

Effect of h-BN on the mechanical and dielectric properties of porous h-BN/Si₃N₄ composite ceramics prepared by gel casting

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Abstract

Porous h-BN/Si₃N₄ composite ceramics with different h-BN contents (5vol.%, 10vol% and 15vol.%) have been fabricated by gel casting. Sintering was carried out at 1750°C for 1h under a 0.1MPa nitrogen atmosphere. For comparison, porous Si₃N₄ ceramic was also prepared following the same route. The h-BN content has strong influence on the rheological behaviors of the suspensions, and the slurry has a suitable viscosity when h-BN content is lower than 10vol.%. Effects of h-BN content on the microstructure, mechanical properties, dielectric properties and thermal shock resistance of h-BN/Si₃N₄ composite ceramics were investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies showed that h-BN particles homogeneously scattered in the β-Si₃N₄ matrix, and the porous h-BN/Si₃N₄ composite ceramics show a superiorly comprehensive performance compared with porous Si₃N₄. For the 10vol.%h-BN/Si₃N₄ composite ceramics with a porosity of 49.4%, the flexural strength of 106.6MPa, dielectric constant of about 3.8 and a tangent loss of $(3\sim 7) \times 10^{-3}$ indicating that it could be one of the most ideal candidates for wave-transparent applications.

Keywords: Gel casting; Rheological behaviors; Porous; h-BN/Si₃N₄; Mechanical properties; Thermal shock resistance; Dielectric properties

1. Introduction

Silicon nitride (Si₃N₄) ceramics are one of the most promising wave-transparent materials due to its excellent properties such as high mechanical properties, good thermal shock resistance and moderate dielectric properties.^[1,2] However, relatively high dielectric constant and dielectric loss tangent at elevated temperatures limit its applications in advanced aircrafts.^[3] In addition, further utilization of Si₃N₄ ceramics has been restricted mainly attributed to its catastrophic fracture behavior, which brought by their brittle and hard nature. This makes the machinability of the as-sintered Si₃N₄ parts extremely poor, especially for those with complex shapes.

In order to improve the dielectric properties of Si₃N₄ ceramics at elevated temperatures, pores^[4,5] or hexagonal boron nitride (h-BN) particles^[6] were introduced as a second-phase dispersion into the Si₃N₄ matrix. In recent years, based on the weak boundary phase (WBP) concept,^[7] attempts have been made to develop various machinable ceramics by means of introducing WBP in matrices, and pores^[8] or h-BN^[9,10] was also regarded as a WBP. In h-BN/Si₃N₄ composite ceramics, the cleavage behavior of plate-like structured h-BN particles endowed the material with good machinability, together with superior high thermal shock resistance.^[11] Yet unfortunately, a remarkable decrease in fracture strength caused by the aggregation of h-BN particles has been observed when h-BN content in h-BN/Si₃N₄ composite

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increased to a certain level.^[12] Therefore, the homogeneous dispersion of h-BN particles into the matrix is probably an effective way to ensure the mechanical properties of h-BN/Si₃N₄ composite ceramics. To achieve this goal, hot pressing h-BN/Si₃N₄ ceramic nanocomposites have been fabricated by many researchers,^[9,13-15] and the nanocomposites exhibited improved mechanical properties. According to their researches, boric oxide/acid and organic reducing agent (urea) were used to prepare turbostratic BN (t-BN) powder or t-BN coating on α -Si₃N₄ particles. During subsequent sintering, t-BN is converted into the thermodynamically stable h-BN, and then the homogeneous dispersion of h-BN particle in h-BN/Si₃N₄ nanocomposite was obtained. However, in order to prevent the loss of urea, this process requires excess urea and a small gas overpressure, making it difficult to control the stoichiometry of B and N source.

Gel casting is a near-net-shape technology and is well-established to fabricate homogeneous, complex-shaped and machinable green body with high green strength.^[16,17] In past decades, many researchers have demonstrated that gel casting was one of the most promising ways to increase the ceramic reliability and reduce the production costs.^[18-20] Nevertheless, fabrication of h-BN/Si₃N₄ composites by gel casting and subsequently pressureless sintering still has not yet been reported.

In our previous study, we had prepared porous silicon nitride ceramics by gel casting,^[21] based on this work, in this article, we reported on the fabrication of h-BN/Si₃N₄ composite ceramics with homogeneous dispersion of h-BN particles by gel casting technique. Effects of different h-BN content on the rheological behaviors of the slurries were investigated, and the microstructure, mechanical properties, dielectric properties and thermal shock resistance of the h-BN/Si₃N₄ composite ceramics were also discussed in details.

2. Experimental Procedure

2.1 Materials Processing

Si₃N₄ (α -phase > 93%, mean particle size 0.5 μ m) and h-BN (purity = 99.5%, mean particle size 0.5 μ m) employed in this study were commercially available powders. 2wt.% La₂O₃ and 1wt.% Y₂O₃ (Aldrich Chemicals, purity = 99.99%, particle size 50nm) were used as sintering additives.

Aqueous slurries were prepared by mixing distilled water with a small amount (0.2wt%) of ammonium salt of polyacrylic acid dispersant (99%, Tianjin Dengfeng Chemical Factory, Tianjin, China), hydrochloric and ammonia were used to regulate the pH value to 8.5. Solid content of the suspensions were fixed at 40vol.%, and different h-BN content from 0vol.% to 15 vol.% were added. Slurries were ball-milled with Si₃N₄ balls for 24 h in a plastic bottle.

Commercial agarose powder (99.8%, Beijing Aoboxing Bio-tech Co., Beijing, China) was used as gelation, and 3wt.% agarose aqueous solution were made as the method described by I. Santacruz et al.^[22] The agarose was introduced into the ceramic slurry by 0.5wt.% with regard to the powder mass. The suspension was degassed for 10 min before casting, then the resulting slurry was poured into a stainless steel mold (58 mm in diameter and 8 mm in height) which was pretreated at

60°C, and subsequently cooled in a refrigerator with a temperature of 1°C. After consolidation, the green bodies were demoulded and dried at room temperature under controlled humidity to avoid cracking and nonuniform shrinkage caused by rapid drying. After the samples were completely dried, organic removal processing was conducted in a muffle oven at 500°C for 1h in an air atmosphere with a heating rate of 0.5°C/min. Then, the pellets were placed in a graphite crucible in a powder bed with a composition of 50vol%:50vol% for h-BN:Si₃N₄ and sintered in a graphite furnace at 1750°C for 1h under a 0.1MPa N₂ atmosphere.

2.2 Materials Characterization

The rheological properties of ceramic suspensions were determined by a rotary rheometer (Model NSX-11A, Chengdu Instrument Factory, Chengdu, China). Porosity was determined by the Archimedes method using distilled water as a medium. Crystalline phases were identified by X-ray diffraction (XRD, Rigaku, RINT-2000), using CuK α radiation at 40KV and 100mA. Morphologies were observed by scanning electron microscopy (SEM, FEI, Quanta-200). Samples were machined into standard bar samples of 36mm×4mm×3mm and edges was beveled for three-point bending strength test, which was conducted on a mechanical testing machine (Shimadzu, AG-Is50) with a span of 30mm at a crosshead speed of 0.5mm/min, and five specimens were tested to obtain the average strength values. The fracture toughness was measured by a single edge notched beam (SENB) technique, the samples sizes were 20mm×4mm×2mm, with a notch of 2mm in depth and ~0.2mm in width. The fracture toughness testing was conducted by a three-point bending with a span of 15mm and a crosshead speed of 0.05mm/min. For the measurements of dielectric properties, specimens with a size of Φ 18mm×1mm were tested in the frequency range of 21GHz to 38GHz at room temperature by RF impedance/material analyzer (Model 4291B, Agilent, USA).

3. Results and Discussion

3.1 Density

Table 1 Relative density and sintering linear shrinkage of porous h-BN/Si₃N₄ composite ceramics

Samples	Green density (vol.%)	Sintering linear shrinkage (%)	Porosity (%)
Si ₃ N ₄	42.3	6.9	48.1
5BN/95Si ₃ N ₄	42.0	6.8	48.4
10BN/90Si ₃ N ₄	41.8	6.2	49.4
15BN/85Si ₃ N ₄	40.1	5.1	53.3

Variations in the green density, sintering linear shrinkage and apparent porosity of the samples are shown in Table 1, the green density and sintering linear shrinkage decreased with the additions of the h-BN, while the apparent porosity increased. The porosity is a combining result from green density and sintering shrinkage, increasing green density or shrinkage decreases the porosity. Moreover, it was known that the sintering temperature of h-BN was higher than the temperature used in the present work, so the porosity in h-BN/Si₃N₄ ceramics enhanced when more h-BN were added.^[7,9,14]

3.2 Phase Composition and Microstructure

Fig.1 shows the XRD patterns of the obtained h-BN/Si₃N₄ composite ceramics with different h-BN contents. It is revealed that β-Si₃N₄, h-BN and α-Si₃N₄ are the dominate phases for all the three kinds of samples, and La₂O₃ or Y₂O₃ was not detected in the XRD patterns, which due to their amounts being too small to be detected. The diffraction intensity of h-BN enhanced with increasing h-BN amount, indicating that the h-BN did not participate in any reaction during the sintering process.

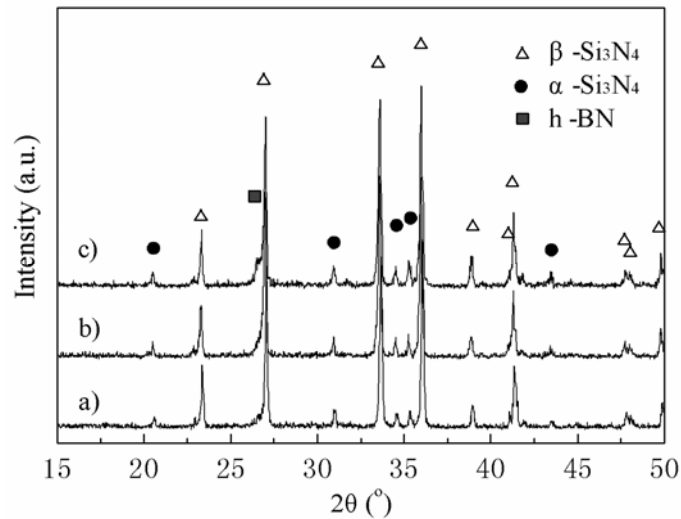


Fig. 1 XRD patterns of porous h-BN/Si₃N₄ composite ceramics
a) 5BN/95Si₃N₄; b) 10BN/90Si₃N₄; c) 15BN/85Si₃N₄

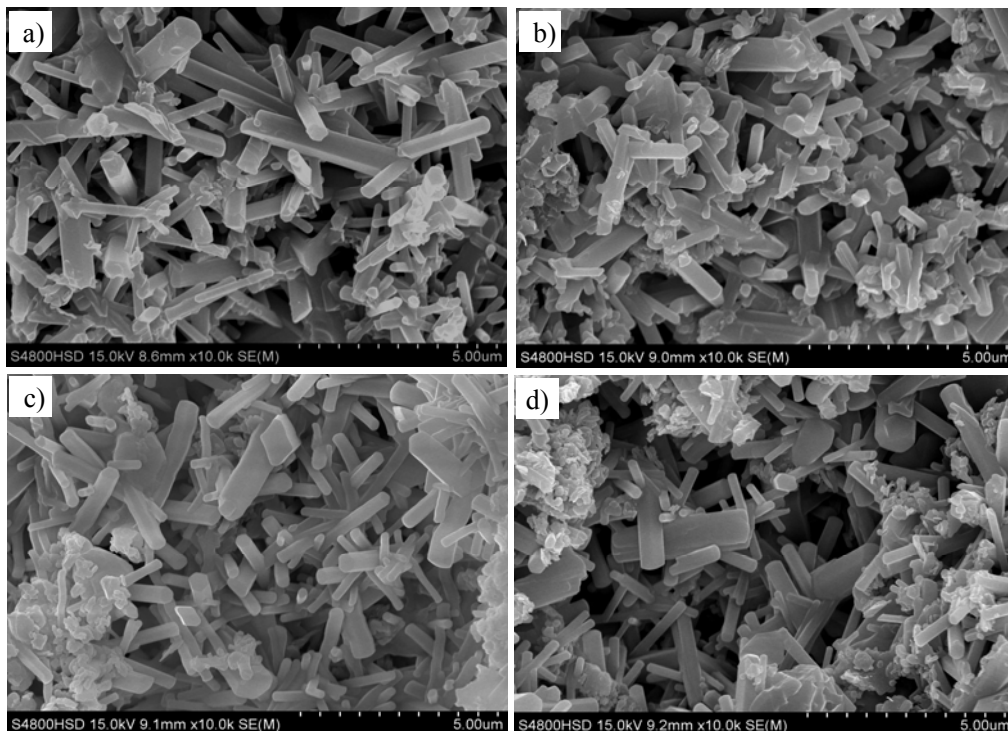


Fig. 2 Fractured surface morphology of porous h-BN/Si₃N₄ composite ceramics
a) Si₃N₄; b) 5BN/95Si₃N₄; c) 10BN/90Si₃N₄; d) 15BN/85Si₃N₄

The fracture surfaces of as-prepared samples observed by SEM are shown in Fig.2. Being different from the conventional h-BN/Si₃N₄ composites, no large h-BN platelets or aggregates were found in the Fig.2b, all of the h-BN particles are well-distributed among the β-Si₃N₄ grains. This indicates that gel casting is a good way to fabricate composites with homogeneous dispersion of ceramic powders. However, to Fig.2c-d, the h-BN aggregates in the composites were detected, and this phenomenon gets more serious when h-BN content increased.

From the SEM micrographs, typically interlocked microstructure that elongated β-Si₃N₄ grains embedded in the small acicular one can also be detected. Formation of this microstructure can be explained by the anisotropic grain growth mechanism of β-Si₃N₄ grains.^[25]

3.3 Mechanical Properties

The mechanical properties of the composites have close relation to its phase composition, porosity and microstructure. Fig.3 shows the mechanical properties of the ceramics as-prepared as a function of h-BN content.

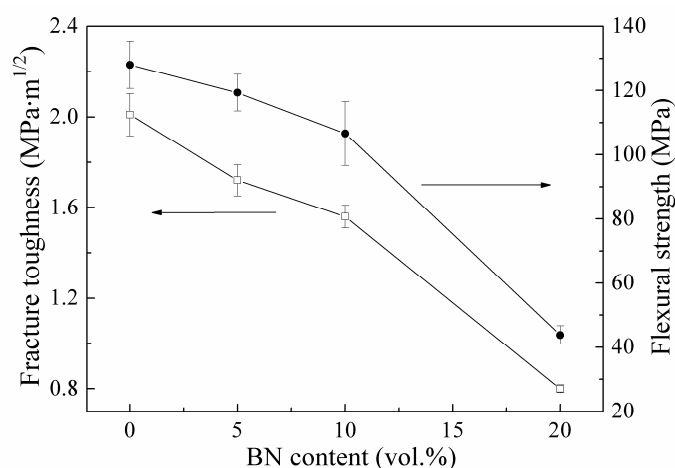


Fig. 3 Effect of h-BN content on the flexural strength and fracture toughness of porous h-BN/Si₃N₄ composite ceramics

As expected, the flexural strength, fracture toughness of the ceramics all decreased monotonously with increasing h-BN content. Since h-BN is a relatively weak phase and the bonds between h-BN and Si₃N₄ were weaker than those between Si₃N₄ grains. When samples were bended, less energy was required with the increase of h-BN.^[7,13,15] So, the more h-BN particles were incorporated, the more flaws were introduced, and the mechanical properties of the composites were deteriorated undoubtedly. Pores were also regarded as a WBP, so the influence of porosity on the mechanical properties of h-BN/Si₃N₄ composites can be explained by the same theories mentioned above.

The changes of the mechanical properties for the composites are also related to their microstructures. The interlocking microstructure formed by rod-like β-Si₃N₄ grains is in favor of enhancing the flexural strength of h-BN/Si₃N₄ composites by pull-out and bridging effect. However, the h-BN agglomerates and porosity increase with increasing h-BN content, and these WBP become the fracture sources which can severely decrease the composites' mechanical properties.

3.4 Dielectric Properties

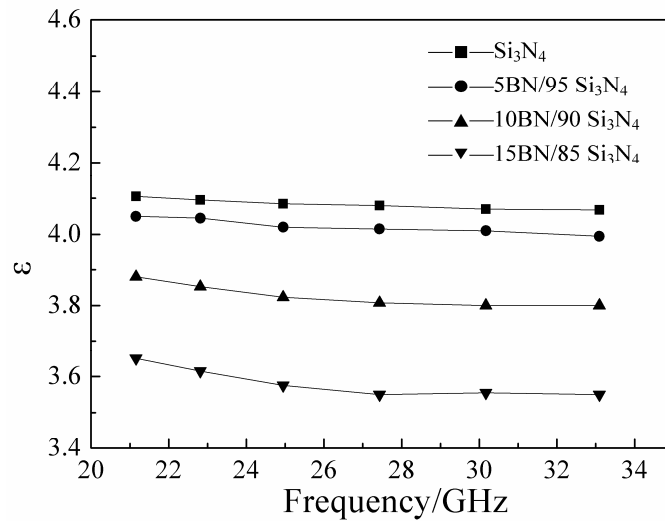


Fig. 4 Variations in dielectric constant values versus h-BN content of porous h-BN/Si₃N₄ composite ceramics

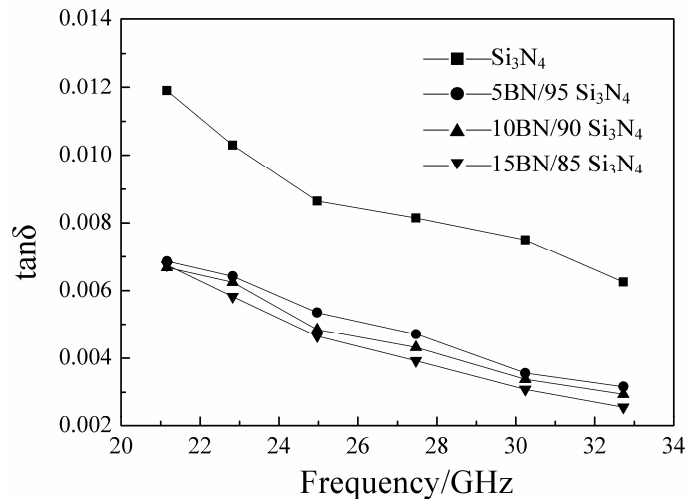


Fig. 5 Variations in dielectric loss tangent values versus h-BN content of porous h-BN/Si₃N₄ composite ceramics

The dielectric property of porous h-BN/Si₃N₄ composite ceramics strongly depends on their porosity, phase components and grain size. In this study, there are relatively little difference in grain size among the four samples, which indicating that the variation of dielectric properties were attributed to the difference in the porosity and phase composition rather than the grain size. The effects of these factors on dielectric properties could be characterized by mixture law. Compared to Si₃N₄, h-BN has excellence dielectric properties, and the dielectric constant (ϵ) and dielectric loss tangent ($\tan\delta$) of pores can regarded as 1 and 0 separately. Therefore, as WBP, h-BN and pores decreased the mechanical properties of a composite ceramic; meanwhile, it also decreases the dielectric constant and dielectric loss tangent. Fig.4 and Fig.5 shows the variations of dielectric constant and dielectric loss tangent versus h-BN content in the frequency range of 21~33GHz, respectively. The results show that the ϵ and $\tan\delta$ of h-BN/Si₃N₄ ceramic composites decreases obviously with the increasing of porosity and h-BN content, which fits well with the mixture law.

4. Conclusions

In this study, porous Si₃N₄ based ceramics with different volume fractions h-BN from 0vol.% to 15vol.% have been fabricated by gel casting technique, the dried green body has enough strength to take pre-processing, and the porosity of as-prepared samples vary from 48.1% to 53.3%. Since the flake structure h-BN, the h-BN content has strong influence on the rheological behaviors of the suspensions, when the h-BN content reached to 15vol.%, the viscosity increased more than 1000mpa·s dramatically, which is detrimental to gel casting processing. Microstructure analysis revealed that h-BN particles can scattered uniformly in the interlocked microstructure formed by β-Si₃N₄ grains when h-BN content is less than 10vol.%. So we can get porous h-BN/Si₃N₄ composite ceramics with excellent overall performance of mechanical properties and dielectric properties when the h-BN content within this range. The thermal shock resistance of porous h-BN/Si₃N₄ composite ceramics was also enhanced with increased h-BN content.

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