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Short communication

Effect of pre-oxidation on the microstructure, mechanical and dielectric properties of highly porous silicon nitride ceramics

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Abstract

Highly porous Si_3N_4 ceramics have been fabricated via freeze casting and sintering. The as-sintered samples were pre-oxidized at 1200–1400 °C for 15 min. The effect of pre-oxidation temperature on the microstructure, flexural strength, and dielectric properties of porous Si_3N_4 ceramics were investigated. As the pre-oxidation temperature increased from 1200 °C to 1400 °C, firstly, the flexural strength of the pre-oxidized specimens remained almost constant at 1200 °C, and then decreased to 14.2 MPa at 1300 °C, but finally increased to 25.6 MPa at 1400 °C, while the dielectric constant decreased gradually over the frequencies ranging from 8.2 GHz to 12.4 GHz. This simple process allows porous Si_3N_4 ceramics to have ultra-low dielectric constant and moderate strength, which will be feasible in broadband radome applications at high temperatures.

Keywords: B. Porosity; C. Dielectric properties; C. Mechanical properties; D. Si_3N_4

1. Introduction

Porous ceramic materials with a tailored microstructure have potential applications as structural components because of their unique properties, such as light weight, good strain and damage tolerance, and good thermal shock resistance. Silicon nitride ceramics are among the well-developed materials through such approaches. Porous Si_3N_4 ceramics with a microstructure of β-Si_3N_4, a high-temperature phase with interconnected fibrous β-Si_3N_4 grains bonded together and reinforcing each other, are of practical importance. These ceramics are suitable for various promising applications at high temperatures because of their excellent mechanical properties at room and elevated temperatures, good thermal shock resistance, and excellent dielectric properties [1–5].

Porous Si_3N_4 ceramics can be prepared in different ways, such as adding fugitive substance [6], freeze casting [7], carbothermal nitridation [5], combustion synthesis [8], in situ reaction bonding [9], and gel casting [10], among others. For example, porous Si_3N_4 ceramics with porosities of 19.4–42.6% were fabricated through the oxidation bonding process, which attained a high flexural strength of 43–137 MPa, a low dielectric constant of 3.1–4.6, and a low dielectric loss of (2.9–4.3) $\times 10^{-3}$ at 1 GHz [11]. Porous Si_3N_4/(Si_3N_4 + BN) sandwich ceramics fabricated via tape casting and hot pressing attained a moderate flexural strength of 53.4 MPa and a low dielectric constant of 3.48 at 1 GHz [12]. However, high porosity decreases the resistance of porous Si_3N_4 ceramics to moisture and mechanical erosion. Therefore, the fabrication of porous Si_3N_4 ceramics with a dense surface is necessary.

Many researchers have attempted to create a dense surface on porous Si_3N_4 ceramics. Recently, a porous Si_3N_4 ceramic has been fabricated via oxidation of Si_3N_4 preform, which attained a high-flexural strength of 137 MPa with a dielectric constant of 4.6 and dielectric loss of 2.9 $\times 10^{-3}$ at 1 GHz [9]. Liu et al. fabricated a dense/porous Si_3N_4 composite using the chemical vapor infiltration process. The composite attained an acceptable strength of 113 MPa and a low-dielectric constant of approximately 4.2–4.3 [13]. Yin and co-workers [14] fabricated a dense/porous Si_3N_4–SiO_2 composite ceramic via a novel process combining oxidation bonding with sol–gel infiltration-sintering. As the content of sol–gel infiltration increased, the dielectric constant of the dense/porous Si_3N_4–SiO_2 composite ceramic increased from 3.08 to 3.80, whereas the dielectric loss

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decreased. Li et al. [15] fabricated a porous Si_3N_4–SiC(BN) ceramic via precursor infiltration pyrolysis. As the annealing temperature increased from 900 °C to 1800 °C, the mechanical properties of porous Si_3N_4–SiC(BN) ceramics exhibited slight improvement, whereas the average real part of porous Si_3N_4–SiC(BN) ceramics increased from 6.91 to 26.20. Several attempts have been proposed to improve the mechanical properties by introducing a dense surface. However, these attempts also resulted in higher dielectric constants of porous Si_3N_4 ceramics. Porous Si_3N_4 ceramics need to maintain ultra-low dielectric constants for broadband radome applications at high temperatures.

Many recent studies have induced a self-crack-healing ability to increase the reliability of structural ceramics by pre-oxidation. Moreover, several works reported on the crack-healing behavior of engineering ceramics, such as Al_2O_3/SiC composites [16,17], Si_3N_4 matrix composites [18,19], ZrB_2–SiC ceramics [20,21], and ternary carbide Ti_3AlC_2 ceramics [22]. Pre-oxidation has been demonstrated to increase mechanical properties, hot corrosion resistance, and thermal shock behavior by forming a dense surface, which could blunt or heal surface flaws. The pre-oxidation and crack-healing behavior of hot-pressed ZrB_2–20 vol.% SiCw composites as a function of temperature and time were studied by Zhang et al. [21]. The flexural strength improved after pre-oxidation, with a maximum increase of strength (15%) for samples after pre-oxidizing at 800 °C for 180 min. Liu et al. [23] studied the effect of pre-oxidation on the hot corrosion behavior of non-oxide Ti_3SiC_2 ceramics in a mixture of 75 wt.% Na_2SO_4 + 25 wt.% NaCl melts at 850 °C. The results indicated that the hot corrosion resistance of the material could be improved greatly by pre-oxidation treatment. Zhang and co-workers [24] studied the effect of pre-oxidation on the thermal shock behavior of $Zr_2Al_4C_5$–20 vol.% SiC composites via a water-quenching technique. The pre-oxidized $Zr_2Al_4C_5$–20 vol.% SiC composites exhibited great improvement in thermal shock resistance compared with the as-sintered specimens.

However, whether pre-oxidation could also improve the mechanical and dielectric properties of porous ceramics is yet to be determined. To the best of our knowledge, few studies in the open literature have been conducted to determine the effect of pre-oxidation on the mechanical and dielectric properties of porous ceramics. In this work, dense/porous Si_3N_4 composite ceramics with high mechanical properties and low dielectric constant were attained by employing the pre-oxidation process. The effect of process parameters on the composition, microstructure, and mechanical and dielectric properties of the porous Si_3N_4 ceramics were measured and analyzed.

2. Experimental procedures

Slurries were prepared by mixing distilled water with 0.3 wt% ammonium polymethacrylate anionic dispersant (Sigma–Aldrich Trading Co., Ltd., Shanghai, China), glycerol (10 wt.% of solvent), 5 wt.% Y_2O_3 (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), 3 wt.% Al_2O_3 (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and Si_3N_4 (Junyu Ceramic Co., Ltd., Shanghai, China). Slurries were ball-milled with alumina balls for 12 h and de-aired by stirring in a vacuum desiccator. The Si_3N_4 powder consisted of 95 wt% α-Si_3N_4 and 5 wt% β-Si_3N_4, and had a mean diameter of 1.5–2.0 μm. The solid loading of the slurries were fixed to 25 vol.%. Highly porous Si_3N_4 ceramics have been fabricated by freeze casting and sintering. The detailed freeze casting process can be found in our previous work [7]. The green compacts were carefully placed into a graphite crucible with a silicon nitride-based powder bed and sintered in a graphite resistance furnace at 1800 °C for 60 min under a 0.05 MPa nitrogen atmosphere. Both the heating and cooling rates were 5 °C/min.

The pre-oxidation process was carried out in a conventional furnace under air atmosphere. In order to eliminate the effect of thermal shock on mechanical properties, the specimens were heated at ∼10 °C/min to the target temperature, held at the target temperature for 15 min, and then left cooling freely inside the furnace.

Porous Si_3N_4 samples of 3 mm × 4 mm × 35 mm were cut off from the as-sintered and pre-oxidized ceramics, and were loaded with a testing machine (Instron 5569, Instron corp., Canton, USA) to test the flexural strength, with a crosshead speed of 0.05 mm/min. All flexural bars were machined with the tensile surface perpendicular to the freezing direction. In order to obtain the average value, more than six samples of each measurement were chosen. The as-prepared and pre-oxidized products were coated with a thin layer of gold and characterized in a scanning electron microscope (FEI Quanta 200, FEI Company, Hillsboro, USA). The dielectric property test is based on measurements of the reflection and transmission moduli between 8.2 and 12.4 GHz, in the fundamental waveguide mode, using standard samples (22.86 mm × 10.16 mm × 3 mm for 8.2–12.4 GHz, Agilent E8326B PNA series network analyzer, USA).

3. Results and discussion

3.1. Microstructure of porous Si_3N_4

Fig. 1(a) shows the typical microstructure of the porous Si_3N_4 ceramics with 25 vol.% solid content obtained through freeze-casting and sintering. The actual porosity of the porous Si_3N_4 ceramics is approximately 62%. As shown in Fig. 1(a), numerous fibrous grains protruding from the internal walls of the macroscopic aligned channels were present in the porous Si_3N_4 samples. The estimated aspect ratio of the fibrous grains is approximately 8, and the average grain size is approximately 4 μm in length and 0.5 μm in width. As shown in Fig. 1(a), the rod-like β-Si_3N_4 particles in the porous Si_3N_4 ceramics intercross with each other to form many open pores that connect well with each other. After pre-oxidation at 1200 °C for 15 min, both α-Si_3N_4 and β-Si_3N_4 were bonded by amorphous SiO_2 from the oxidation of Si_3N_4, which coated the β-Si_3N_4 particles and was well-distributed in the porous Si_3N_4 ceramics [Fig. 1(b)]. This result is supported by the fact that only amorphous SiO_2 can be found in porous Si_3N_4 ceramics by