Research Article

BN Nanoparticles/Si₃N₄ Wave-Transparent Composites with High Strength and Low Dielectric Constant

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Si₃N₄ wave-transparent composites with different volume content of BN nanoparticles (BN_{np}/Si₃N₄) were prepared by gas pressure sintering at 1800°C in N₂ atmosphere. The effects of BN nanoparticles on the dielectric and mechanical properties of BN_{np}/Si₃N₄ composites were investigated. The results showed that the addition of the BN nanoparticles improved the dielectric properties of BN_{np}/Si₃N₄ composites effectively and decreased the mechanical properties. When the volume content of BN nanoparticles was 10%, the dielectric constant and dielectric loss tangent were 4.31 and 0.006, respectively, and the bending strength and fracture toughness still reached 198.9 MPa and 3.36 MPa·m^{1/2}. The high mechanical properties of BN_{np}/Si₃N₄ composites with 10% BN nanoparticles were attributed to homogeneously dispersed BN nanoparticles which were embedded in the pores formed by the rod-like β-Si₃N₄.

1. Introduction

Silicon nitride (Si₃N₄) was one of the most promising ceramic materials for the applications of microwave transparent materials which protected the spacecraft from the influences of harsh environment [1, 2], due to its high mechanical strength, good thermal shock resistance, and excellent rain erosion resistance [3–5]. However, its relatively high dielectric constant and dielectric loss tangent at room and elevated temperatures limited the wider applications as the advanced vehicles [6, 7]. To solve this problem, Xia et al. [8] prepared porous Si₃N₄ ceramics with a porosity of 30–55% for decreasing the dielectric constant, and Zhang et al. [9] prepared BN/Si₃N₄ composites by adding the BN particles with low dielectric constant. All of those methods could effectively decrease the dielectric constant and dielectric loss tangent, yet unfortunately, a drastic degradation of strength occurred unbearably.

It was well known that the addition of nanoparticles to a ceramic matrix could improve the mechanical properties of ceramic nanocomposites [10, 11]. BN/Si₃N₄ nanocomposite with superior mechanical properties, prepared by Gao et

al. alleviated the shortcoming of low strength encountered in conventional BN/Si₃N₄ composite [12]. In this paper, BN nanoparticles were introduced into the Si₃N₄ matrix to fabricate BN_{np}/Si₃N₄ composites by gas pressure sintering. The dielectric and mechanical properties of BN_{np}/Si₃N₄ composites with different volume content of BN nanoparticles were investigated.

2. Experimental Procedure

α-Si₃N₄ powders (α-Si₃N₄ > 93%, D₅₀ < 0.5 μm; UNIS-CERA, Beijing, China) and BN nanoparticles (purity > 99.5 wt.%, D₅₀ < 100 nm; NNT Co., Ltd., Taiwan, China) were used as the starting materials. Figure 1 showed the XRD pattern of Si₃N₄ raw powders, and the principal crystal phase was α-Si₃N₄. The dry gel of yttrium aluminum garnet (YAG), which prepared from yttrium chloride and polyaluminium chloride by sol-gel method, were used as sintering aids [13]. The XRD patterns of dry gel of YAG before and after sintering at current temperature were shown in Figure 2, which indicated that the dry gel of YAG transformed to YAG after sintering.

FIGURE 1: XRD pattern of Si_3N_4 raw powders.

FIGURE 2: The XRD patterns of the dry gel of YAG before and after sintering. (a) dry gel of YAG; (b) dry gel of YAG after sintering.

The Si_3N_4 , BN nanoparticles and 4 vol% dry gel of YAG were ball milled for 24 h in anhydrous ethanol, followed by drying at 70°C for 24 h under vacuum. The mixture was then molded by isostatic pressing method under 120 MPa. The green body was sintered at 1800°C for 120 minutes under the pressure of 6–8 MPa in N_2 atmosphere.

The apparent porosity and density were determined by Archimedes' displacement method. The bending strength was measured by the three-point bending test and the fracture toughness was determined by the single-edge-precracked beam (SEPB) method. The samples were machined into $22.76 \times 10.06 \times 5$ mm to measure the dielectric properties by the method of completely filled short circuited waveguide technique at a frequency of 9.36 GHz. The phase composition and microstructure was investigated by the XRD (PANalytical X'Pert Alpha-1) and SEM (ZEISS).

FIGURE 3: XRD patterns of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites with different contents of BN nanoparticles. (a) 5 vol %; (b) 10 vol %; (c) 15 vol %; (d) 20 vol %.

3. Results and Discussion

Figure 3 shows the XRD patterns of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites with different volume content of BN nanoparticles. As can be seen, the principal crystal phase in all the four samples is $\beta\text{-Si}_3\text{N}_4$, which indicates that the $\alpha\text{-Si}_3\text{N}_4$ raw powders transform to β phase during sintering process. But the random diffraction peaks can be seen in sample (b) and (d) near 31° (2θ), which indicates that trace $\alpha\text{-Si}_3\text{N}_4$ does not transform to β phase. Distinct reflections of h-BN are observed in the XRD pattern at 26.7° (2θ), and the diffraction peak intensities of the h-BN increase with the increasing of BN nanoparticles. However, YAG phase is not detected in XRD patterns due to the amount being too small to be detected. Because the dielectric constant and dielectric loss tangent of YAG were higher than BN and Si_3N_4 , the composites using fewer amounts of YAG as sintering aids could possess lower dielectric constant and dielectric loss tangent.

Figure 4 shows the SEM images of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites. The fracture surfaces of the composites with 10 vol % and 20 vol % BN nanoparticles were shown in Figures 4(a), and 4(b), and the surfaces that were polished and chemically etched in molten NaOH were shown in Figures 4(c), and 4(d). From the SEM graphs, the massive rod-like $\beta\text{-Si}_3\text{N}_4$ can be observed, that is consistent with the result of XRD patterns shown in Figure 3. The dense packing rod-like $\beta\text{-Si}_3\text{N}_4$ grains form tough interlocking microstructure, which could absorb more energy during the fracture process. For the dielectric properties, a large amount of rod-like grains accumulate together to form a lot of pores with the size of $0.5\text{--}1\ \mu\text{m}$, which may decrease the dielectric constant of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites effectively. Furthermore, as can be seen in Figures 4(a), and 4(c), the homogeneously dispersed BN nanoparticles, which embed in the submicron pores formed by rod-like $\beta\text{-Si}_3\text{N}_4$ grains, may prevent the crack

FIGURE 4: The SEM images of the $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites. (a) 10 vol% fracture surface; (b) 20 vol% fracture surface; (c) 10 vol% polished and etched surface; (d) 20 vol% polished and etched surface.

propagating along the submicron pores or prolong the crack propagation path. So $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites with 10% BN nanoparticles maintained relatively good mechanical properties. But when the content of BN nanoparticles increases to a high level in Figures 4(b), and 4(d), agglomerate structure of BN nanoparticles could cause a drastic loss of strength inevitably.

Figures 5 and 6 show the apparent porosity and dielectric properties of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites with different volume content of BN nanoparticles. It can be seen that the dielectric constant and dielectric loss tangent of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites decreases obviously with the increasing of BN nanoparticles and the apparent porosity increases. When the volume content of BN nanoparticles is 10%, the dielectric constant and dielectric loss tangent are 4.31 and 0.006, respectively. Because, for the well-distributed two-phase composites, the addition of the BN nanoparticles with lower dielectric constant could decrease the dielectric constant

FIGURE 5: The apparent porosity and density of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites.

FIGURE 6: The dielectric constant and dielectric loss tangent of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites.

FIGURE 7: The bending strength and fracture toughness of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites.

and dielectric loss tangent of the composites according to Lichtencker's logarithmic equation [14]. Furthermore, the apparent porosity increases with the addition of BN nanoparticles, and the increasing of apparent porosity could also decrease the dielectric constant and dielectric loss tangent of the composites [7, 8].

Figure 7 shows the bending strength and fracture toughness of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites. As can be seen, the bending strength and fracture toughness of the composites decrease monotonously with the increasing of BN nanoparticles. It is attributed to not only the increase of apparent porosity but also the weaker bonds between BN and Si_3N_4 [15]. When the content of BN nanoparticles increases to a high level, a drastic loss of strength occurs inevitably for the agglomeration of BN nanoparticles. However, the bending strength and fracture toughness of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites with 10% BN nanoparticles still reach 198.9 MPa and $3.36 \text{ MPa} \cdot \text{m}^{1/2}$. The

homogeneous distribution of BN nanoparticles should be responsible for the high strength of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites.

4. Conclusion

The $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites with low dielectric constant and excellent mechanical properties were prepared. The dielectric constant and dielectric loss tangent of $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites decreased obviously with the addition of the BN nanoparticles, and the bending strength and fracture toughness decreased. When the volume content of BN nanoparticles was 10%, the dielectric constant and dielectric loss tangent were 4.31 and 0.006, respectively, and the bending strength and fracture toughness still reached 198.9 MPa and $3.36 \text{ MPa} \cdot \text{m}^{1/2}$. Distinct reflections of h-BN were observed in the XRD pattern, along with the reflections of β - Si_3N_4 . The homogeneously dispersed BN nanoparticles may improve the mechanical properties of the $\text{BN}_{\text{np}}/\text{Si}_3\text{N}_4$ composites.

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