Effects of oxidation treatment on properties of SiO$_2$/SiO$_2$-BN composites

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Abstract: The silica fiber reinforced silica and boron nitride-based composites (SiO$_2$/SiO$_2$-BN) were prepared firstly via the sol-gel method and then the urea route, and the effects of oxidation treatment on the component, structure, mechanical and dielectric properties of the composites were investigated. The results show that the oxidation treatment at 450 °C will not impair the structure of boron nitride, and carbon is the main impurity with the excessive urea. The density of SiO$_2$/SiO$_2$-BN composites is 1.81 g/cm$^3$, and the flexural strength and elastic modulus are 113.9 MPa and 36.5 GPa, respectively. After oxidation treatment, the density varies to 1.80 g/cm$^3$, and the flexural strength and elastic modulus are decreased to 58.9 MPa and 9.4 GPa, respectively. The mechanical properties of the composites are severely damaged, but they still exhibit a good toughness. The composites show excellent dielectric properties with the dielectric constant and loss tangent being 3.22 and 0.0039, respectively, which indicates that the oxidation treatment is ineffective to improve the dielectric properties of SiO$_2$/SiO$_2$-BN composites.

Key words: radome; boron nitride; urea route; composites; oxidation treatment; wave-transparent structure; mechanical properties; dielectric properties

1 Introduction

In recent years, continuous fiber reinforced ceramic matrix composites have received considerable attention for structural and functional applications, of which the silica fiber reinforced silica composites (SiO$_2$/SiO$_2$) are especially attractive due to their low dielectric constant and loss tangent, high ablation resistance, thermal shock damage resistance and chemical stability [1−4]. With these excellent properties, SiO$_2$/SiO$_2$ composites have been widely used in the field of high temperature wave-transparent structures, like an electromagnetic window or a radome [5−7].

However, a severe drawback of SiO$_2$/SiO$_2$ composites prepared by sol-gel method is their high porosity, which in turn leads to low density, low strength and low rain erosion resistance, as well as the poor moisture-proof ability, and this to a large extent limits their applications on the aircrafts of higher Mach numbers [1, 2, 4].

As one of the most important nitride ceramics, boron nitride (BN) possesses a number of highly desirable properties [8−10]. Its high thermal stability (as high as 2 800 °C in the air), fine dielectric properties over a wide temperature range, excellent thermal shock resistance, coupled with its good corrosion resistance, make it a promising material to overcome the above-mentioned problems. To bring BN particles to SiO$_2$/SiO$_2$ composites is considered as a useful method to increase the density and decrease the porosity of the material, which may make a good structural integrity. In addition, SiO$_2$ grains will be coated by the BN particles, leading to the improvement of the moisture-proof ability.

Urea route is a smart method to fabricate the nitride ceramics because of its low cost, convenience and feasibleness as well as its possibility to prepare nanomaterials, which has attracted an increasing number of researches on it during these years, and many kinds of nitride ceramics and composites have been synthesized such as BN, TiN, Fe$_3$Mo$_3$N, SiC/BN and ZrO$_2$/BN [10−15]. LH et al [10] have prepared turbostratic boron nitride (t-BN) films on carbon fibers and graphite substrates by dip-coating in methanolic boric acid and urea solutions followed by nitriding in an ammonia flow at 1 000 °C. GOMATHI et al [11−12] have obtained nanoparticles of BN, TiN and NbN as well as the ternary metal oxynitrides like Fe$_3$Mo$_3$N by heating mixtures of H$_3$BO$_3$, TiCl$_4$, NbCl$_5$ and the corresponding metal oxides...
with urea in the temperature range of 850–1 000 °C. SUN et al [13] have synthesized TiN powders by reactive ball milling of titanium powders and urea at room temperature. SiC/BN nanocomposite powders have been fabricated via a chemical reaction of boric acid and urea on the surface of SiC particles in a nitrogen gas by WANG et al [14]. In the research of LI et al [15], 3Y-ZrO2/BN ceramic composites with nano-sized BN have been obtained via in situ reaction between boric acid and urea on the surface of 3Y-ZrO2 particles in nitrogen gas. However, until now, there have been few reports about the silica fiber reinforced silica and boron nitride-based (SiO2f/SiO2-BN) composites via the urea route. In our previous work [16], urea and boron acid were used to prepare SiO2f/SiO2-BN composites, which exhibited superior mechanical and dielectric properties. Whereas, the carbon produced by urea during the high preparation temperature would be adverse to the properties of the composites. One of the effective methods to remove carbon is the oxidation treatment above 400 °C, which may in turn cause some bad effects on the composites.

In this work, based on the preparation of SiO2f/SiO2-BN composites, the effects of oxidation treatment on the component, structure, mechanical and dielectric properties of the composites were primarily investigated.

2 Experimental

2.1 Raw materials

Silica fibers used in the present work were produced by Feilihua Quartz Glass Corporation (Jingzhou, China) with the following characteristics: purity ≥99.95%, density 2.2 g/cm³, tensile strength 1.7 GPa, elastic modulus 78 GPa and diameter 6–8 μm. The fibers were woven into 2.5-dimensional fabric with a fiber volume fraction about 45% by Beijing FRP Research and Design Institute (Beijing, China). Boron acid (H3BO3, AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and urea (CO(NH2)2, AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were also used.

2.2 Preparation process

As the starting materials, SiO2f/SiO2 composites were prepared by the sol-gel method based on the above-mentioned silica fiber fabric and silica sol. SiO2f/SiO2-BN composites were fabricated via the urea route as follows. Firstly, the solution for infiltration was made by mixing CO(NH2)2 and H3BO3 at a molar ratio of 3:2 with ethanol to a total volume of 500 mL. Secondly, SiO2f/SiO2 composites were infiltrated with the solution in vacuum at about 70 °C for 5 h. Finally, the composites were dried and heated in flowing nitrogen at about 900 °C for 2 h.

To discuss the effects of oxidation treatment on the properties of SiO2f/SiO2-BN composites, they were heat-treated in the air at 450 °C for 2 h and then cooled to room temperature.

2.3 Measurement and characterization

Thermogravimetric-differential thermal analysis of boron nitride was conducted using a thermal analyzer (TG-DTA, Rigaku Thermoflex, DT-40, Japan) in oxygen atmosphere with a flow rate of 40 mL/min. The samples were heated at 10 °C/min to the final temperature of 1 250 °C. An investigation of bondings was performed via Fourier transform infrared spectrometer (FT-IR, Avatar 360, Nicolet Instrument Corp., Wisconsin, USA) on discs pressed from composite powders mixed with KBr. X-ray diffractometer (XRD, D8 Advance, Bruker/Axs Corp., Germany) was employed to examine the crystalline phase and its preferred orientation using Cu Kα radiation. The bulk density of composites was calculated from the mass to volume ratio. Three-point flexural testing was performed on a computer controlled universal testing machine (WDW-100, Changchun Research Institute of Testing Machines, China) with a span of 30 mm and crosshead speed of 0.5 mm/min carried out on specimens with a dimension of 3 mm×4 mm×35 mm. Five specimens were used to calculate the average values. The fracture surface of the composites was examined by scanning electron microscope (SEM, FEI Sirion 200, Holland). The dielectric properties (dielectric constant ε and loss tangent tanδ) were evaluated in Kα band range at room temperature by a resonant cavity method using the TE010 mode. It was examined using a vector network analyzer (Hewlett-Packard, Hp8720ES) with 1 Hz resolution. The size of the specimens was 15.8 mm×7.9 mm×(5–10) mm.

3 Results and discussion

3.1 Effects of oxidation treatment on component and structure of composites

It has been already reported that the main process for the synthesis of BN by using boric acid and urea can be written as follows [10, 12, 14]:

\[ 2CO(NH_2)_2(s) \xrightarrow{\sim 200 \degree C} NH_3(g) + H_2N-CO-NH-CO-NH_2(s) \]  
\[ 2H_2BO_3(s) \xrightarrow{\sim 300 \degree C} B_2O_3(s) + 3H_2O(g) \]  
\[ B_2O_3(s) + 2NH_2(g) \xrightarrow{\sim 850 \degree C} 2BN(s)(amorphous) + 3H_2O(g) \]

So, we can see that boron nitride prepared at 900 °C is amorphous. Figure 1 shows the TG-DTA curves of boron nitride powders heated in oxygen atmosphere. The