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Electrical, dielectric and microwave-absorption properties of polymer derived SiC ceramics in X band

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ABSTRACT

Porous silicon carbide ceramics were successfully fabricated by pyrolysis of a polycarbosilane precursor. The direct-current electrical conductivity, dielectric and microwave absorption properties over the frequency range of 8.2–12.4 GHz (X band) were investigated. Polymer derived silicon carbide is composed of SiC nano-crystals and free carbon nanodomains. The high-temperature direct-current conductivities of samples indicate the transformation of amorphous semiconductor into polycrystalline semiconductor with the increase of the annealing temperature. After annealed at 1500 °C, the real permittivity, imaginary permittivity and the loss tangent increase from 3.6, 0.17 and 0.05 to 8.49, 10.01 and 1.18, respectively. The increases of the relative complex permittivity and loss tangent are ascribed to the appearance of SiC nano-crystals and free carbon nanodomains. The average reflectivity of the polymer derived SiC ceramics annealed at 1400 °C is −9.9 dB, which exhibits a promising prospect as microwave absorbing materials.

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1. Introduction

In recent years, a lot of interests have been attracted on the electromagnetic (EM) absorption materials for their wide applications in the protection of the workspace and the environment from the radiation emitted by telecommunication as well as in the stealth technology [1]. In order to fabricate materials with excellent microwave absorption properties, the dielectric constant (real part of the permittivity) should be close to 1, and the dielectric loss (conductivity or imaginary part of the permittivity) should be high enough [2,3]. In order to fulfill the above requirements, the microwave absorption agents are usually dispersed in the nonconductive matrix to fabricate the microwave absorption materials [4].

Silicon carbide (SiC) is a wide band gap semiconductor which possesses many practical and potential applications in electromagnetic wave absorption at severe environments. The dielectric and microwave absorption properties of SiC, such as SiC particles [5], SiC nanowires [6], and elements (e.g., B, N, and Al) doped-SiC particles [7–10], have been widely investigated. Owing to the special dielectric and electrical properties, SiC possesses excellent microwave absorption properties, especially for the nano-structural materials. The dielectric properties of SiC nanowires synthesized by the infiltration process are good and associated with the length of nanowires [6]. By the self-propagating high-temperature synthesis method (SHS), Ni-doped SiC nanopowders have been fabricated, which improve the dielectric properties of pure SiC [11]. However, these nano-structural materials are usually dispersed in the polymer or SiO_2 matrix [4–10], which limit their potential usages at high temperatures. On the other side, it is difficult to disperse the nanoparticles into the matrix. In situ formation of nano-SiC in the matrix is an effective way to solve the issues. By low pressure chemical vapor infiltration (LPCVI), nano-sized SiC are in situ formed in the SiBC ceramics, the loss tangent of which can reach 0.8 [12].

Compared with other processing, polymer derived ceramics (PDCs) can be used to in situ fabricate nano-sized SiC in matrix. Through the design of the molecular structures of precursors, various SiC based materials can be fabricated, such as PDC-SiC [13], PDC-SiCN [14], PDC-SiBCN [15], and magnetic element doped-PDC-SiCN [16]. During the polymer-to-ceramic conversion, the microwave absorption agents such as SiC and/or carbon phase are in situ formed in the PDCs, which are beneficial to the increase of microwave absorption properties [17,18]. The PDCs exhibit excellent high-temperature creep resistance and oxidation resistance [19,20], making it attractive for the applications at high temperatures.

In this study, a carbon-rich PDC-SiC precursor (polycarbosilane) is used to fabricate the porous PDC-SiC. The effects of annealing temperature on microstructure, direct-current electrical conductivity, dielectric properties, and microwave absorption properties of the PDC-SiC are studied.

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2. Experimental details

2.1. Materials preparation

SiC ceramics were fabricated from a liquid polycarbosilane (PCS, Xiamen University). The precursor had a highly branched structure with a Si—CH_2—Si chain and Si—H, Si—CH_3, CH═CH_2 functionalities [21]. For preparing ceramic samples, the PCS was first cross-linked at 300 °C for 2 h in a high-purity N_2 atmosphere. 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 a dimension of 70 mm × 15 mm × 4 mm under a pressure of 70 MPa. Finally, the green bodies were pyrolyzed at 900 °C for 2 h with heating rate of 1 °C/min and then annealed at 1100 °C, 1200 °C, 1300 °C, 1400 °C, 1500 °C and 1600 °C in a high purity N_2 environment in an Al_2O_3 tube for 2 h with heating rate of 5 °C/min, respectively. For convenience, the samples were designated as S1, S2, S3, S4, S5 and S6 according to the annealing temperature.

2.2. Materials characterization

The phase compositions of samples were analyzed by the X-ray diffraction (XRD, Rigaku-D/max-2400, and Tokyo, Japan). The element compositions of SiC were analyzed by a combination of carbon–sulfur analyzer and oxygen–nitrogen analyzer (EMIA-320 V/EMGA-620 V, HORIBA Ltd., Hakata-ku, Japan). The density and open porosity of the samples were measured by Archimedes method according to ASTM C-20 standard.

The direct-current electrical conductivities of the samples were measured through a four-point probe setup (ET9000, Eastchanging, China). As shown in Fig. 1, the four point probe setup had four tungsten metal tips, which were supported by a spring. Steady electrical current was supplied by a high impedance current source (6220, Keithley, USA) through the probe 1 and 4. The voltage between probe 2 and 3 was measured by a high impedance voltmeter (2182A, Keithley, USA). Because of the high input impedance voltmeter in the circuit, the probe 2 and 3 draw no current, which avoided the voltage drop at probe 2 and 3 caused by contact resistance between probe and the sample. The resistance (R) was obtained directly by the equipment, and the electrical resistivity (ρ) was calculated according to the following equations:

$$\rho = C\frac{2\pi R}{S} \tag{1}$$

$$S = \left(\frac{1}{S1} + \frac{1}{S3} - \frac{1}{S2 + S3} - \frac{1}{S1 + S2}\right) \tag{2}$$

where C was the prefactor. C was ≈1 in the present work. For testing the high-temperature direct-current electrical conductivity, a heating apparatus was placed beneath the sample, and a thermocouple was used to record temperature. The high-temperature resistance was recorded from room temperature to 673 K.

The relative complex permittivities of samples were measured through waveguide method according to ASTM D 5568-08. As shown in Fig. 2, the measurement setup consisted of a vector network analyzer (VNA, MS4644A, Japan), waveguide cavity, and sample holder. In addition, a set of calibration kits were used to calibrate the measurement system. The microwave scattering parameters were directly measured by the VNA, and the permittivities of samples were calculated according to the NRW algorithm. The relative complex permittivities 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). The gaps between the sample and the sample holder would affect the signal of the scattering parameters, which may result in the errors. [22] In some researches [22,23], the materials were directly injected into the sample holder, which eliminated the gaps. In the paper, thin conductive taps were used to seal the gaps in order to avoid the errors.

3. Results and discussion

3.1. Microstructure and element compositions of porous PDC-SiC

The open porosity and the density of porous SiC are shown in Table 1. The open porosity and the density of samples S1–S5 are about 41% and 1.43 g/cm^3, respectively. The open porosity of sample S6 increases to 49% and the density decreases to 1.27 g/cm^3.

The element compositions of C, O and N in samples were characterized by a combination of carbon–sulfur and oxygen–nitrogen analyzer. The results are shown in Table 1. In addition to Si and C elements, the O and N elements also exist in the samples which are probably introduced into the samples during the heat treatment [24]. It can be seen that the element compositions of the samples S1, S2 and S3 are almost the same, indicating the samples are thermally stable up to 1300 °C. With the increase of the annealing temperature, the weight ratio of O element in samples S4, S5 and S6 decreases from 9.6% to 4.5%, which are mainly attributed to the release of SiO and CO during the heat treatment, as shown in the following equations [25]:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \tag{3}$$

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g) \tag{4}$$

The release of SiO also results in the obvious increase of the open porosity and the decrease of the density of sample S6. It is noted that with the increase of annealing temperature, the C/Si mole ratios in samples increase from 1.39 to 1.58, which suggests that a large quantity of excess carbon exists in the samples. The contents of N in sample S4, S5 and S6 are 4.0%, 4.3% and 6.1%, which are much larger than those in S3, S2 and S1. The increase of N content in samples may have pronounced effect on the electrical and dielectric properties of the samples.

3.2. Phase compositions of PDC-SiC

The phase compositions of samples were revealed by the XRD spectra, as shown in Fig. 3. Obviously, a weak SiC peak at about 35.6° appears in sample S1, which means the PDC-SiC begins to crystallize at about 1100 °C. Compared with samples S1 and S2,

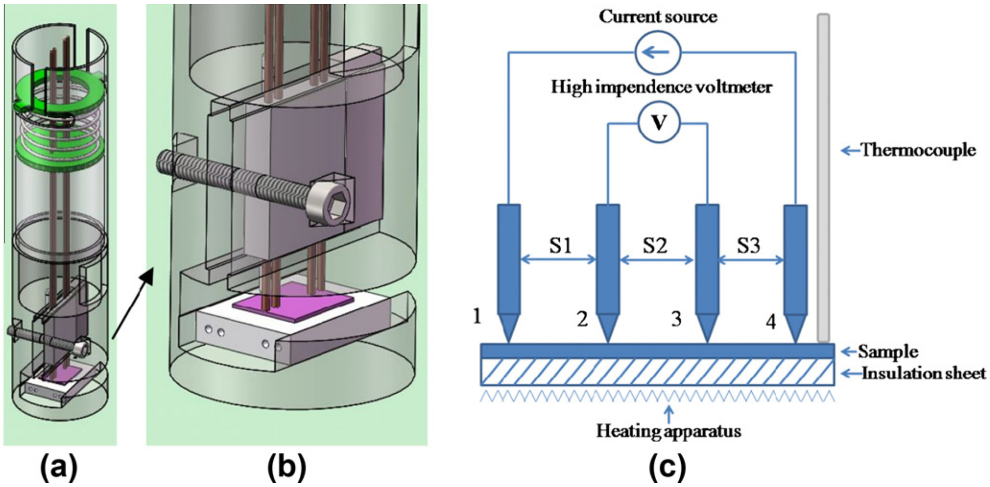

Fig. 1. (a) and (b) 3D map of the four probe equipment set up, and (c) diagram of the four probe equipment.

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