Effect of h-BN on the mechanical and dielectric properties of porous h-BN/Si$_3$N$_4$ composite ceramics prepared by gel casting

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Abstract

Porous h-BN/Si$_3$N$_4$ 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 Si$_3$N$_4$ 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/Si$_3$N$_4$ composite ceramics were investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies showed that h-BN particles homogeneously scattered in the β-Si$_3$N$_4$ matrix, and the porous h-BN/Si$_3$N$_4$ composite ceramics show a superiorly comprehensive performance compared with porous Si$_3$N$_4$. For the 10vol.%h-BN/Si$_3$N$_4$ 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 (3~7) × 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/Si$_3$N$_4$; Mechanical properties; Thermal shock resistance; Dielectric properties

1. Introduction

Silicon nitride (Si$_3$N$_4$) 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. However, relatively high dielectric constant and dielectric loss tangent at elevated temperatures limit its applications in advanced aircrafts. In addition, further utilization of Si$_3$N$_4$ 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 Si$_3$N$_4$ parts extremely poor, especially for those with complex shapes.

In order to improve the dielectric properties of Si$_3$N$_4$ ceramics at elevated temperatures, pores or hexagonal boron nitride (h-BN) particles were introduced as a second-phase dispersion into the Si$_3$N$_4$ matrix. In recent years, based on the weak boundary phase (WBP) concept attempts have been made to develop various machinable ceramics by means of introducing WBP in matrices, and pores or h-BN was also regarded as a WBP. In h-BN/Si$_3$N$_4$ 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. 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/Si$_3$N$_4$ composite

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increased to a certain level. Therefore, the homogeneous dispersion of h-BN particles into the matrix is probably an effective way to ensure the mechanical properties of h-BN/Si$_3$N$_4$ composite ceramics. To achieve this goal, hot pressing h-BN/Si$_3$N$_4$ ceramic nanocomposites have been fabricated by many researchers, 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 $\alpha$-Si$_3$N$_4$ 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/Si$_3$N$_4$ 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. 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. Nevertheless, fabrication of h-BN/Si$_3$N$_4$ 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, based on this work, in this article, we reported on the fabrication of h-BN/Si$_3$N$_4$ 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/Si$_3$N$_4$ composite ceramics were also discussed in details.

2. Experimental Procedure

2.1 Materials Processing

Si$_3$N$_4$ ($\alpha$-phase $>$ 93%, mean particle size 0.5 $\mu$m) and h-BN (purity = 99.5%, mean particle size 0.5 $\mu$m) employed in this study were commercially available powders. 2wt.% La$_2$O$_3$ and 1wt.% Y$_2$O$_3$ (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 Si$_3$N$_4$ 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. 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:Si$_3$N$_4$ and sintered in a graphite furnace at 1750°C for 1h under a 0.1MPa N$_2$ 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 CuKα 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-I50) 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 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>
<thead>
<tr>
<th>Samples</th>
<th>Green density (vol.%)</th>
<th>Sintering linear shrinkage (%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$</td>
<td>42.3</td>
<td>6.9</td>
<td>48.1</td>
</tr>
<tr>
<td>5BN/95Si$_3$N$_4$</td>
<td>42.0</td>
<td>6.8</td>
<td>48.4</td>
</tr>
<tr>
<td>10BN/90Si$_3$N$_4$</td>
<td>41.8</td>
<td>6.2</td>
<td>49.4</td>
</tr>
<tr>
<td>15BN/85Si$_3$N$_4$</td>
<td>40.1</td>
<td>5.1</td>
<td>53.3</td>
</tr>
</tbody>
</table>

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/Si$_3$N$_4$ 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/Si$_3$N$_4$ composite ceramics with different h-BN contents. It is revealed that β-Si$_3$N$_4$, h-BN and α-Si$_3$N$_4$ are the dominate phases for all the three kinds of samples, and La$_2$O$_3$ or Y$_2$O$_3$ 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.

![XRD patterns of porous h-BN/Si$_3$N$_4$ composite ceramics](image1)

Fig. 1 XRD patterns of porous h-BN/Si$_3$N$_4$ composite ceramics
a) 5BN/95Si$_3$N$_4$; b) 10BN/90Si$_3$N$_4$; c) 15BN/85Si$_3$N$_4$

![Fractured surface morphology of porous h-BN/Si$_3$N$_4$ composite ceramics](image2)

Fig. 2 Fractured surface morphology of porous h-BN/Si$_3$N$_4$ composite ceramics
a) Si$_3$N$_4$; b) 5BN/95Si$_3$N$_4$; c) 10BN/90Si$_3$N$_4$; d) 15BN/85Si$_3$N$_4$
The fracture surfaces of as-prepared samples observed by SEM are shown in Fig.2. Being different from the conventional h-BN/Si$_3$N$_4$ 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-Si$_3$N$_4$ 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-Si$_3$N$_4$ 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-Si$_3$N$_4$ 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/Si$_3$N$_4$ composite ceramics](image)

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 Si$_3$N$_4$ were weaker than those between Si$_3$N$_4$ 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/Si$_3$N$_4$ 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-Si$_3$N$_4$ grains is in favor of enhancing the flexural strength of h-BN/Si$_3$N$_4$ 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

The dielectric property of porous h-BN/Si$_3$N$_4$ 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 Si$_3$N$_4$, h-BN has excellence dielectric properties, and the dielectric constant ($\varepsilon$) and dielectric loss tangent (tan$\delta$) of pores can regarded as 1 and 0 separately. Therefore, as WBPs, 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 $\varepsilon$ and tan$\delta$ of h-BN/Si$_3$N$_4$ 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 0 vol.% to 15 vol.% 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 15 vol.%, the viscosity increased more than 1000mpa·s dramatically, which is detrimental to gel casting processing. Microstructure analysis revealed that h-BN particles can scattered uniformity in the interlocked microstructure formed by β-Si₃N₄ grains when h-BN content is less than 10 vol.%. 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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Reference