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Improved dielectric properties of PDCs-SiCN by in-situ fabricated nano-structured carbons

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ABSTRACT

In order to enhance dielectric properties of polymer derived SiCN ceramics (PDCs-SiCN), nano-structured carbons were in-situ fabricated in PDCs-SiCN by pyrolysis of ferrocene-modified polysilazane. Microstructure evolutions, dielectric and microwave absorption properties of PDCs-SiCN decorated with nano-structured carbons were investigated. Nano-structured PDCs-SiCN ceramics are composed of carbon nanowires as well as interpenetrating graphene-like free carbons, SiC nano-crystals, Si_3N_4 nano-crystals and amorphous SiCN. Relative complex permittivities of nano-structured PDCs-SiCN increase with increasing ferrocene contents and annealing temperatures. Free carbons in PDCs-SiCN play a dominating role on the improved dielectric properties. Polarization loss is the primary dielectric loss. Loss tangent of PDCs-SiCN exceeding 0.7 is obtained when free carbons are only 2.57% in weight. Nano-structured PDCs-SiCN exhibit good microwave absorption property. The reflectivity is smaller than −14 dB in the whole X band when material is composed of both impedance and microwave absorption materials.

1. Introduction

Polymer derived ceramic (PDC) is an attractive route to fabricate nano-structured composite ceramic. The unique nanostructures render PDCs special functional properties, such as semi-conductivity property and piezoresistance property [1–10]. Recently, dielectric and electromagnetic wave absorption (EMA) properties of PDCs in the gigahertz have been developed for their potential applications in severe environment [11–18]. Some reported dielectric properties of PDCs at 10 GHz are summarized in Fig. 1. As shown in Fig. 1, crystallized PDCs possess much higher real permittivities (ε'), imaginary permittivities (ε'') and loss tangents ($\tan\delta = \varepsilon''/\varepsilon'$) than amorphous PDCs. The improved dielectric properties of crystallized PDCs are also ascribed to their special nanostructures, which comprise interpenetrating nano microwave absorption agents (free carbons, SiC) in insulating matrices (amorphous ceramic phase, Si_3N_4, or SiO_2).

However, in addition to PDCs-SiC, pure pre-ceramic polymer derived ceramics exhibit low dielectric losses, especially for PDCs-SiCN. As shown in Fig. 1, imaginary permittivity and loss tangent of PDCs-SiCN are smaller than 7 and 0.49, respectively [12]. Low dielectric loss means low microwave attenuation efficiency. Therefore, some efforts are made to improve dielectric losses of PDCs. An effective method is introducing nano microwave absorption agents (nano-SiC or CNT) into PDCs [18]. As shown in Fig. 1, loss tangent of 8 wt.%-CNT/SiBCN composite annealed at 1500 °C is about 1 at 10 GHz [18]. It is worth noting that the required compositions and microstructures of PDCs can be obtained through modifications of their precursors [13,19]. The in-situ growths of nano-SiC (SiC nano-crystals or SiC nanowires) or nano-carbons (carbon nanotubes, carbon nanowires, graphene-like carbons, or onion-like carbons) can be promoted in PDCs by catalytic metals (Fe, Co and Ni) decorated precursors [20–26]. Therefore, another effective method for improvement of dielectric properties of PDCs is in-situ growth of nano-structured absorption agents in PDCs.

Ferrocene comprising one iron element and two cyclopentadienes in a molecular is a kind of organometallic compounds, which can be directly used to fabricate carbon nanotubes owing to coexistence of carbon source and catalytic agent [27,28]. Ferrocene is also a good catalytic candidate for PDCs. On one hand, ferrocene can be homogeneously dissolved into and react with precursor, which gives rise to more free carbons in the final PDCs. On the other hand, the iron can promote growths of nano-structured carbons and SiC nano-crystals. In the paper, ferrocene-modified polysilazane was used as precursor to fabricate nano-structured carbons decorated SiCN ceramics. Microstructure evolutions, dielectric properties and

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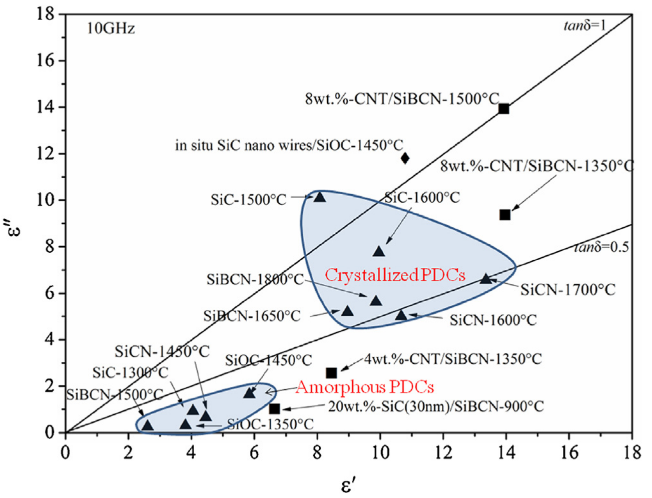

Fig. 1. Some reported dielectric properties of PDCs-SiC [11], SiCN [12], SiOC [14], SiBCN [16], SiC/SiBCN [17] and CNT/SiBCN [18].

EMA properties of PDCs-SiCN were investigated. The mechanisms of dielectric losses for PDCs-SiCN were also discussed.

2. Experimental

2.1. Materials preparation

A commercially available polysilazane (PSN-2, Institute of Chemistry, Chinese Academy of Science) was used as pre-ceramic precursor, which comprised Si-N main chain and Si-Methyl, Si-Vinyl, and Si-H functionalities [12]. Ferrocene ($Fe(C_5H_5)_2$, purity > 99%) was used to modify the precursor. First, PSN-2 was mixed with ferrocene by weight ratios of 3%, 5% and 7%, respectively. The as-received mixtures were stirred in a three-necked flask in a flowing Ar until mixtures became clear red. Then, mixtures were cross-linked at 350 °C for 2 h with a heating rate of 1 °C/min in a flowing Ar environment. During cross-link, reactions between functional groups (Si-vinyl or Si—H) of PSN-2 and cyclopentadienes of ferrocene may occur following formulation shown in Fig. 2. The obtained $(CH_2–CH_2)_X$ chains were beneficial for the formations of free carbons. The cross-linked products were ball milled for 4 h and passed through a 200 mesh sieve. The as-received powders were cold pressed into green bodies with dimensions of 70 mm × 15 mm × 4 mm under a pressure of 70 MPa. Finally, green bodies were pyrolyzed at 900 °C for 2 h with a heating rate of 1 °C/min and then annealed at 1250 °C, 1300 °C, 1350 °C, 1400 °C and 1450 °C in a flowing Ar atmosphere for 2 h with a heating rate of 5 °C/min, respectively. As shown in Table 1, samples were designated as SCN0 to SCN7 according to annealing temperature and ferrocene content. Samples were oxidized at 500 °C in air for 15 h and weight reductions after oxidation were also shown in Table 1.

2.2. Microstructure characterization

Thermal behaviors of cross-linked products were analyzed by simultaneous thermogravimetric analysis and differential scanning calorimetry coupled with mass spectrometry (TG-DSC-MS), which were performed using a quadrupole mass spectrometer QMS 403C Aëolos (Netzsch Group, Germany) at a temperature range between 40 and 1400 °C. Densities and open porosities of samples were measured by Archimedes method according to ASTM C-20 standard. Phase compositions of samples were analyzed by X-ray diffraction (XRD, Rigaku-D/max-2400, and Tokyo, Japan). Carbon phases in the samples were characterized by Raman spectra using a laser confocal Raman microscopy (RMS, Renishaw, UK). Microstructures of samples were characterized by scanning electron microscope (SEM, S-4700, Hitachi, Tokyo, Japan) and transmission electron microscope (TEM, G-30, FEI-Tecnai, Hillsboro, USA).

2.3. Electrical conductivity, dielectric and EMA measurement

Direct-current electrical conductivities (σ_{dc}) of samples were measured through a four-point probe setup (ET9000, Eastchanging, China) [11]. Relative complex permittivities ($\varepsilon_r = \varepsilon' - j\varepsilon''$) of samples with dimensions of 22.86 mm × 10.16 mm × 3 mm were measured in the frequency range of 8.2–12.4 GHz (X band) through waveguide method using a vector network analyzer (VNA, MS4644A, Japan) according to ASTM D 5568-14.

Reflectivity (R) was calculated according to metal back-up panel model for prediction of EMA property. Reflectivity was calculated according to following equation:

$$R = 20\log 10\left(\frac{Z_{in}-1}{Z_{in}+1}\right) \tag{1}$$

where Z_{in} was normalized input impedance of EMA material. The lower reflectivity meant the better EMA property. When reflectivity was smaller than −10 dB, more than 90% microwave energy was absorbed. In order to obtain wide frequency band absorption ($R < -10$ dB in the whole X band), material was usually designed as multilayer structure [13]. When EMA material was only single layer, Z_{in} was calculated according to following equation:

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left[j\frac{\omega}{c}\sqrt{\mu_r\varepsilon_r}d\right] \tag{2}$$

where $\omega = 2\pi f$ (f is frequency), c was velocity of light, d was thickness of EMA material, μ_r was relative complex permeability, respectively. When EMA material was composed of two layers (microwave absorption layer and impedance layer), Z_{in} was calculated according to following equation:

$$Z_{in} = \sqrt{\frac{\mu_{r1}}{\varepsilon_{r1}}} \frac{\left[\sqrt{\mu_{r2}/\varepsilon_{r2}}\tanh(j\omega/c\sqrt{\mu_{r2}\varepsilon_{r2}})d_2 + \sqrt{\mu_{r1}/\varepsilon_{r1}}\tanh(j\omega/c\sqrt{\mu_{r1}\varepsilon_{r1}}d_1)\right]}{\left[\sqrt{\mu_{r1}/\varepsilon_{r1}} + \sqrt{\mu_{r2}/\varepsilon_{r2}}\tanh(j\omega/c\sqrt{\mu_{r2}\varepsilon_{r2}})d_2\tanh(j\omega/c\sqrt{\mu_{r1}\varepsilon_{r1}}d_1)\right]} \tag{3}$$

where μ_{r1} and μ_{r2} were relative complex permeabilities, and ε_{r1} and ε_{r2} were relative complex permittivities of impedance layer and microwave absorption layer, respectively. Owing to poor magnetic properties, relative complex permeabilities of samples was thought as 1.

3. Results and discussion

3.1. Thermal behaviors of ferrocene-modified PSN-2

TG and DSC curves of pure PSN-2 and ferrocene-modified PSN-2 are shown in Fig. 3(a) and (b), respectively. A small weight loss occurs at temperature range of 150–400 °C and a main weight loss occurs at temperature range of 400–800 °C for all samples. The final ceramic yield of sample at 1400 °C increases from 74.4 to 78.1 wt.% when ferrocene content increases from 0 to 7 wt.%. As shown in Fig. 3(c) and (d), MS curves of pure PSN-2 and ferrocene-modified PSN-2 are different at temperature range of 40–400 °C. Thermal behaviors of pure PSN-2 at temperature range of 40–400 °C

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