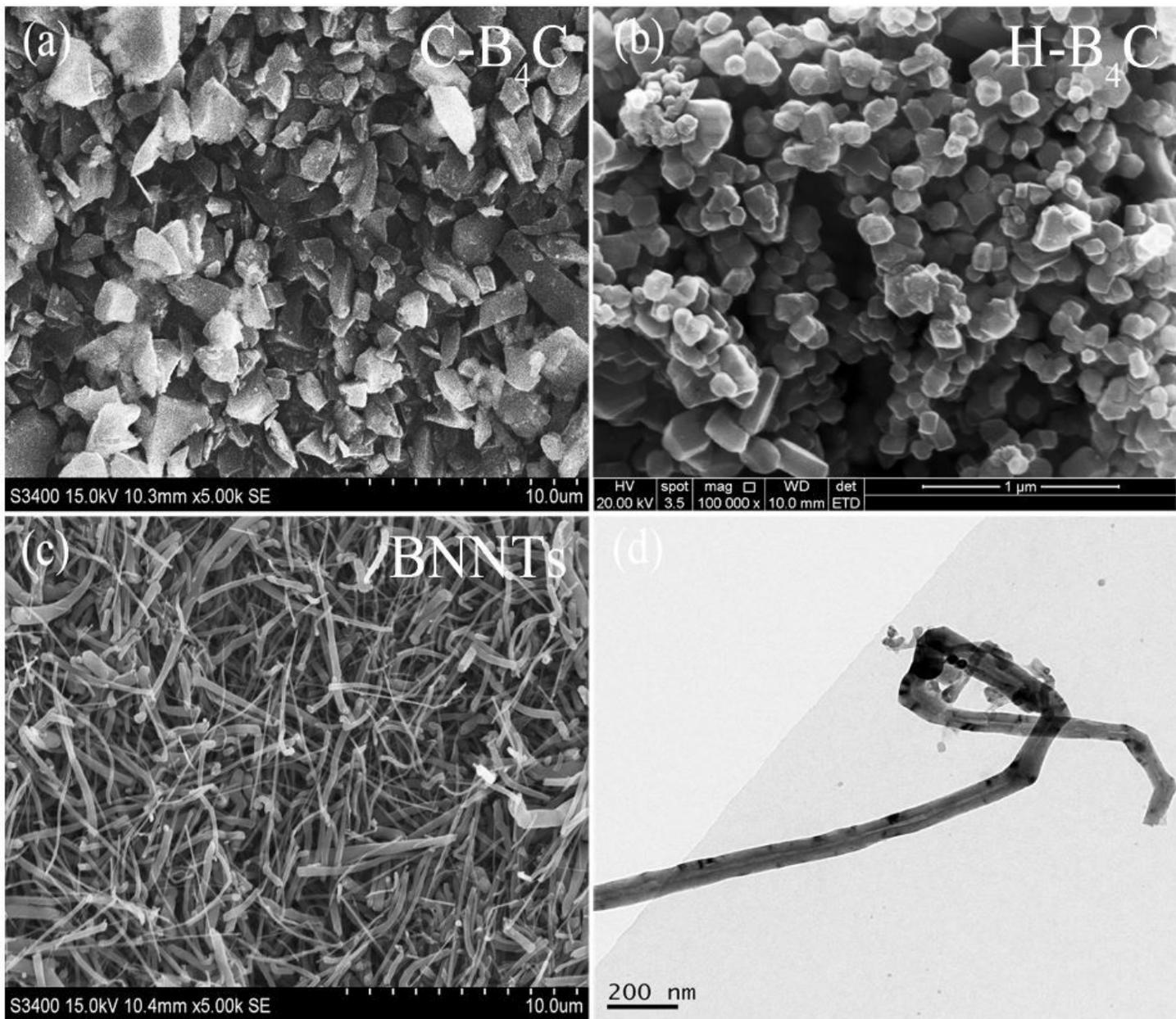


Figure 1

The typical SEM images of C-B₄C (a), H-B₄C (b) and BNNTs (c), (d).

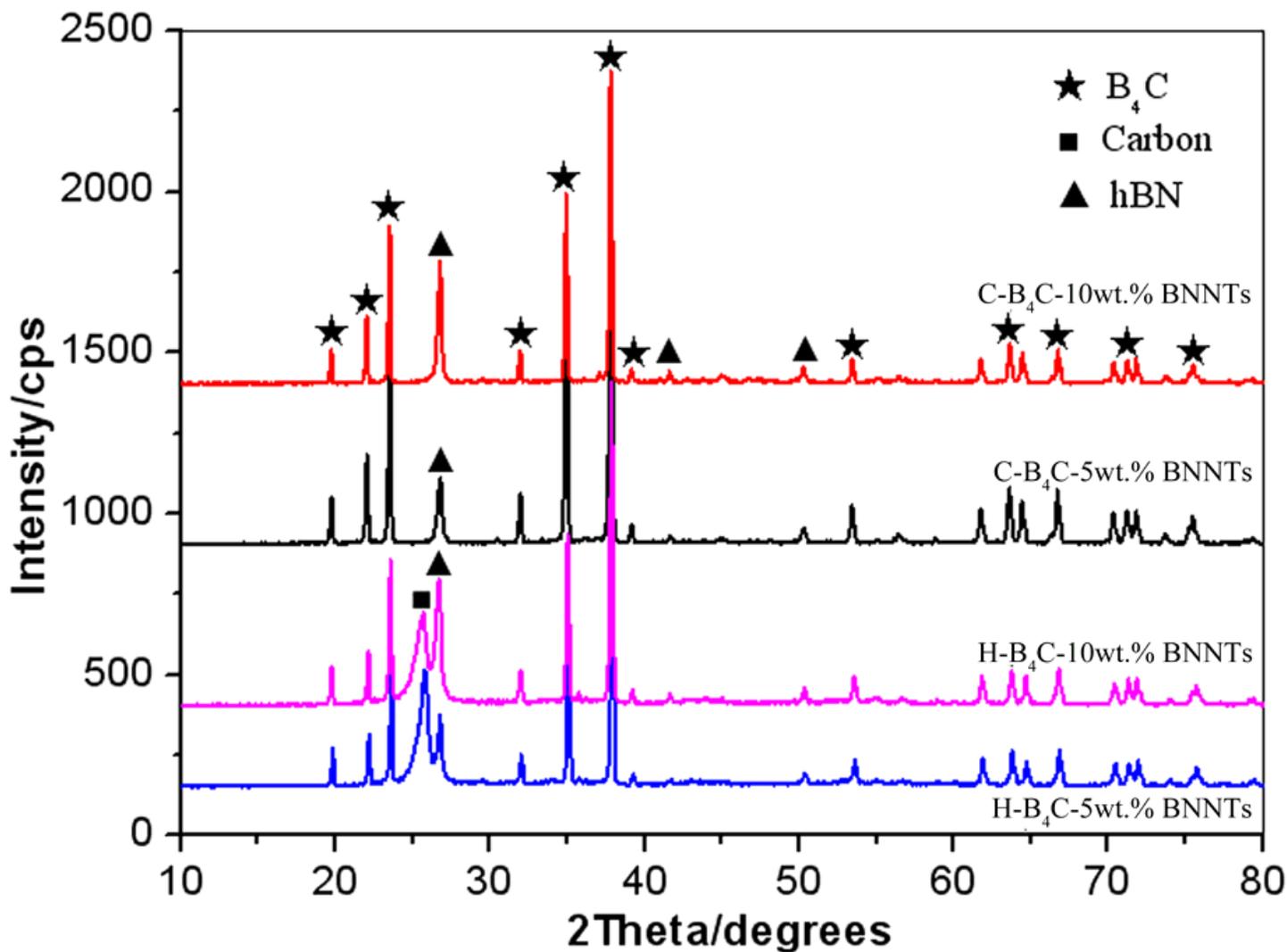


Figure 2

XRD patterns of B_4C samples fabricated by sintering at $1700^{\circ}C$ with different adding amounts of BNNTs (wt.%).

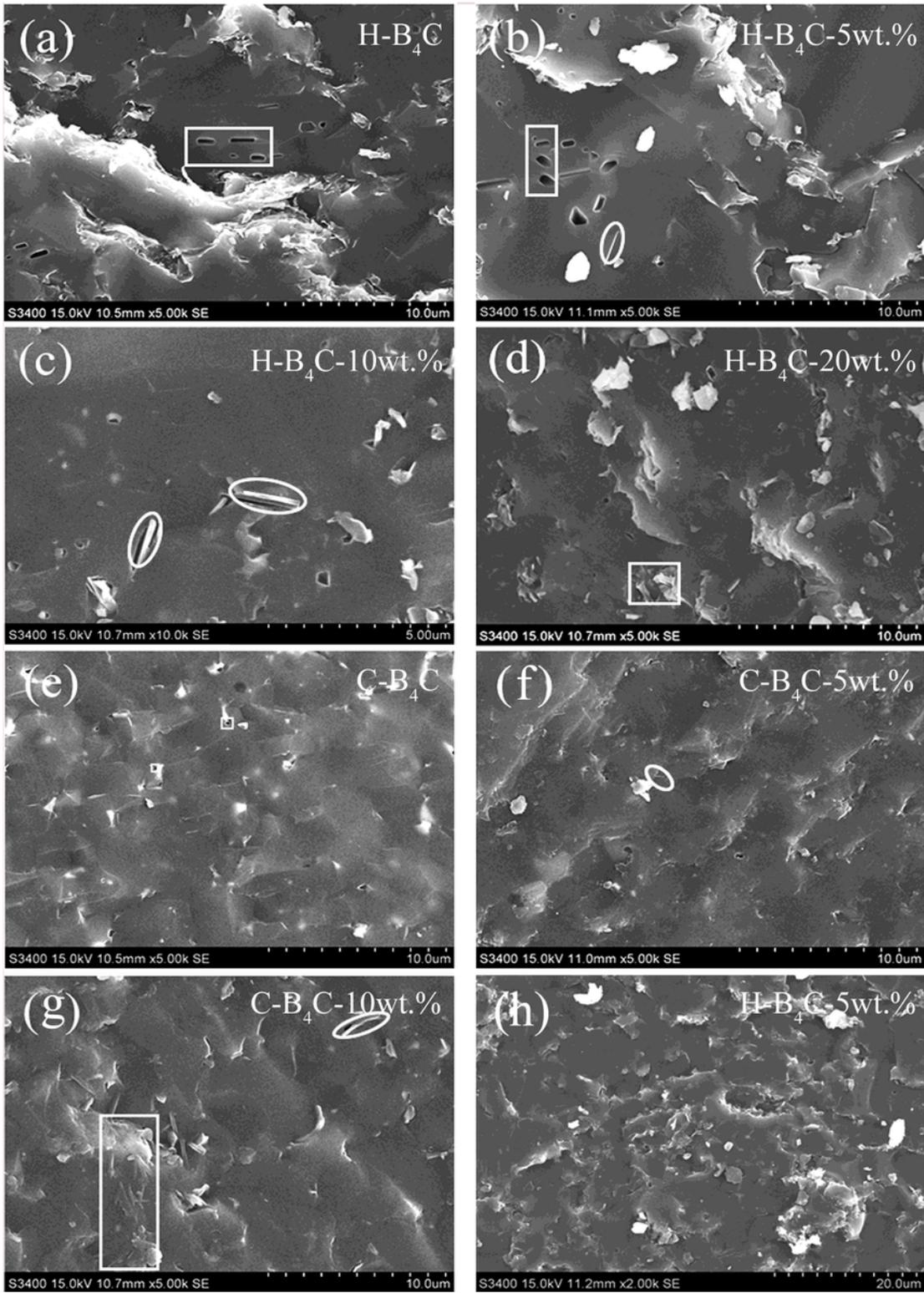


Figure 3

SEM images of the fracture surfaces of B₄C samples fabricated with different adding amounts of BNNTs.

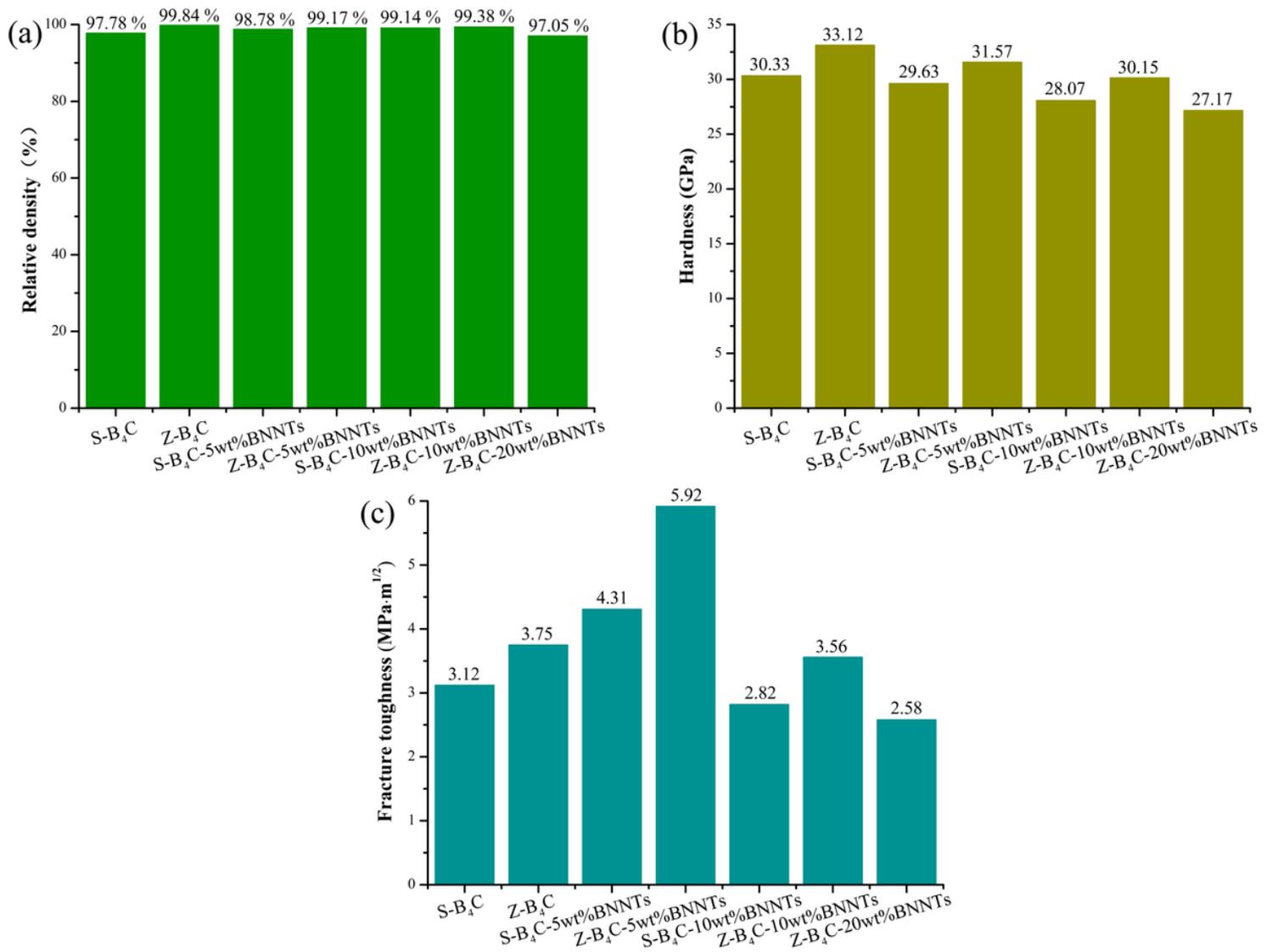


Figure 4

The relative densities, microhardness and fracture toughness of B₄C samples prepared by sintering at 1700°C with different adding amounts of BNNTs.

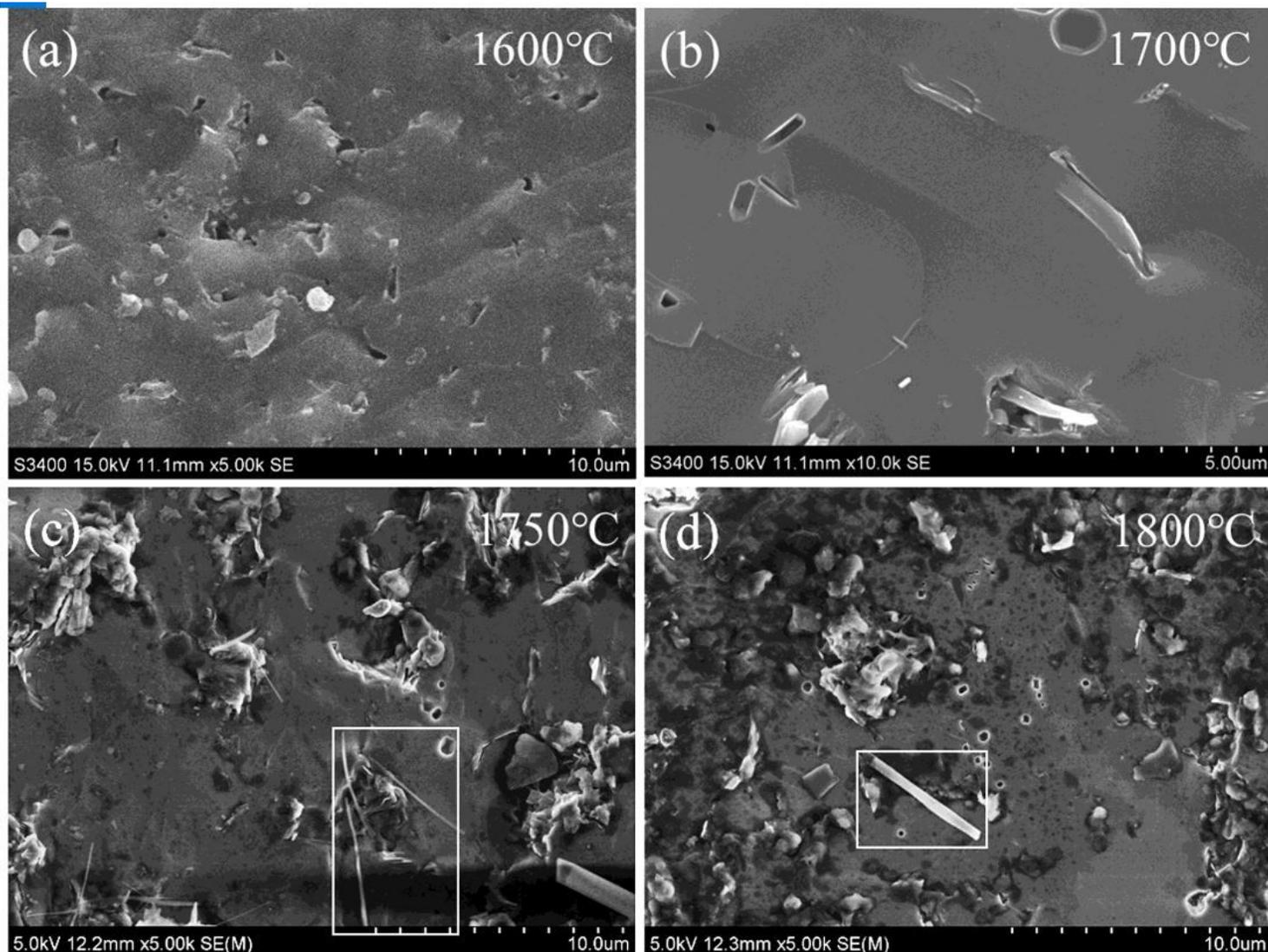


Figure 5

SEM images of the fracture surfaces of H-B4C ceramics fabricated by sintering at different temperatures with adding 5wt.% BNNTs.

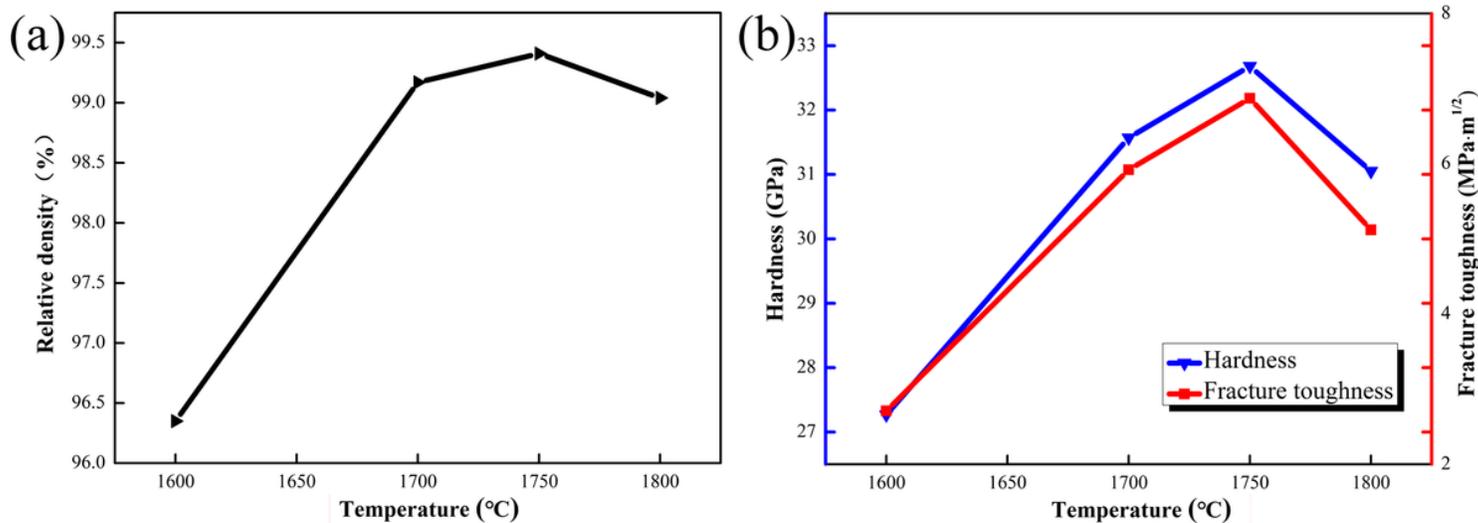


Figure 6

The relative densities and mechanical properties of B4C samples fabricated at different sintering temperatures with adding 5wt.% BNNTs.

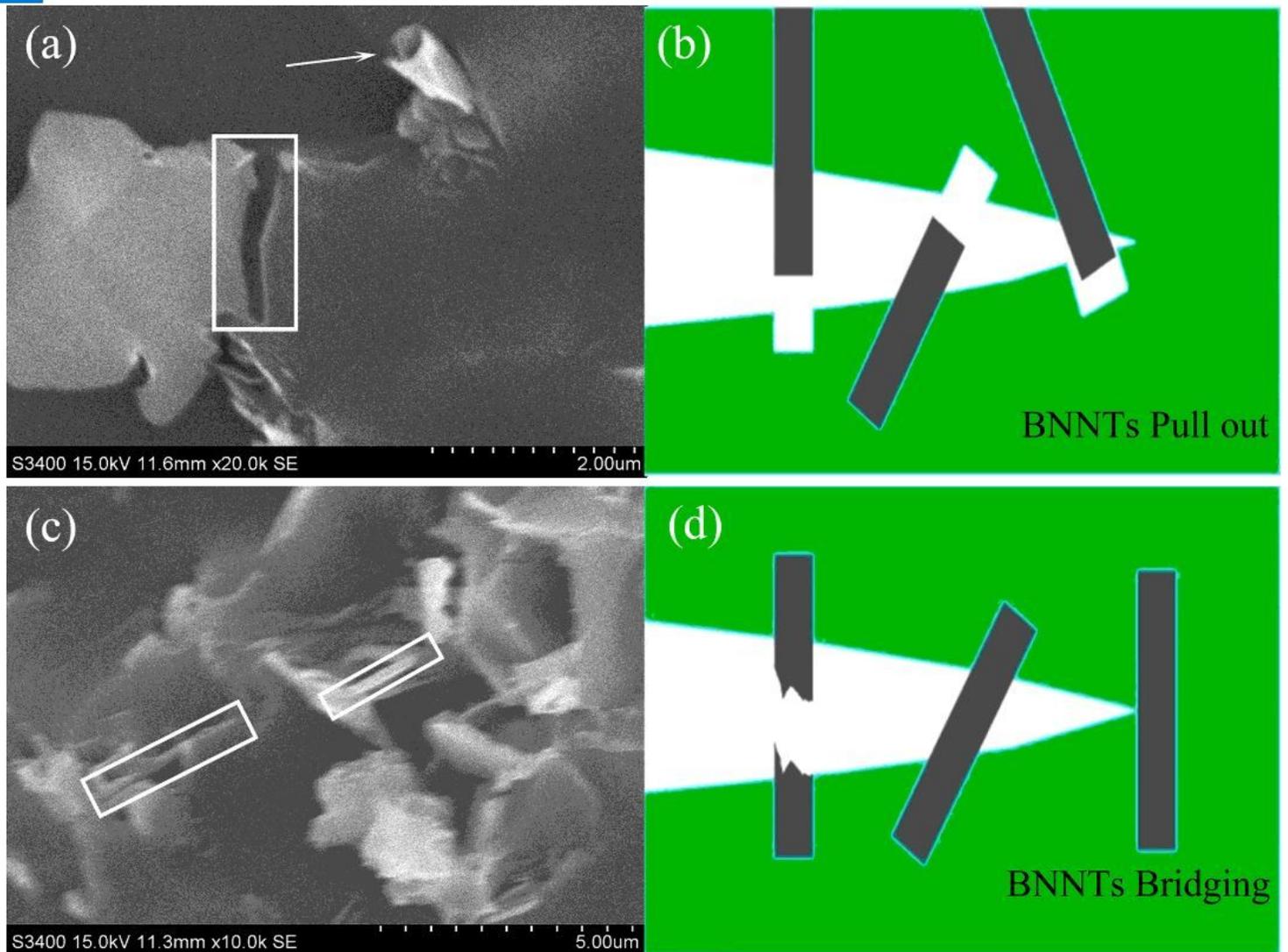


Figure 7

SEM images of the BNNTs/B4C composites: (a) and (c) fracture surface. The schematic indicated various toughening mechanisms: (b) BNNTs pull out. (d) BNNTs bridging.