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High-temperature dielectric and electromagnetic interference shielding properties of SiC_f/SiC composites using Ti_3SiC_2 as inert filler

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ABSTRACT

Ti_3SiC_2 filler has been introduced into SiC_f/SiC composites by precursor infiltration and pyrolysis (PIP) process to optimize the dielectric properties for electromagnetic interference (EMI) shielding applications in the temperatures of 25–600 °C at 8.2–12.4 GHz. Results indicate that the flexural strength of SiC_f/SiC composites is improved from 217 MPa to 295 MPa after incorporating the filler. Both the complex permittivity and $\tan\delta$ of the composites show obvious temperature-dependent behavior and increase with the increasing temperatures. The absorption, reflection and total shielding effectiveness of the composites with Ti_3SiC_2 filler are enhanced from 13 dB, 7 dB and 20 dB to 24 dB, 21 dB and 45 dB respectively with the temperatures increase from 25 °C to 600 °C. The mechanisms for the corresponding enhancements are also proposed. The superior absorption shielding effectiveness is the dominant EMI shielding mechanism. The optimized EMI shielding properties suggest their potentials for the future shielding applications at temperatures from 25 °C to 600 °C.

1. Introduction

Electromagnetic interference (EMI) shielding materials have attracted more and more interests because of the facts that various electronic devices for communication, automation and computation processes are widely used in commercial and military applications [1,2]. The EMI shielding materials aim at shielding against the penetration of external electromagnetic radiation that generates from the developed electronic devices working at gigahertz frequencies. The electromagnetic radiation can seriously affect the function of nearby wide range of electrical circuitry and cause potential health hazards for human beings when exposed to the electromagnetic fields [3,4]. Therefore, various materials such as metal-based materials, carbon-based materials [5,6] and conducting polymer-based materials [7,8] have been developed for the attenuation of EMI during the past decades. Metal-based materials in the form of thin sheets or sheathing typically serve as excellent EMI shielding agents, but the disadvantages of heavy weight and prone to environmental degradation often make them undesired choices for many current devices [9]. Conversely, carbon-based materials such as carbon nanotubes, carbon black and carbon fibers are generally used as conducting fillers by incorporating them into polymers to form conducting polymer composites for EMI shielding, which are normally lightweight, physical flexible and corrosion resistant [10–14]. Though polymer-based materials offer distinct advantages against metals, it is very difficult to achieve the satisfactory improvements in EMI shielding properties because the high specific surface area of these nanofillers leads to their agglomerations, non-uniform properties and failure to realize their full potentials [15]. What is more worse, the susceptibility to oxidation of carbon materials and polymers has hampered their wide applications at high temperatures [16]. Consequently, for an application such as aerospace industry, especially for the high-temperature components which require high strengths as well as EMI shielding capabilities [1,3], SiC fiber reinforced SiC matrix (SiC_f/SiC) composites have been developed in recent years as promising structural and functional materials for the replacement of orthodox metallic aluminium and ferrous alloys in this respect, due to their excellent high-temperature strength, good thermo-chemical stability, low density, oxidation resistance, and special dielectric and electrical properties [17,18].

Generally, the EMI shielding materials could result in the attenuation of external electromagnetic wave by three shielding mechanisms including the reflection, absorption and multiple reflections [3,19]. Reflection relies on the mobile charge carriers, such as electrons, being present within the materials. Therefore, this shielding characteristic is found to be enhanced by a high electrical

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conductivity. Significant absorption of electromagnetic waves by the shield requires electric or magnetic dipoles in the materials. And the absorption loss is proportional to the shield thickness and relative electrical conductivity. The multiple reflections often take place at the surface or interfaces within the shield. Thus, the presence of large surface areas or interfaces is beneficial to this mechanism. Based on the previous studies [20,21], it has been identified that there exist amounts of excess carbon and β-SiC microcrystals including many dangling bonds and vacancies defects in the fibers and matrix of SiC_f/SiC composites fabricated by precursor infiltration and pyrolysis (PIP) process, which contributes to enhancing the electrical and dielectric properties of the composites. Several papers have investigated the EMI shielding effectiveness (SE) of SiC_f/SiC composites at ambient temperature. Ding et al. reported that SiC_f/SiC composites containing PyC interphase exhibited a remarkable EMI SE of 25 dB at 8.2–12.4 GHz, and its dominant shielding mechanism shifted from absorption to reflection as the PyC thickness increased [22]. We have prepared SiC_f/SiC composites by combined chemical vapor infiltration (CVI) and PIP processes and found that the final composites showed an evident EMI SE of 30 dB at 8.2–12.4 GHz [23]. However, up to now, the reports on EMI SE of SiC_f/SiC composites at high temperatures are rare.

Accordingly, the EMI SE of a composite material strongly depends on the filler's intrinsic conductivity, dielectric constant and aspect ratio [4,19]. From the mechanical standpoint, the incorporating filler can effectively improve the infiltration efficiency during the PIP process and act as strengthening phase to enhance the mechanical properties of the composites [24]. Thus, in the present work, titanium silicon carbide (Ti_3SiC_2) was introduced into the polycarbosilane (PCS) precursor as inert filler to optimize the dielectric and EMI shielding properties of SiC_f/SiC composites, owing to its nano-laminate structure, good electrical and thermal conductivities, low specific gravity, and excellent oxidation resistance at elevated temperatures [25]. We report the results of the first study on the dielectric and EMI shielding properties of SiC_f/SiC composites with Ti_3SiC_2 filler at temperatures from 25 °C to 600 °C in the frequency range of 8.2–12.4 GHz, and the mechanisms of their evolutions with the increasing temperatures are also proposed.

2. Experimental procedure and characterization

2.1. Composites preparation and characterization

The 2.5D KD-I SiC fabrics and PCS powders were used as the reinforcement and precursor of SiC matrix respectively, which were both provided by National University of Defense Technology, China. The detailed parameters of SiC fibers and PCS precursor were characterized in Ref. [26]. Ti_3SiC_2 powders with the diameters of 0.5–2 μm were used as the inert filler, which were supplied by Jinghe Chemical Reagent Factory, Hebei, China. The density and electrical conductivity of Ti_3SiC_2 powders were 4.5 g/cm^3 and 4.0×10^6 S/m respectively.

Prior to matrix preparation, the SiC fabric was coated by BN interphase with a thickness of 200 nm, and its preparation process was conducted according to our previous study [27]. In this work, PCS/xylene solution with 9 wt.% Ti_3SiC_2 powders (mass ratio of PCS:xylene:Ti_3SiC_2 = 1:1:0.2) was adopted as the infiltrating slurry. The detailed preparation routes of the infiltrating slurry and final composites with Ti_3SiC_2 filler were represented in Ref. [24]. The PIP cycles of the final composites were repeated for 9 times until the mass gain was less than 1 wt.%. By comparison, the SiC_f/SiC composites without filler were fabricated using the 50 wt.% PCS/xylene solution and the PIP cycles were repeated for 15 times.

The open porosity and density of the composites were measured by the Archimedes method. The flexural strength was measured by a three-point bending test (specimen size of $40^l\ \text{mm} \times 4^w\ \text{mm} \times 3^t\ \text{mm}$) with a cross-head speed of 0.5 mm/min and support span length of 30 mm using a universal testing machine (Haida Qualitative Analysis, HD-609B). The fracture surfaces of the composites after three-point bending tests were characterized by scanning electron microscope (Model SUPRA-55, Zeiss, Germany). The resistance of the composites was measured by the two-probe direct current method from 25 °C to 600 °C (25, 200, 400 and 600 °C) [28], and the DC electrical conductivity (σ_{dc}) was calculated by: $\sigma_{dc} = L/RS$, where R is the resistance parallel to the warp direction of the composites, S is the cross-sectional area perpendicular to the warp direction, and L is the length parallel to the warp direction.

2.2. Evaluation of dielectric properties and EMI SE

The dielectric properties of the composites were characterized by the real part (ε') and imaginary part (ε'') of complex permittivity (generally expressed by $\varepsilon_r = \varepsilon' - j\varepsilon''$). The EMI SE was determined by calculations of the magnitudes of complex scattering parameters (S-parameters) that correspond to reflection (S_{11} or S_{22}) and transmission (S_{21} or S_{12}). The complex permittivity and S-parameters were measured by the rectangular waveguide method using a two-port vector network analyzer (Agilent technologies E8362B: 10 MHz to 20 GHz) at four temperature spots from 25 °C to 600 °C (25, 200, 400 and 600 °C) in the frequency range of 8.2–12.4 GHz (X band). Fig. 1 schematically shows the waveguide method set-up for complex permittivity and S-parameters measurements at high temperatures. As shown in Fig. 1b, the testing composites were arranged perpendicularly to the incident microwave through the thickness orientation and heated by an inner heater at a rate of 10 °C/min. Each temperature spot was stabilized for 10 min in order to ensure the accuracy of measurement. The dimensions of the measured samples were $22.86^l\ \text{mm} \times 10.16^w\ \text{mm} \times 3.0^t\ \text{mm}$.

When defining the performance of a shielding material, the total SE (SE_T) can be applied and characterized as follows [29,30]:

$$SE_T(\text{dB}) = 10\log(P_iP_t) = SE_A + SE_R + SE_M \tag{1}$$

where P_i and P_t are the incident and transmitted power density of microwave through the shielding materials; SE_A and SE_R are the absorption and reflection SE respectively; SE_M is induced by the multiple internal reflections inside the shielding materials, which is negligible when $SE_T > 15$ dB [31]. Thus, Eq. (1) can be taken as: $SE_T = SE_A + SE_R$. The SE_R and SE_A can be calculated by the reflection coefficient (R) and transmission coefficient (T):

$$SE_R = -10\log(1 - R) \tag{2}$$

$$SE_A = -10\log[T/(1 - R)] \tag{3}$$

where R and T are directly given by $R = |S_{11}|^2 = |S_{22}|^2$ and $T = |S_{12}|^2 = |S_{21}|^2$.

3. Results and discussion

3.1. Microstructures and mechanical properties of SiC_f/SiC composites with and without filler

Fig. 2 displays the XRD patterns of Ti_3SiC_2 filler before and after heat treatment to investigate its phase transformation during the pyrolysis process. As seen from Fig. 2, the narrow diffraction peaks of as-received Ti_3SiC_2 filler reveal that the Ti_3SiC_2 is highly crystallized. The XRD patterns of Ti_3SiC_2 filler show no obvious differences before and after heat treatment, and the broad peaks of SiC