

Combustion Synthesis of Si_3N_4 -BN-SiC Composites by *in-situ* Introduction of BN and SiC

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Abstract: Si_3N_4 -BN-SiC composites present desirable potential for engineering applications because of their improved mechanical properties and oxidation resistance. In present work, Si_3N_4 -BN-SiC composites were successfully fabricated by combustion synthesis using Si, Si_3N_4 diluent, B_4C , and Y_2O_3 as initial powders. BN and SiC were *in situ* introduced into Si_3N_4 ceramics by the reaction between Si, B_4C , and N_2 gas. The obtained Si_3N_4 -BN-SiC composites were composed of elongated β - Si_3N_4 matrix and hollow spherical composites. The formation mechanism of the hollow spherical microstructure was investigated. The results show that the generated SiC and BN particles and glass phase cover on the raw materials, and hollow spherical microstructure is formed when raw particles are depleted. Furthermore, the impacts of B_4C content on the mechanical properties of Si_3N_4 -BN-SiC composites were investigated in detail. The *in-situ* introduction of BN and SiC is beneficial to improving mechanical properties of the composites to some extent. Finally, Si_3N_4 -BN-SiC composites with bending strength of 28–144 MPa, fracture toughness of 0.6–2.3 $\text{MPa}\cdot\text{m}^{1/2}$, Young's modulus of 17.4–54.5 GPa, and porosity of 37.7%–51.8% were obtained for the samples with 0–20% (in mass) B_4C addition.

Key words: combustion synthesis; Si_3N_4 -BN-SiC composites; *in situ* introduction; phase compositions; hollow sphere; formation mechanism

Silicon nitride (Si_3N_4) ceramics have been extensively used as structural and/or functional components in various engineering fields such as filtration, aerospace, and membrane support. It possesses low thermal expansion coefficient, excellent mechanical properties, good thermal shock resistance, and high chemical stability due to its strongly covalent bonds between atoms^[1–3]. Several technologies can be used to fabricate Si_3N_4 ceramics, including pressureless sintering^[4–5], reactive sintering^[6–7], carbothermal synthesis^[8], and combustion synthesis (CS)^[9–10]. Among these approaches, combustion synthesis can achieve rapid and low-cost fabrication of Si_3N_4 ceramics by the self-propagating of combustion waves using Si as starting material^[9].

Compared with Si_3N_4 ceramics, Si_3N_4 -BN-SiC composites present some improved properties such as lower dielectric constant, lower thermal expansion coefficient, and higher flexural strength, which draws attractive at-

tentions in engineering applications^[11–12]. The traditional introduction way of an additional phase is to add the required phase into the initial powders^[13]. However, the introduced phase is difficult to disperse homogeneously into the sintered product. *In-situ* introduction can solve this difficulty and achieve good interface bonding between the matrix and introduced phases^[14]. But investigations involving the *in-situ* introduction of BN or SiC into Si_3N_4 matrix are limited. Kusunose *et al.*^[15] reported the preparation of Si_3N_4 /BN nanocomposites by hot-pressing the t-BN coated α - Si_3N_4 powders, t-BN was *in situ* synthesized by the reducing reaction between boric acid and urea. Zheng *et al.*^[16] used B_4C and Si as raw materials to prepare h-BN-SiC composites *via* their combustion reaction at high-pressure N_2 gas (60–120 MPa). Inspired by the above work, present study attempts to *in situ* introduce BN/SiC into Si_3N_4 matrix by B_4C addition. The microstructural evolution of the *in-situ* fabricated

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BN/SiC and its effects on the properties of the sintered Si₃N₄-BN-SiC composites is studied.

1 Experimental

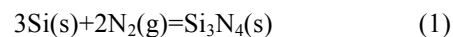
The initial powders were Si powder (Peixian Tiannayuan Silicon Materials Co., Ltd., Jiangsu, China; purity $\geq 99.99\%$; $d_{50}=4.1\text{ }\mu\text{m}$), Si₃N₄ powder (Yantai Tomley Hi-Tech Advanced Materials Co., Ltd., Shandong, China; purity $\geq 99.9\%$; α -phase content=42.3% (in mass); $d_{50}=22\text{ }\mu\text{m}$), B₄C powder (Dalian Jinma Boron Technology Group Co., Ltd, Shandong, China; purity $\geq 99.99\%$; $d_{50}=1.5\text{ }\mu\text{m}$), and Y₂O₃ powder (Yuelong New Material Co., Ltd, Shanghai, China; purity $\geq 99.999\%$; $d_{50}=5.04\text{ }\mu\text{m}$). The weight ratio of initial powders was determined as Si: Si₃N₄: B₄C: Y₂O₃=40 : (60- x) : x : 2 ($x=0, 5, 10, 15, 20$). The samples were named SBC00, SBC05, SBC10, SBC15, and SBC20 according to the weight ratio of B₄C, respectively. To obtain homogeneous mixtures, the ceramic powders were ball-milled for 3 h in ethyl alcohol with a ball/charge weight ratio of 2 : 1. After dried and sieved through a 150 μm (100 mesh) screen, each homogeneous mixture was cold-pressed into a rectangular compact (40 mm \times 40 mm \times 10 mm) at 10 MPa. The obtained compact was immersed into a powder bed (homogeneous mixture of 40% Si and 60% Si₃N₄ (in mass)) and ignited under 5 MPa N₂ atmosphere. Schematic diagram of the reactor and detailed preparation process was mentioned in previous work^[17].

The reaction temperature was obtained from the W-Re5/26 thermocouple immersed into the powder bed. Rectangular bars with the dimensions of 3.0 mm \times 4.0 mm \times 36.0 mm were prepared to measure the bending strength and Young's modulus by three-point bending method (Instron-3443, Instron, USA). Fracture toughness was tested by single-edge notched beam method (SEBN) on pre-notched bars (3.0 mm \times 6.0 mm \times 30.0 mm). The microstructure of the sample was observed by scanning electron microscope (SU-1000, Hitachi, Japan) and transmission electron microscope (JEM-2100F, JEOL Company, Japan). The phase composition of the sample

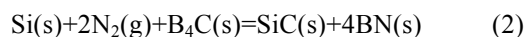
was performed by XRD (Diffractor meter D8, Bruker, Germany), and the content of each crystalline phase was calculated based on the XRD results. The open porosity of sintered sample was determined by the Archimedes method in the distilled water. The total porosity (P) was calculated from the measured bulk density (ρ_b), theoretical density (ρ , calculated based on the phase content of each phase) using following equation: $P=1-\rho_b/\rho$.

2 Results and discussion

The possible reactions during the fabrication process are shown in Eq. (1-2). Both the reactions are exothermic, but the adiabatic temperature of reaction (2) is reported to be lower than that of reaction (1)^[18-19]. It meets the experimental results as shown in Table 1, the measured reaction temperature decreases from 1850 °C to 1765 °C with the increase of B₄C content. Meanwhile, the reaction time increases with the B₄C content increasing, it can be ascribed to the generation of SiC and BN which restrain the propagating of combustion wave as an inert phase.



$$\Delta G^0 = -725.615\text{ kJ/mol}$$



$$\Delta G^0 = -914.459\text{ kJ/mol}$$

Fig.1 displays the phase identification of the obtained composites. The detected crystalline phase of sample SBC00 without B₄C is β -Si₃N₄. With the increase of B₄C content, the content of BN and SiC increase evidently. Besides, it is worth noting that peak broadening is observed for BN, which reveals that its crystallization is unsatisfactory in such a rapid combustion process. When B₄C content is equal to or greater than 10% (in mass), residual Si is detected, which reveals that the nitridation of Si is suppressed by the newly formed BN and SiC. Meanwhile, residual α -Si₃N₄ is also detected for samples prepared with high B₄C addition. The fabrication mechanism of Si₃N₄ ceramics is primarily controlled by the dissolution of α -Si₃N₄ and precipitation of β -Si₃N₄^[20]. The decreasing reaction temperature as shown in Table 1

Table 1 Reaction parameters during combustion synthesis and physical properties of the sintered samples with different B₄C contents

Sample	Reaction temperature/°C	Reaction time/s	Open porosity/%	Total porosity/%	Bending strength/MPa	Fracture toughness/(MPa·m ^{1/2})	Young's modulus/GPa
SBC00	(1850 \pm 15)	(16 \pm 3)	(51.8 \pm 1.0)	52.0	(120 \pm 12.0)	(2.2 \pm 0.4)	(49.5 \pm 1.6)
SBC05	(1825 \pm 20)	(18 \pm 5)	(47.3 \pm 0.5)	48.5	(144 \pm 8.4)	(2.3 \pm 0.2)	(54.5 \pm 1.7)
SBC10	(1795 \pm 12)	(21 \pm 2)	(43.3 \pm 0.6)	47.5	(108 \pm 5.0)	(1.7 \pm 0.2)	(46.2 \pm 3.0)
SBC15	(1778 \pm 20)	(26 \pm 5)	(42.3 \pm 0.5)	46.9	(30 \pm 7.4)	(0.7 \pm 0.2)	(18.5 \pm 2.1)
SBC20	(1765 \pm 14)	(30 \pm 3)	(37.7 \pm 1.7)	45.2	(28 \pm 3.9)	(0.6 \pm 0.1)	(17.4 \pm 1.2)

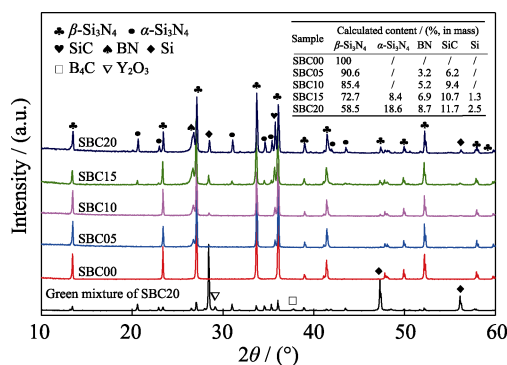


Fig. 1 XRD patterns of the green mixture and sintered samples with varied B₄C contents

is unfavorable to the phase transition from α -Si₃N₄ to β -Si₃N₄, which results in the residual α -Si₃N₄ in materials. Besides, the formed BN and SiC disperse in the liquid phase and restrain the mass transport, which is also a significant factor leading to the residual α -Si₃N₄.

Fig. 2 shows the microstructure of green mixture of SBC20, and fracture-surface microstructure of the CS-fabricated specimens with varied B₄C contents. It could be seen that the microstructure varies evidently after CS process. Before CS process, the green mixture is particulate. After CS process, sample SBC00 without B₄C is composed of interlocking β -Si₃N₄ grains with high aspect ratio. As B₄C is added to the raw materials, the development of β -Si₃N₄ grains is evidently inhibited. Average aspect ratio of β -Si₃N₄ grains decreases significantly with

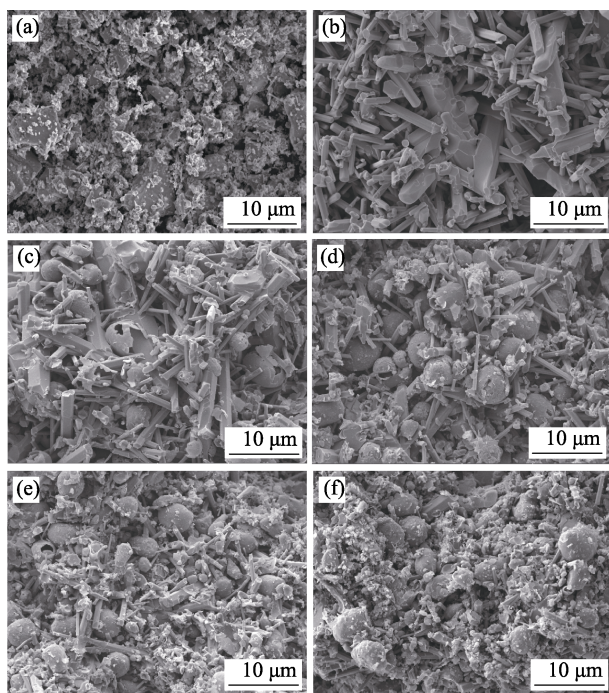


Fig. 2 Microstructure of green mixture of SBC20 (a) and fracture-surface microstructures of the CS-fabricated specimens with B₄C contents at (b) 0, (c) 5%, (d) 10%, (e) 15%, and (f) 20% (in mass)

the increase of B₄C content, almost no elongated grains can be observed when B₄C content is 20% (in mass). Furthermore, hollow spherical microstructure is observed for the samples prepared with B₄C addition. The hollow spheres have very thin wall and evident micropores on their surfaces when B₄C content is 5% (in mass). With the increase of B₄C content, the thickness of the wall increases and closed hollow sphere is gradually formed. This hollow spherical microstructure is different from that of flaky BN-SiC composites prepared at 60–120 MPa N₂ gas^[16], which illustrates that the microstructure of Si₃N₄-BN-SiC composites is evidently influenced by the N₂ gas pressure.

The properties of the sintered samples are shown in Table 1, the open porosity of sample SBC00 is 51.8%. With the increase of B₄C content, the open porosity of the sample decreases apparently. When the B₄C content is 20% (in mass), the open porosity of the obtained Si₃N₄-BN-SiC composites is 37.7%. The significant decrease in porosity can be attributed to the higher volume expansion (170%) of reaction (2) than that of nitridation of Si (21.2%)^[16], more pores are filled by the generated SiC and BN grains. However, the calculated total porosity based on the XRD results is higher than open porosity, especially for samples prepared with higher B₄C content. On one hand, closed pores are formed with increasing addition of B₄C as discussed above. On the other hand, B₄C might form glass phase with native SiO₂ film and Y₂O₃ during the high-temperature CS process, the theoretical density calculated based on the XRD results is higher than the actual value of sample, thus leading to the increasing total porosity. This behavior could be proven from the calculated content of each phase by XRD. According to the law of conservation of mass of reaction (2), the content of the generated BN and SiC should be higher than the calculated content. It illustrates that B₄C partially forms glass phase instead of BN and SiC after CS process, which could not be detected by XRD.

To investigate the reaction mechanism of the CS process, transmission electron microscope (TEM), high-resolution transmission electron microscope (HRTEM), energy dispersive spectroscopy (EDS) analysis, and selected area electron diffraction (SAED) are conducted on sample SBC10 and the results are shown in Fig. 3. The results demonstrate that the hollow sphere is a mixture of polycrystalline phase and amorphous phase. The crystalline phase should be BN and SiC combining the XRD analysis in Fig. 1. The amorphous phase consists of multiple elements including B, C, Si, N, and a little amount of O. On one hand, it has the characteristics of SiBCN ceramics^[21]. It is well known that SiBCN ceramics have two compositions of amorphous SiC_xN_{4-x} (x=1–4) and graphite-like BN(C)^[22]. The above-mentioned broadening of BN peak derives from the formation of amorphous BN(C). On the other hand, the amorphous phase contains evident glass phase

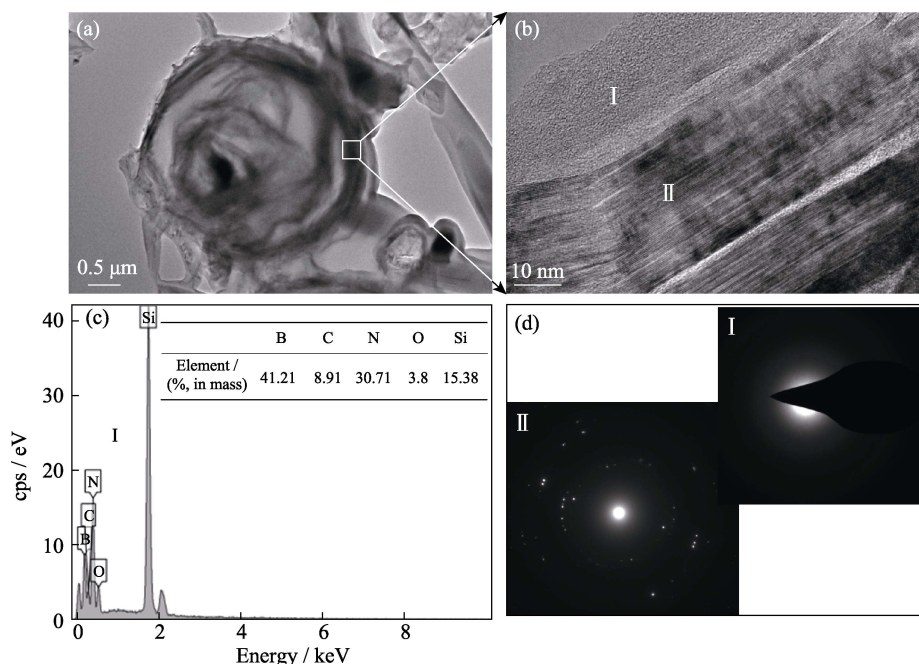


Fig. 3 (a) TEM image, (b) HRTEM image, (c) EDS analysis, and (d) SAED images of sample SBC10

combining the SEM image. The formation of the hollow spherical microstructure may originate from the comparatively low N_2 gas pressure and the formation of glass phase. At the initial stage of the combustion reaction, eutectic liquid phase, and small BN and SiC particles are formed and cover the surfaces of raw particles, but the small BN flakes could not grow up because of the low N_2 gas pressure and restriction of liquid phase. As the reaction proceeding, the newly formed products continue to cover the surfaces thus forming hollow spheres when raw particles are depleted. Ultimately, eutectic liquid phase forms glass phase during the rapid cooling of CS process.

As listed in Table 1, the mechanical properties of the obtained Si_3N_4 -BN-SiC composites fluctuate with different contents of B_4C addition. Compared to the monolithic Si_3N_4 ceramics, the composites prepared with 5% (in mass) B_4C has higher bending strength of 144 MPa and higher Young's modulus of 54.5 GPa. These improvements mainly result from the decrease of porosity of the sample according to the well-known negative relationship between bending strength and porosity of porous material^[23]. Additionally, the generated BN and SiC grains may also benefit the mechanical properties of composites because of their pinning effects within the grain boundary. But the fracture toughness of composites does not show apparent increase. It could be ascribed to the introductions of BN and SiC grains, resulting in more lattice defects in Si_3N_4 grains. The elongated Si_3N_4 grains become new crack sources, which is unfavorable to the fracture toughness of composites. With the further increase of B_4C content, the porosity of the obtained Si_3N_4 -BN-SiC composites decreases continuously from 47.3% to 37.7%, but their mechanical properties, including bending strength, Young's modulus, and fracture tough-

ness, degrade sharply. These behaviors indicate that the variation of microstructure is the predominated factor degrading the mechanical properties. On the one hand, the introduction of hollow spheres instead of elongated Si_3N_4 grains presents lower mechanical properties than that of Si_3N_4 ceramics with elongated morphology. On the other hand, the growth of Si_3N_4 grain is restrained because of the introduction of B_4C and the consequent generation of BN and SiC. Therefore, the degraded average aspect ratio is also a significant factor decreasing the mechanical properties of the Si_3N_4 -BN-SiC composites according to the theory of crack deflection^[24].

3 Conclusion

In this research, Si_3N_4 -BN-SiC composites with hollow spherical microstructure were successfully fabricated by combustion synthesis. The microstructural evolution of the *in-situ* introduced BN/SiC and its impacts on the properties of the obtained Si_3N_4 -BN-SiC composites were studied. As the B_4C content increases, the reaction temperature decreases and the porosity of sintered sample decreases evidently. Besides, the nitridation of Si, phase transition from α - Si_3N_4 to β - Si_3N_4 , and growth of β - Si_3N_4 grains are suppressed with the introduction of B_4C . Therefore, residual Si and α - Si_3N_4 are detected for samples prepared with high B_4C content. The bending strength and Young's modulus of the obtained Si_3N_4 -BN-SiC composites increase firstly and then decrease with the B_4C content increasing because of the decreasing porosity and degradation of microstructure. Optimal mechanical properties with bending strength of 144 MPa, fracture toughness of $2.3 \text{ MPa} \cdot \text{m}^{1/2}$, and Young's modulus of 54.5 GPa are achieved when B_4C content is 5% (in mass).

References:

- [1] WANG W D, YAO D X, CHEN H B, *et al.* ZrSi₂-MgO as novel additives for high thermal conductivity of β -Si₃N₄ ceramics. *J. Am. Ceram. Soc.*, 2020, **103**(3): 2090–2100.
- [2] SUN S Y, XIE Z P, CHEN K X. Precisely controlled carbothermal synthesis of spherical β -Si₃N₄ granules. *Ceram. Int.*, 2020, **46**(8): 10879–10884.
- [3] HAMPSHIRE S. Silicon nitride ceramics—review of structure, processing and properties. *J. Achieve. Mater. Manuf. Eng.*, 2007, **24**(1): 43–50.
- [4] LI X Q, YAO D X, ZUO K H, *et al.* Microstructure and gas permeation performance of porous silicon nitride ceramics with unidirectionally aligned channels. *J. Am. Ceram. Soc.*, 2020, **103**(11): 6565–6574.
- [5] KALEMTAS A, TOPATES G, OZCOBAN H, *et al.* Mechanical characterization of highly porous β -Si₃N₄ ceramics fabricated via partial sintering & starch addition. *J. Eur. Ceram. Soc.*, 2013, **33**(9): 1507–1515.
- [6] YANG J G, WU P, ZHANG Y P, *et al.* Synthesis of Si₃N₄ whiskers by rapid nitridation of silicon droplets. *Int. J. Appl. Ceram. Technol.*, 2020, **17**(1): 296–303.
- [7] MATSUNAGA C, ZHOU Y, KUSANO D, *et al.* Nitridation behavior of silicon powder compacts of various thicknesses with Y₂O₃ and MgO as sintering additives. *Int. J. Appl. Ceram. Technol.*, 2017, **14**(6): 1157–1163.
- [8] ZHI Q, WANG B, ZHAO S, *et al.* Synthesis and mechanical properties of highly porous ultrafine-grain Si₃N₄ ceramics via carbothermal reduction-nitridation combined with liquid phase sintering. *Ceram. Int.*, 2019, **45**(17): 21359–21364.
- [9] ZHANG Y, YU X, GU H, *et al.* Microstructure evolution and high-temperature mechanical properties of porous Si₃N₄ ceramics prepared by SHS with a small amount of Y₂O₃ addition. *Ceram. Int.*, 2021, **47**(4): 5656–5662.
- [10] CANO I G, BOROVINSKAYA I P, RODRIGUEZ M A, *et al.* Effect of dilution and porosity on self-propagating high-temperature synthesis of silicon nitride. *J. Am. Ceram. Soc.*, 2002, **85**(9): 2209–2211.
- [11] LOJANOVÁ S, TATARKO P, CHLUP Z, *et al.* Rare-earth element doped Si₃N₄/SiC micro/nano-composites—RT and HT mechanical properties. *J. Eur. Ceram. Soc.*, 2010, **30**(9): 1931–1944.
- [12] LI X L, ZHANG L, YIN X, *et al.* Mechanical and dielectric properties of porous Si₃N₄-SiC(BN) ceramic. *J. Alloys Compd.*, 2010, **490**(1/2): 40–43.
- [13] WANG S J, JIA D C, YANG Z H, *et al.* Effect of BN content on microstructures, mechanical and dielectric properties of porous BN/Si₃N₄ composite ceramics prepared by gel casting. *Ceram. Int.*, 2013, **39**(4): 4231–4237.
- [14] WANG S J, YANG Z H, DUAN X M, *et al.* Fabrication and characterization of *in situ* porous Si₃N₄-Si₂N₂O-BN ceramic. *Int. J. Appl. Ceram. Technol.*, 2014, **11**(5): 832–838.
- [15] KUSUNOSE T, SEKINO T, CHOA Y H, *et al.* Fabrication and microstructure of silicon nitride/boron nitride nanocomposites. *J. Am. Ceram. Soc.*, 2002, **85**(11): 2678–2688.
- [16] ZHENG Y T, LI H B, ZHOU T. Microstructure and mechanical properties of h-BN-SiC ceramic composites prepared by *in situ* combustion synthesis. *Mater. Sci. Eng. A-Struct.*, 2012, **540**(1): 102–106.
- [17] ZHANG Y, YAO D, ZUO K, *et al.* Fabrication and mechanical properties of porous Si₃N₄ ceramics prepared via SHS. *Ceram. Int.*, 2019, **45**(12): 14867–14872.
- [18] LI H B, ZHENG Y T, HAN J C. *In-situ* combustion synthesis of h-BN-SiC high-temperature ceramics. *Key Eng. Mater.*, 2007, **353–358**: 1501–1504.
- [19] ZHANG Y, YAO D, ZUO K, *et al.* Effects of N₂ pressure and Si particle size on mechanical properties of porous Si₃N₄ ceramics prepared via SHS. *J. Eur. Ceram. Soc.*, 2020, **40**(13): 4454–4461.
- [20] LAI K R, TIEN T Y. Kinetics of β -Si₃N₄ grain-growth in Si₃N₄ ceramics sintered under high nitrogen pressure. *J. Am. Ceram. Soc.*, 1993, **76**(1): 91–96.
- [21] RIEDEL R, KIENZLE A, DRESSLER W, *et al.* A silicoboron carbonitride ceramic stable to 2,000 °C. *Nature*, 1996, **382**(6594): 796–798.
- [22] THIYAGARAJAN G B, DEVASIA R. Simple and low-cost synthetic route for SiBCN ceramic powder from a boron-modified cyclotrisilazane. *J. Am. Ceram. Soc.*, 2019, **102**(1): 476–489.
- [23] YANG J F, ZHANG G J, OHJI T. Fabrication of low-shrinkage, porous silicon nitride ceramics by addition of a small amount of carbon. *J. Am. Ceram. Soc.*, 2001, **84**(7): 1639–1641.
- [24] FABER K T, EVANS A G. Crack deflection processes- I. Theory. *Acta Metall.*, 1983, **31**(4): 565–576.

原位引入 BN-SiC 燃烧合成 Si₃N₄-BN-SiC 复合材料

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摘 要: Si₃N₄-BN-SiC 复合材料以其良好的力学性能和抗氧化性能而具有良好的工程应用前景。本研究以 Si、Si₃N₄ 稀释剂、B₄C 和 Y₂O₃ 为原料, 采用燃烧合成法成功制备了 Si₃N₄-BN-SiC 复合材料。通过 Si、B₄C 和 N₂ 气之间的反应, 在 Si₃N₄ 陶瓷中原位引入 BN 和 SiC, 制备的 Si₃N₄-BN-SiC 复合材料由长棒状的 β -Si₃N₄ 和空心球形复合材料组成。实验研究了空心球微结构的形成机理, 结果表明, 生成的 SiC、BN 颗粒及玻璃相覆盖在原料颗粒上, 当原料颗粒反应完全时, 形成空心球形微结构。并进一步研究了 B₄C 含量对 Si₃N₄-BN-SiC 复合材料力学性能的影响。原位引入 SiC 和 BN 在一定程度上可以提高复合材料的力学性能。当 B₄C 添加量为质量分数 0~20% 时, 获得了抗弯强度为 28~144 MPa、断裂韧性为 0.6~2.3 MPa·m^{1/2}, 杨氏模量为 17.4~54.5 GPa, 孔隙率为 37.7%~51.8% 的 Si₃N₄-BN-SiC 复合材料。

关 键 词: 燃烧合成; Si₃N₄-BN-SiC 复合材料; 原位引入; 相组成; 空心球; 形成机理

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