Mechanical Properties of Boron Nitride Nanosheets (BNNSs) Reinforced Si_3N_4 Composites

Guandong Liang, Jianqiang Bi, Guoxun Sun, Yafei Chen and Weili Wang

Abstract The boron nitride nanosheets (BNNSs)/silicon nitride (Si_3N_4) composite ceramics were prepared by SPS sintering. BNNSs with few layers and transverse size in micron-scale were prepared by ball-milling and ultrasound-assisted liquid-phase stripping. In this work, it was found that the BNNSs prepared by these two methods could enhance the mechanical properties of silicon nitride ceramics, and of BNNSs/Si_3N_4 composite ceramics exhibit better bending strength when adding the ultrasound-assisted liquid-phase stripping BNNSs. The bending strength and fracture toughness of BNNSs/Si_3N_4 composite ceramics was increased by 36% and 51%, respectively, when 2 wt% BNNSs prepared by ball-milling method were added. The pullout of BNNSs, the bridging of cracks, and the deflection of cracks are the main factors of improving the toughness.

Keywords Boron nitride nanosheets · BNNSs/Si_3N_4 composite ceramics · Mechanical properties

Introduction

Graphene has been widely used as a reinforcement for ceramic matrix composites due to its excellent mechanical properties [1–3]. BNNSs, commonly known as "white graphene", has similar structural and mechanical properties to graphene. BNNSs also exhibit unique dielectric properties, insulating properties, and high temperature resistance, thus has become a promising enhancer [4].

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When graphene is employed as a reinforcing agent, it is easily oxidized by high temperature in the air, which greatly limits its application under high-temperature conditions [5]. In addition, due to its superior electrical conductivity, the application of graphene is also limited in wave-transparent materials and insulating materials. Boron nitride nanosheets have excellent dielectric properties [6] and high temperature resistance [5, 7], thus can replace graphene materials as reinforcing agents for composite materials in this field.

Silicon nitride ceramics have been widely used in high-speed cutting tools, engine parts, and aerospace radome materials due to their high strength, hardness, toughness, excellent wear resistance, thermal shock resistance, low dielectric constant and dielectric loss, and good creep resistance [4, 8–11]. In order to further improve the mechanical properties of the silicon nitride ceramics at high temperature, some reinforcing agents with excellent mechanical properties can be added, and it is obvious that the graphene materials have their limitations. Employing the BNNSs to enhancing the silicon nitride ceramics not only can improve the toughness of the silicon nitride ceramic, but can also reduce the dielectric constant of the silicon nitride ceramic, thus improving the wave transmission performance of the silicon nitride ceramic.

The efficient preparation of boron nitride nanosheets is one of the problems that has been plaguing researchers. Common preparation methods of boron nitride nanosheets include ball-milling, liquid-phase stripping, and chemical-vapor-deposition. The ball-milling method introduces a large number of defects into the nanosheet during the process, but its yield is high and the process is simple [12, 13]; the liquid-phase stripping method has low yield and is not easy to prepare in large quantities, but the prepared boron nitride nanosheets can keep the original crystal structure and have few defects [14–16]; the chemical-vapor-deposition method is expensive, and there are difficulties in that the nanosheet and the substrate are difficult to peel off, but it can realize the controllable preparation of the number of nanosheets [17].

Each of the above three methods for preparing boron nitride nanosheets has its own advantages. As far as we know, there are few reports about silicon nitride composite ceramics containing BNNSs nanosheets. In this paper, boron nitride nanosheets are prepared by ball-milling and liquid-phase stripping, respectively; the effects of nanosheets prepared by two methods on the mechanical properties of silicon nitride composite ceramics were also studied.

Experimental

Preparation of Boron Nitride Nanosheets

Preparation of BNNSs by Ultrasonic-Assisted Liquid-Phase Stripping

A mixed liquid of anhydrous ethanol and deionized water was used as a dispersion. 0.5 g of h-BN powder was added per 1000 ml of the dispersion (55 vol.% of absolute ethanol and 45 vol.% of deionized water [18]), and the mixture was continuously ultrasonicated for 20 h. After 48 h of standing, 40% of the liquid in the upper layer of the mixed disperse solution was taken for filtration, and the powder on the filter membrane was dried at 80 °C for 10 h, and then BNNSs was collected.

Ball-Milling Stripping BNNSs

Weigh 2.5 g of h-BN powder, add 250 ml of absolute ethanol (the ratio of grinding ball to material is 100:1, solvent to material ratio is 80:1) to two ball mill jars with a capacity of 500 ml, according to the ratio. The zirconia grinding ball was added, and after 18 h of ball-milling, a milky white solution with uniform peeling was obtained. The solution was sonicated for 2 h, then filtrated, and dried for 10 h to obtain BNNSs.

Preparation of BNNSs/Silicon Nitride Composite Ceramics

According to the experimental group, BNNSs with different mass fractions were weighed separately (Table 1). After adding a small amount of absolute ethanol, ultrasound was conducted for 2 h. Quantitative powders of silicon nitride, yttrium oxide (6 wt%), and alumina (4 wt%) were obtained according to the proportion. The above substances and a suitable amount of anhydrous ethanol were jointly added to the ball-milling jar. The uniform composite powder was obtained by wet-grinding zirconia ball for 6 h and drying for more than 24 h.

Each group of sufficient mixed powders was added to the graphite mold with a diameter of 30 mm and sintered by SPS. The mixture powders were then heated at a rate of 100 °C/min from room temperature and hot-pressing sintered at 1600 °C for 1 h under the pressure of 50 MPa in a flowing Ar atmosphere before the furnace cooled down to room temperature.

Table 1 Contents of each component in the mixed powder

Group	1	2	3	4	5	6
Mass fraction of BNNSs (%)	0	0.1	0.5	2	0.1	0.5
Mass fraction of Si_3N_4 (%)	90	89.9	89.5	88	89.9	89.5
Mass fraction of Al_2O_3 (%)	4	4	4	4	4	4
Mass fraction of Y_2O_3 (%)	6	6	6	6	6	6

Note BNNSs doped in No. 2, No. 3, and No. 4 are obtained by ball-milling method, while BNNSs doped in No. 5 and No. 6 are obtained by ultrasound-assisted peeling method

Tests and Characterization

The bending strength of the bar specimens (3.0 mm × 4.0 mm × 25 mm) was measured by a three-point bending test with a span of 20 mm at a crosshead speed of 0.5 mm/min. Three specimens were tested in each group. Besides, fracture toughness of three specimens (2.0 mm × 4.0 mm × 25 mm) for each sample was measured by the single-edge notched beam (SENB) method. A notch of 2.0 mm in depth and 0.3 mm in width was introduced in the middle of each specimen by a thin diamond blade. Both the bending strength and fracture toughness tests were conducted on a CMT5105 electromechanical universal testing machine (Shenzhen SANS Testing Machine Co., Ltd., Shenzhen, Guangdong, China). In addition, the morphology of BNNSs and the fracture surfaces of the composites were examined via thermal field emission scanning electron microscope (FESEM; Hitachi SU-70, Tokyo, Japan).

Results and Discussion

Figure 1 shows the SEM images of BNNSs prepared by two methods. From Fig. 1a, b, it can be seen that many fragments are adsorbed on the surface of boron nitride nanosheets prepared by ball-milling. One possible reason is that some nanosheets are grounded into fragments by high-speed rotating grinding balls, and these fragments are easily adsorbed on the surface of large-scale nanosheets. In contrast, few fragments were found in boron nitride nanosheets prepared by ultrasound-assisted liquid-phase peeling in Fig. 1c, d.

By comparing the two methods, it can be found that the nanosheets prepared by ultrasonic peeling have larger transverse size, but the nanosheets prepared by ball-milling are thinner. There are some transparent and edge-curled nanosheets in the nanosheets prepared by the two methods, and the transverse size is in the micron level. It shows that both methods can produce a few layers and large sheets of boron nitride nanosheets [5], but the quality of the nanosheets prepared by ultrasound-assisted liquid-phase peeling is better.

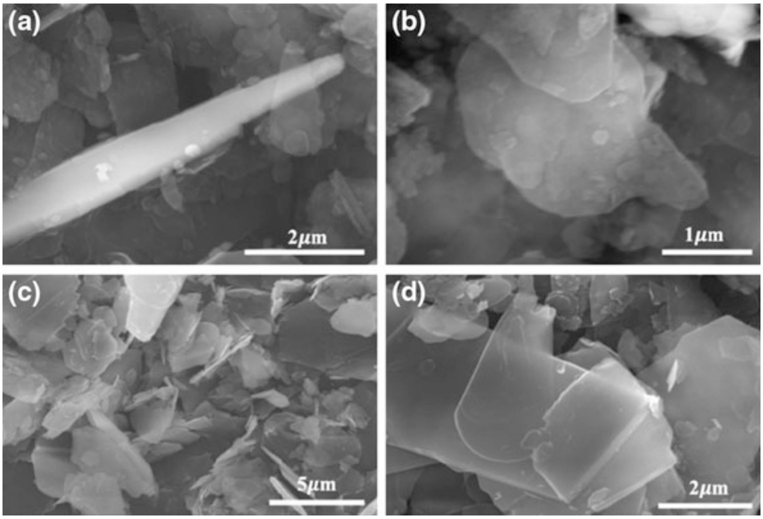

Fig. 1 FESEM images of BNNSs. **a** and **b** are BNNSs prepared by ball-milling, **c** and **d** are BNNSs prepared by ultrasonic-assisted liquid-phase stripping

Figure 2 showse the fracture scanning images of BNNSs/Si_3N_4 composites. Figure 2a–f shows that most of the composites are rod-like β-phase grains, which indicates that the conversion of silicon nitride powder from α-phase to β-phase is sufficient during sintering. These different orientations of the β-phase grains have a positive impact on the mechanical properties of silicon nitride ceramics [19]. The presence of boron nitride nanosheets can be observed in Fig. 2c, d, f, which can further improve the mechanical properties of silicon nitride composite ceramics. In Fig. 2b, e, no boron nitride nanosheets were found, possibly due to the small amount of added nanosheets.

Figure 3 shows a histogram of mechanical properties of Si_3N_4 composite ceramics prepared by adding ultrasound-assisted liquid-phase peeling BNNSs. The results show that the bending strength and fracture toughness of the composite ceramics increase to a certain extent with the increase in the amount of BNNSs prepared by ultrasonic-assisted liquid-phase peeling. The bending strength of BNNSs/Si_3N_4 composite ceramics increased from 402.0 MPa to 482.7 MPa, and the fracture toughness increased from 3.61 MPa·$m^{1/2}$ to 4.16 MPa·$m^{1/2}$, after adding 0.5 wt% BNNSs nanosheets prepared by ultrasonic-assisted liquid-phase peeling. The bending strength and fracture toughness of boron nitride nanosheets prepared by 0.1 wt% ultrasound-assisted liquid-phase peeling increased significantly, which may be related to the measurement errors caused by many notches on the surface of the sample during processing.

Figure 4 shows a histogram of mechanical properties of silicon nitride composites prepared by adding boron nitride nanosheets obtained by ball-milling. Similarly, the flexural strength and fracture toughness of the composite ceramics

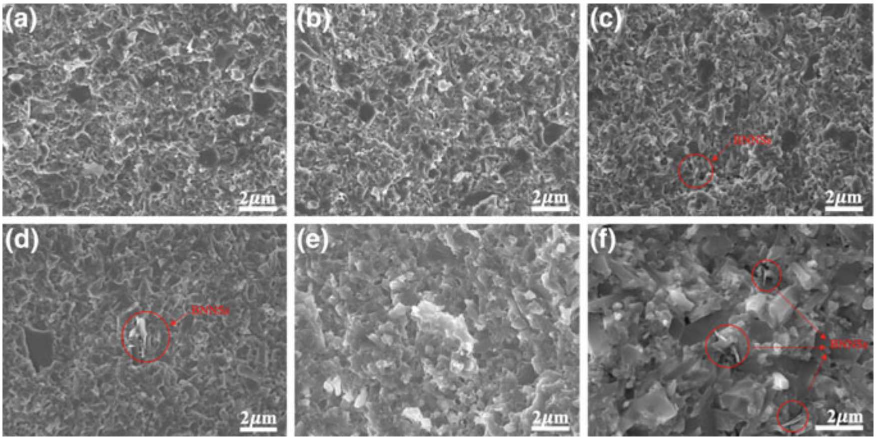

Fig. 2 FESEM images of the fracture surfaces of BNNSs/Si_3N_4 composites: **a**–**f** correspond to samples no. 1–6 in Table 1, respectively

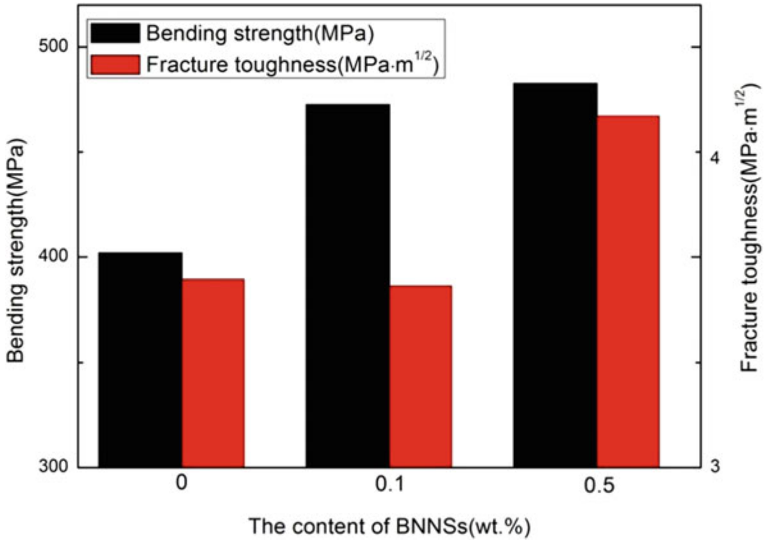

Fig. 3 Mechanical properties of BNNSs/Si_3N_4 composite ceramics prepared by ultrasonic-assisted liquid-phase stripping BNNSs

increased with the addition of nanosheets; the flexural strength and fracture toughness of the composite ceramics reached the maximum, 547.0 MPa and 5.47 MPa·m$^{1/2}$, respectively, when adding 2 wt% BNNSs obtained. Compared with the Si_3N_4 ceramics without boron nitride nanosheets, the flexural strength and fracture toughness are 36% and 51% higher, respectively.

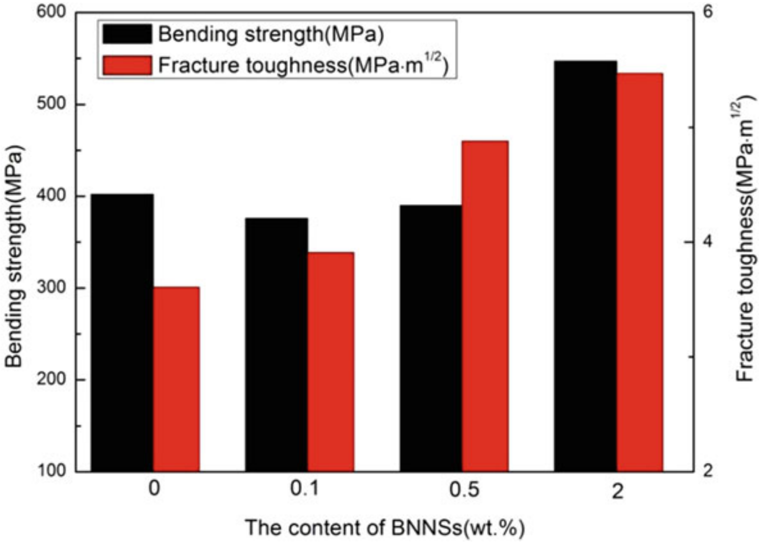

Fig. 4 Mechanical properties of BNNSs/Si_3N_4 composite ceramics prepared by ball-milling BNNSs

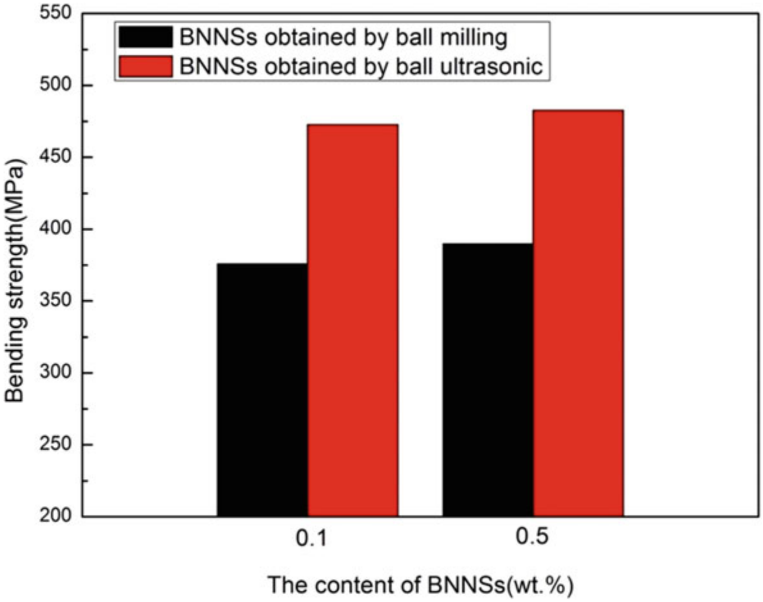

Fig. 5 Comparison of bending strength of BNNSs/Si_3N_4 composite ceramics after adding BNNSs prepared by different methods

Figure 5 shows a comparison of the bending strength of composite ceramics after adding the same mass fraction of boron nitride nanosheets prepared by two methods. It can be seen from the figure that when the same mass fraction of boron nitride nanosheets is added, the bending strength of silicon nitride ceramics can be enhanced more when the ultrasound-assisted liquid-phase stripping BNNSs are added. This is because boron nitride nanosheets obtained by ultrasound-assisted liquid-phase stripping method have fewer defects and more complete crystal structure than those obtained by ball-milling method.

The toughening mechanisms were clearly identified from the FESEM images of the indentation crack propagation paths and the fracture surfaces. FESEM images of Vickers indentation imprints performed on the sample surface are presented in Fig. 6. The pulling mechanism of boron nitride nanosheets can be clearly observed from Fig. 6c, d, and some nanosheets remain in the ceramic matrix [5, 20]. From the crack growth path of indentation, the deflection of the crack and the bridging phenomenon of the boron nitride nanosheets can be clearly observed, and the crack growth path is serrated. These will consume a lot of fracture energy, which is conducive to the improvement of fracture toughness of composite ceramics [21].

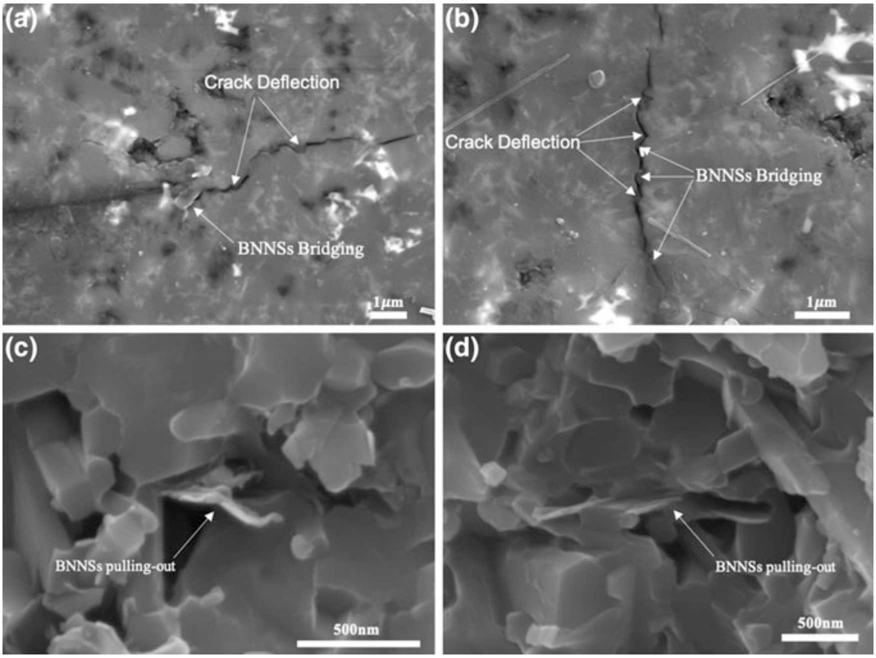

Fig. 6 Toughening mechanisms. **a** and **b** details of indentation crack propagation with crack deflection and BNNSs bridging in sample 6. **c** and **d** FESEM images of the fracture surface of sample 6 after three-point bending tests

Conclusion

BNNSs with few layers and transverse size in micron-scale were prepared by ball-milling and ultrasound-assisted liquid-phase stripping. We found that the BNNSs prepared by two methods could enhance the mechanical properties of silicon nitride ceramics, and the silicon nitride ceramics show better mechanical properties with the addition of ultrasound-assisted liquid-phase stripping BNNSs. The bending strength and fracture toughness of silicon nitride composite ceramics were increased by 36% and 51%, respectively, when BNNSs prepared by ball-milling method of 2 wt% were added. The pullout of BNNSs, the bridging of cracks, and the deflection of cracks are the main factors to improve the toughness.

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