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Dielectric and microwave-absorption properties of SiC nanoparticle/SiBCN composite ceramics

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Abstract

SiC nanoparticles with different contents (5–20 wt%) were mixed with liquid polyborosilazane. The compound was used to prepare SiC nanoparticle/polymer-derived SiBCN ceramics (SiC/PDCs-SiBCN). Thermal gravity tests (25–1400 °C) in air and helium atmosphere were used to investigate the thermal stability of SiC/PDCs-SiBCN. Dielectric and microwave-absorption properties of SiC/PDCs-SiBCN were determined at frequencies of 8.2–12.4 GHz by waveguide method. Results show that the addition of SiC nanoparticles increased the thermal stability of SiBCN ceramics. The permittivity, dielectric loss and absorption coefficient of ceramics increased as an elevated SiC content, resulting from the increase of carrier concentration. To understand the high-temperature dielectric property of SiC/PDCs-SiBCN, the permittivity of SiBCN ceramics with 15 wt% of SiC was measured at temperatures of 293–773 K. The composite ceramics were found to have a visible increase in the permittivity and dielectric loss, indicating their great potential as the high-temperature microwave absorption materials.

Keywords: SiC nanoparticle; PDCs-SiBCN; Dielectric property; Electromagnetic property

1. Introduction

The development of Si-based polymer-derived ceramics (PDCs) has enabled lots of significant technological breakthroughs in ceramic science and technology.[1–3] Generally, Si-based PDCs exhibit enhanced thermo-mechanical properties with respect to creep and oxidation, crystallization, or phase separation up to 1500 °C.[4,5] In some special cases, the high-temperature stability of PDCs-SiBCN in terms of decomposition is remarkable even at 2200 °C. The excellent thermo stability coupled with the remarkably high chemical and mechanical stability makes PDCs-SiBCN possess a very promising potential in the applications of high-temperature structural materials.[6]

Recently, the advanced researches on the functional properties of PDCs have been carried out including the electrical, magnetic and optical properties.[7–9] The literatures on electrical properties of PDCs cover the SiCO, SiCN and SiBCN systems. Some novel insights into their microstructure at the nanoscale level have been established connection with their semi-conducting behavior.[10,11] The conductivity of PDCs can be changed by adding fillers to the preceramic matrix.[12] Based on the Debye theory of dielectric, the dielectric property of a dielectric material is related to its electrical property, which is considered as one of the most important evaluation of the electromagnetic (EM) absorbing ability of materials.[13,14] However, few reports on the dielectric and EM properties of PDCs have been found so far, and there were scarcely any ones about PDCs-SiBCN except our previous research on the effect of annealing temperature on the dielectric property of PDCs-SiBCN.[15]

According to the previous works, the as-pyrolyzed PDCs-SiBCN are usually amorphous and single-phase materials, which can be reasonably considered as an electrically insulating matrix.[15,16] The introduction of conductive particles into ceramics is necessary for the improvement of electrical conductivity and dielectric property of ceramics. As a wide band gap semiconductor, SiC is regarded as an excellent absorbent in the microwave-absorption applications.[17,18] Besides, SiC has received the growing attention owing to the excellent thermal, electrical and optical properties with wide applications in microelectronics devices, integrated circuit, aerospace and nuclear industry.[19,20] Lee et al. prepared PDCs-SiBCN with SiC fillers, which had the increased resistance to creep and

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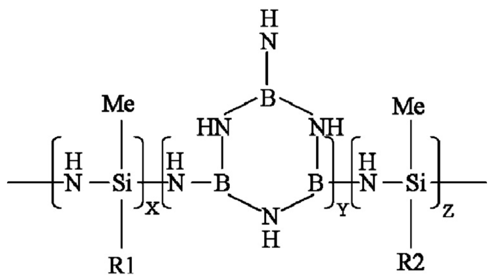

Fig. 1. The molecule structural formula of liquid PBSZ.

oxidation compared with SiBCN ceramics. The material can be used as the matrix candidate of fiber-reinforced ceramic matrix composites with high thermo stability.[21] It follows that the addition of SiC fillers in ceramics is probably feasible for developing the promising potentials of SiBCN ceramics as the novel high-temperature structural and wave-absorbing materials.

Based on the above considerations, in this paper, SiC nanoparticles with different contents were added into liquid polyborosilazane. The compound was used to prepare SiC nanoparticle/polymer-derived SiBCN composite ceramics (SiC/PDCs-SiBCN). The effects of SiC nanoparticles on the morphology, microstructure and phase composition, thermal stability, dielectric, electrical and EM absorbing properties of SiBCN ceramics were investigated.

2. Experimental

2.1. Material preparation

Liquid polyborosilazane (PBSZ) and SiC nanoparticles were used as the starting materials. The molecular structure of PBSZ is shown in Fig. 1. Fig. 2 reveals the composition and microstructure of SiC nanoparticles used in this study. The nanoparticles contained silicon, carbon and little oxygen element according to EDS analysis result, and the purity of nanoparticles reached 99.5 vol% by suppliers' data. XRD pattern illustrated that they mainly consisted of β-SiC, with few α-SiC. In Raman spectrum, the peak at 795.167 cm^{-1} of β-SiC was clearly seen, and the broadened peak around 940 cm^{-1} also corresponded to β-SiC. The broadening of peak can be relative to the nanoscale of SiC particles and fluorescence effect during testing. The nanoparticles had an average grain diameter of 30 nm as shown in TEM image.

SiC nanoparticles as wave-absorbing agents were added in PBSZ at 5, 7, 10, 15 and 20 wt%, respectively. They were mixed by a digital thermostat magnetic stirrer (Puguang 85–2, Pudong physical optical instrument plant, China) and a precision force electric Blender (Puguang JJ-1, Pudong physical optical instrument plant, China). The thermal gravimetric-differential scanning calormetry (TG-DSC) analysis of cross-linked PBSZ with different contents of SiC was performed at temperatures of 30–1450 °C using a thermogravimetric analyzer (TGA, Netzsch STA 409 C/CD, Germany). Fig. 3 (a) shows the TG curves of samples. There were all three weight loss stages, illustrating the conversion of organic polymer into inorganic ceramic. The weight loss was remarkable from 400 to 700 °C (Stage 1), began to slow down until 800 °C (Stage 2), and was almost invariable above 900 °C (Stage 3). In the third stage, the conversion rate of ceramics was improved with the increase of SiC content, which can be attributed to the positive role of fillers in promoting the cross-linking and curing of precursor.[1] From the DSC analysis in Fig. 3(b), it is found that all the curves had a decalescence peak corresponding to the sharp fall stage of TG curves, indicating that the conversion from polymer to ceramics was an endothermic process. The endothermic sidestep at 1125 °C reflected the change of specific heat, which gradually became an endothermic peak as the content of SiC increased, probably predicting the gradual intensification of structural rearrangement before the crystallization of ceramics. The exothermic peak at 1350 °C illustrated the beginning of crystallization, and the peak intensity gradually increased as the elevated content of SiC, probably related to the improved crystallinity.

Based on TG-DSC analysis, the liquid PBSZ with different contents of SiC was first cast into an alumina crucible, and heated at 170 °C for 2 h in high-purity nitrogen atmosphere to attain the cross-linking and curing. The cured bodies were milled into fine powders, which were uniformly filled into a metal die and compressed into a bulk at a pressure of 70 MPa. The bulk samples were pyrolyzed at 900 °C for 2 h in high-purity nitrogen atmosphere. The as-pyrolyzed ceramics samples were respectively marked as 0(/5/7/10/15/20)SiC/PDCs-SiBCN.

2.2. Morphology, microstructure and phase composition characterization

The surface morphology of the composite ceramics was observed by a scanning electron microscope (SEM, S-4700, Hitachi, Japan). The element composition of SiC nanoparticles used in this study was qualitatively analyzed by an energy dispersive spectrometer (EDS, Genesis XM2, EDXA, USA) attached to SEM. Laser Raman micro-spectroscopy (LRMS) of SiC nanoparticles was taken on a Renishaw Ramoscope (Confocal Raman Microscope, inVia Reflex, Renishaw, UK) equipped with a He-Ne laser (514 nm). The phase composition of SiC nanoparticles and as-received ceramics was conducted by X-ray diffractometer (XRD, X'Pert Pro, Philips, Netherlands) using Cu Kα (λ = 1.54 Å) radiation. The TEM analysis of SiC nanoparticles and as-received ceramics was performed on a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan).

2.3. Performance testing

Thermal gravity tests (from 25 to 1400 °C) in air and helium (He) atmosphere were used to investigate the thermal stability of SiC/PDCs-SiBCN, using a Netzsch STA 429 (C/CD, Germany). The relative complex permittivity ($\varepsilon = \varepsilon' - \varepsilon''j$, ε' is the real part and ε'' is the imaginary part) of ceramics samples (22.86 mm × 10.16 mm × 3.7 mm) was measured using a vector network analyzer (VNA, MS4644A, Anritsu, Japan) by waveguide method at frequencies of 8.2–12.4 GHz (X-band). In order to understand the high-temperature dielectric property of SiC/PDCs-SiBCN, the permittivity of 15SiC/PDCs-SiBCN was