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Silicon nitride/boron nitride ceramic composites fabricated by reactive pressureless sintering

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Abstract

Using Si and BN powders as raw materials, silicon nitride/hexagonal boron nitride (Si_3N_4/BN) ceramic composites were fabricated at a relatively low temperature of 1450 °C by using the reaction bonding technology. The density and the nitridation rate, as well as the dimensional changes of the specimens before and after nitridation were discussed based on weight and dimension measurements. Phase analysis by X-ray diffraction (XRD) indicated that BN could promote the nitridation process of silicon powder. Morphologies of the fracture surfaces observed by scanning electron microscopy (SEM) revealed the fracture mode for Si_3N_4/BN ceramic composites to be intergranular. The flexural strength and Young's modulus decreased with the increasing BN content. The reaction-bonded Si_3N_4/BN ceramic composites showed better machinability compared with RBSN ceramics without BN addition.

Keywords: RBSN; Ceramic composites; Boron nitride; Silicon nitride

1. Introduction

Si_3N_4 and h-BN are very versatile materials which have low density, excellent chemical and thermal properties, superior insulating properties, good dielectric properties, and good corrosion resistance [1,2]. They can be used as crucibles for metallurgy industry, substrate for semiconductor parts, windows in microwave apparatus, refractory materials for high-temperature furnaces [1–3], and so on. However, the sinterability of BN is very poor and BN ceramics are generally produced by hot pressing or hot isostatic pressing at high temperatures over 1800 °C [4–8], which is relatively expensive for their widespread utilization. The development of Si_3N_4 ceramics has also been limited due to its intrinsic brittleness and poor machinability [2]. To solve these problems, Si_3N_4 and BN can be used together to form Si_3N_4/BN ceramic composites, which have shown good properties [9,10]. Kusunose et al. [9] produced high strength Si_3N_4/BN nanocomposites by hot pressing using *in-situ* synthesized composite powders. Mazdiyasni and Ruh [10] prepared Si_3N_4/BN composites with good thermal shock resistance by conventional hot pressing method. The temperatures in the above hot press processing are usually at about 1750 °C. Although hot pressing is an effective way to prepare small and simply shaped samples, it is not suitable for the preparation of large pieces with complex shapes.

It is well known that *in-situ* nitridation of Si powders, usually called as reaction bonding of silicon nitride (RBSN), is a feasible way to fabricate Si_3N_4 ceramics due to its low processing temperature of about 1400 °C, low cost and handling facility [2,11]. Furthermore, it is easy to control the dimensions, which is favorable for the production of large or complex-shaped components. The obtained RBSN ceramic materials usually have a porosity of about 20% and contain some residual silicon in the microstructures. Post-sintering technique such as gas-pressure sintering (GPS) at higher temperatures can reduce both the porosity and the content of residual silicon [12–14]. In the present work, Si_3N_4/BN ceramic composites were prepared by the RBSN technology using Si and BN as starting powders at 1450 °C, and the properties of the obtained materials were characterized.

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Table 1
Sample designation and the corresponding compositions.

Sample no.	Starting materials (wt.%)				Theoretical final phase composition
	Si	BN	Al_2O_3	Y_2O_3	
BN0	100.0	0	3.00	2.00	Si_3N_4–0 vol%BN–1.8 wt.%Al_2O_3–1.2 wt.%Y_2O_3
BN20	77.1	22.9	2.72	1.81	Si_3N_4–20 vol%BN–1.8 wt.%Al_2O_3–1.2 wt.%Y_2O_3
BN40	55.8	44.2	2.47	1.65	Si_3N_4–40 vol%BN–1.8 wt.%Al_2O_3–1.2 wt.%Y_2O_3
BN60	36.0	64.0	2.22	1.49	Si_3N_4–60 vol%BN–1.8 wt.%Al_2O_3–1.2 wt.%Y_2O_3
BN80	17.4	82.6	2.01	1.34	Si_3N_4–80 vol%BN–1.8 wt.%Al_2O_3–1.2 wt.%Y_2O_3
BN95	4.2	95.8	1.85	1.23	Si_3N_4–95 vol%BN–1.8 wt.%Al_2O_3–1.2 wt.%Y_2O_3

2. Experimental procedure

Starting powders of commercial Si (purity >99.5%, mean particle size about 20 μm, Yinfeng Silicon Co., Jinan, China) and h-BN (purity >99.5%, mean particle size <0.5 μm, Sanxing Ceramic Materials Co. Ltd., Gongyi, China) were used in this investigation. Y_2O_3 (purity >99.5%, ChemPur, Germany) and Al_2O_3 (purity >99.5%, ChemPur, Germany) were added as sintering aids. Polyethylene glycol 300 (CP, SCRC, Shanghai, China) was used as binder to strengthen the green body of the specimen without BN addition. The sample designation and the corresponding compositions were listed in Table 1. The weight percents of silicon and h-BN were calculated by the final composition of Si_3N_4 and h-BN based on the hypothesis that silicon would transformed into silicon nitride completely.

The starting powders, binder, Si_3N_4 balls, and ethanol were placed in a polyethylene bottle and ball milled for 12 h. The slurry was dried by a rotary evaporator and then sieved through a 60-mesh screen. The mixed powders were shaped into a 30 mm × 37 mm green body by uniaxial pressing in a stainless-steel die followed with cold isostatic pressing at 250 MPa. The binder was burned out in a flowing N_2 atmosphere (>99.99%) at 700 °C for 150 min. Finally, the compacts were placed in a graphite furnace for nitridation and reaction bonding. The furnace chamber was evacuated to about 5 Pa firstly, and then was heated to 1000 °C. Pure nitrogen atmosphere was introduced slowly into the chamber, and kept it flowing at the rate of about 0.5 L/min. Then the temperature was increased to 1450 °C very slowly, and kept at that temperature for 30 min.

The nitridation behavior was characterized by the relative density of green compacts and sintered samples, the nitridation rate, as well as the change of the samples' volume. The phase composition was determined by XRD and the microstructure was observed by SEM. Flexural strength via three-point bending was tested on 3 mm × 4 mm × 35 mm bars using 30 mm spans, and the crosshead speed was 0.5 mm/min. A total of five bars were fractured to determine the average strength and the standard deviation. Young's modulus was obtained from the slope of flexural curve at the initial linear domain. Holes drilling by an electric drill using WC/Co aiguilles were used to evaluate the machinability of the BN40 sample.

3. Results and discussion

3.1. Nitridation behavior

The nitridation results of different samples are summarized in Table 2. The relative density of the green compacts firstly increased, and then decreased as the BN content increased. This should be related to the particle size of the raw materials. As shown in Fig. 1a, the relative density of the green compact of Si powders was only about 60%. When the small particles of BN were added, they could disperse in the Si skeleton and fill in the void space between large particles of Si. Furthermore, the lubricating effect of h-BN was also favorable for the compaction of the irregular Si particles. Thus, the relative density of the green body increased, and a maximum value of 73.09% was achieved in the specimen with BN content of 40%, as shown in Fig. 1b. However, when the BN content was further increased, the relative density of the green bodies decreased. Due to the initial tiny card structure, h-BN could not compact tightly, though not shown clearly in Fig. 1c.

It is well known that there is often a thin layer of SiO_2 coated on the surface of Si particle. The SiO_2 layer can react with Si to form SiO vapor at high temperature, and this can cause weight loss [11]. Besides, some B_2O_3 impurity included in BN powder would result in evaporation at temperature above 600 °C. Accordingly, in order to get the true nitridation rate from the weight change during the nitridation process, the weight loss of

Table 2
Relative densities, nitridation rate and bulk expansion of the samples.

Sample no.	Relative density of the green body (%)	Nitridation rate (%)	Relative density of the sintered sample (%)	Bulk expansion (%)
BN0	62.28	91.3	75.47	−0.06
BN20	70.79	89.8	79.60	1.75
BN40	71.48	92.6	76.04	2.75
BN60	68.38	96.4	70.54	3.52
BN80	67.05	98.9	65.61	5.44
BN95	66.90	100.7	63.50	6.08

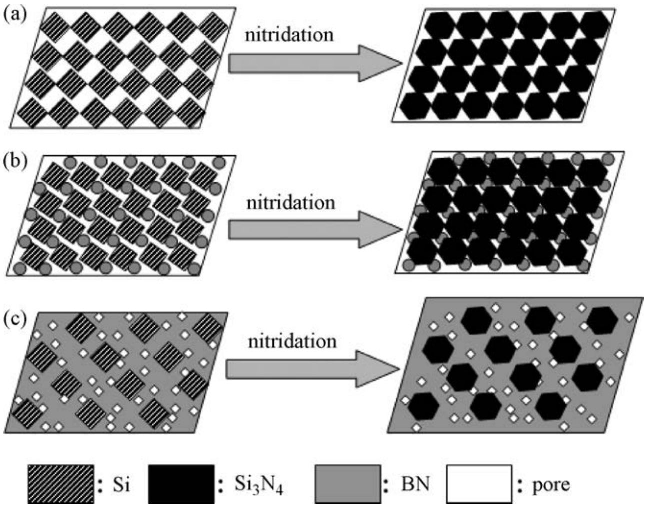

Fig. 1. The compact of the green body and the sketch map of the volume expansion (a) without BN; (b) BN particles dispersed in Si skeleton; (c) Si particles dispersed in BN skeleton.

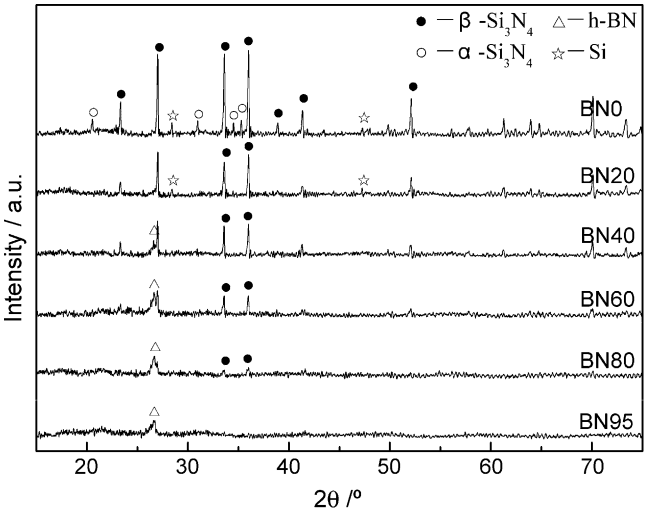

Fig. 2. XRD patterns of the nitrided samples.

Si and BN after heat treatment in Ar atmosphere at 1450 °C was measured separately. The calculated nitridation rates were also listed in Table 2. It is revealed that the addition of BN can promote the nitridation of Si powders, and nearly full nitridation could be reached with high BN contents.

The relative densities of the sintered samples are between 60% and 80%, which are lower than those of hot pressed Si_3N_4/BN composites [15]. This should be attributed to the fact that the conversion of Si to Si_3N_4 only involves an internal volume expansion of approximately 22% without skeleton shrinkage [2,16]. Different from the specimens without BN addition, there were obvious bulk expansions after nitridation for the specimens with BN. The bulk expansion increased with the increase of BN content. For BN80 and BN95, this expansion resulted in the decrease of the relative density after nitridation process, as shown in Table 2.

3.2. Phase composition and microstructures

The internal volume expansion mentioned above could close the internal pore network in the compacts, which would prevent the penetration of the nitrogen gas into the structure and reduce the nitridation of Si particles. So there could be a little residual Si in the sintered samples. Fig. 2 shows the XRD patterns of the

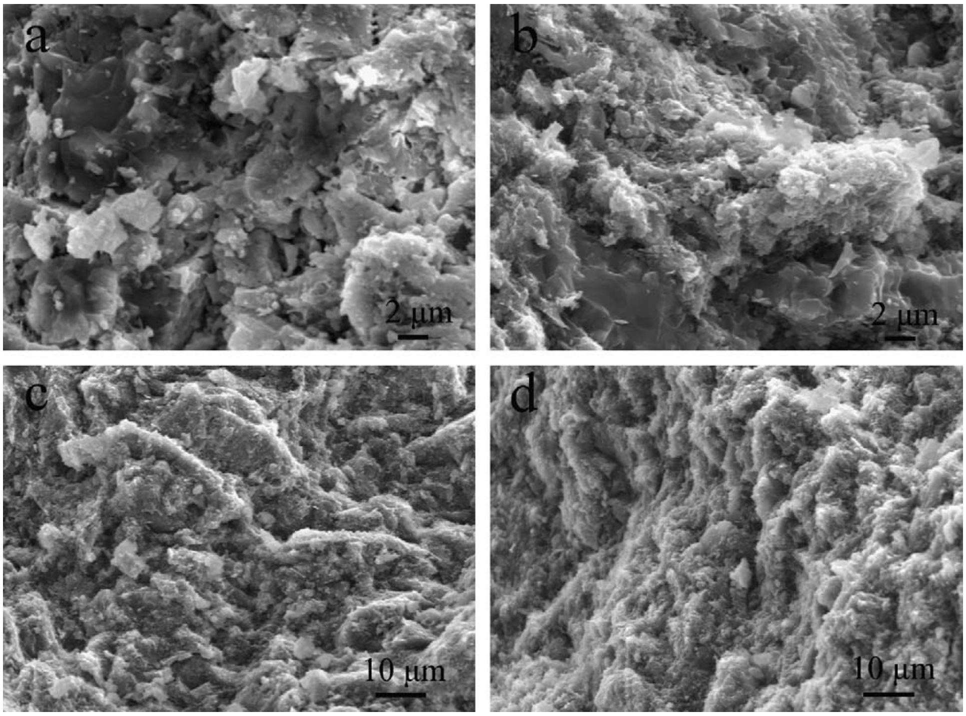

Fig. 3. Fracture surfaces of the nitrided samples: (a) BN0; (b) BN20; (c) BN40; (d) BN80.

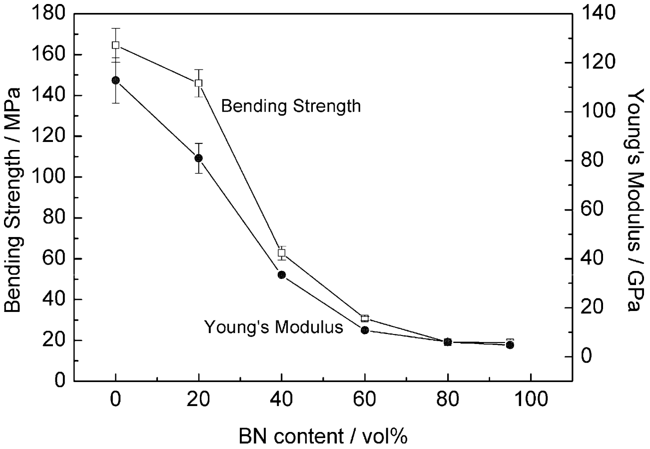

Fig. 4. Flexural strength and Young's modulus of the nitrided samples.

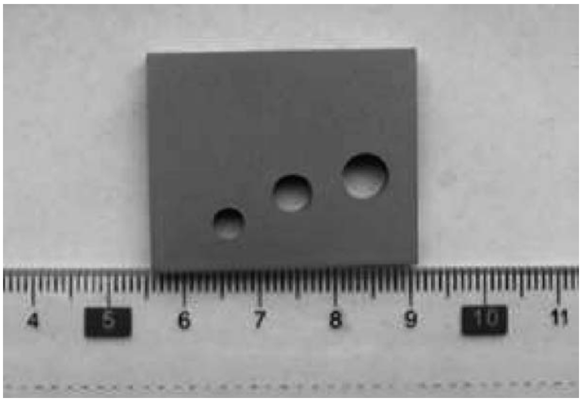

Fig. 5. Photograph of BN40 after machining.

sintered composites with different BN contents. The peaks of residual Si are identified in BN0 and BN20, while they disappeared in BN40 to BN95, which is attributed to the increasing of BN content for keeping the penetration tunnels for nitrogen. Because BN powder is hard to be sintered, it can act as grog addition, which maintain an open pore structure in the sample and promote the nitridation. The similar phenomenon was reported in previous works, where Si_3N_4 powder were used as grog addition to maintain the open pore structure and increase the nitridation rate of Si compacts [16,17]. XRD results of BN0–BN95 also show that the main phases are β-Si_3N_4, h-BN and α-Si_3N_4. The peaks of Si_3N_4 do not appear in BN95 due to the low content of initial Si.

The fracture surfaces of BN0, BN20, BN40, BN80 observed by SEM are shown in Fig. 3. The major fracture mode for these samples was intergranular. To BN0, cracks could nucleate at the interfaces of Si_3N_4 grains and propagate along Si_3N_4 grain boundaries, as shown in Fig. 3a. From Fig. 3b–d, it can be found that with the BN content increased, cracks preferred to nucleate at BN grain boundaries, due to the low bonding strength of BN grains and the weak interfaces between BN and Si_3N_4 grains.

3.3. Mechanical properties

Fig. 4 shows the flexural strength and Young's modulus as a function of volume fraction of BN. When no BN was contained, the bending strength and Young's modulus were 160 MPa and 110 GPa, respectively. The flexural strength and Young's modulus decreased a little when 20 vol.% BN was added, and then sharply while more BN was added. The strengths of the reactive pressureless sintering Si_3N_4/BN ceramic composites are lower than that of hot pressed Si_3N_4/BN ceramic composites [15] due to the high porosities.

Fig. 5 shows the machinability of the BN40 sample. The holes were drilled with WC/Co aiguilles. Compared with sample BN0 (RBSN ceramics without BN addition), BN40 showed much better machinability due to the existence of the Si_3N_4/BN weak interfaces and the cleavage behavior of BN particles [9], which was expected to absorb and disperse the damage force during machining operation and prevent the machining crack from penetrating deep into the material, while allowing easy material removal [15].

4. Conclusions

Using Si and BN powders as raw materials, Si_3N_4/BN ceramic composites were fabricated by reactive pressureless sintering, which was low cost and easy to operate. With the addition of BN, the bending strength and Young's modulus decreased while the nitridation rate of silicon compacts increased and nearly full nitridation could be reached at high BN contents. The fracture mode for BN/Si_3N_4 ceramic composites was intergranular. The Si_3N_4/BN ceramic composites showed much better machinability due to the weak interfaces compared with the RBSN ceramics without BN addition.

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