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Journal of the European Ceramic Society 34 (2014) 2229–2237

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Multiwalled carbon nanotubes–$BaTiO_3$/silica composites with high complex permittivity and improved electromagnetic interference shielding at elevated temperature

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Received 12 November 2013; received in revised form 23 January 2014; accepted 2 February 2014
Available online 5 March 2014

Abstract

Composites with silica matrix and mixed filler of multiwalled carbon nanotubes (MWCNTs) and $BaTiO_3$ powder were fabricated. Excellent uniform dispersion of MWCNTs can be obtained using a two-step mixing method. Both of the real and imaginary parts of complex permittivity increased with increasing MWCNT content and measured temperature. The electromagnetic interference (EMI) shielding results showed that the absorption mechanism is the main contribution to the total EMI shielding effectiveness (SE). Compared with the EMI SE resulting from reflection, the absorption showed more dependence on the MWCNT content, measured temperature and frequency. The total EMI SE is greater than 20 dB at 25 °C and 50 dB at 600 °C in the whole frequency range of 12.4–18 GHz with a 1.5 mm composite thickness, which suggests that the MWCNT–$BaTiO_3$/silica composites could be good candidates for the EMI shielding materials in the measured frequency and temperature region.
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Keywords: Functional composites; High-temperature properties; Complex permittivity; Multiwalled carbon nanotubes; Electromagnetic interference

1. Introduction

Carbon nanotubes (CNTs) are new one-dimensional carbon materials with excellent mechanical, electrical, thermal and chemical stability properties. Especially, CNTs can be utilized to impart electrical conductivity to dielectric hosts because of their fascinating electrical properties (metallic or semiconducting) as well as large aspect ratio.[1–3] Researches of CNTs as novel fillers to fabricate electromagnetic interference (EMI) shielding composites and microwave absorber have grown expeditiously over the past decade.[4–9] Xiang et al. prepared dense fused silica composites filled with multiwalled carbon nanotubes (MWCNTs) by hot-pressing. Experimental results show that such composites exhibit high complex permittivity in the frequency range of 8.2–12.4 GHz, indicating that such composites have excellent microwave attenuation properties.[9] Furthermore, the EMI shielding effectiveness (SE) and microwave absorbing properties of the CNTs filled composites can be improved by adding the other fillers, such as metal particles, conductive polymer, magnetic and/or dielectric particles.[10–13] For example, MWCNTs and $BaTiO_3$ particles filled polyvinylidene fluoride composites with high dielectric constant and low dielectric loss can be obtained.[13] In addition, MWCNT/$BaTiO_3$ ceramics with high electrical conductivity also have been studied,[14,15] indicating that the composite filled with MWCNTs and $BaTiO_3$ can be used as EMI shielding materials with excellent microwave attenuation property.

However, for the introduction of CNTs into ceramic matrix composites, two key issues are generally deemed as barriers: the first one is how to evenly disperse CNTs into ceramic slurries, and the second one is how to achieve a tight interface bonding between the CNTs and the surrounding matrix,

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http://dx.doi.org/10.1016/j.jeurceramsoc.2014.02.007
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without damaging the CNTs.[16] Therefore, it is valuable to fabricate uniform dispersed CNTs filled ceramic composites under moderate condition. In this work, two-step mixing method was adopted to obtain MWCNTs and $BaTiO_3$ powder filled silica composites with excellent dispersion of MWCNTs, and such composites were prepared under moderate condition to avoid damaging the structure of CNTs. The microstructure, complex permittivity and EMI SE of the MWCNT–$BaTiO_3$/silica composites in the frequency range of 12.4–18 GHz (Ku-band), based on different contents of MWCNTs and measured temperatures, were measured and analyzed. The effects of MWCNT contents and measured temperatures on the EMI shielding mechanism (absorption and reflection) of the overall EMI SE were also investigated.

2. Experimental

2.1. Materials

The MWCNTs used as a conductive filler in this work were fabricated by the catalytic decomposition of CH_4 and supplied by the Shenzhen Nanotech Port Co., Ltd., China. The diameter of MWCNTs was ranging from 60 to 100 nm, and length was ranging from 2 to 5 μm, and the purity was 95%. Tetragonal-phase $BaTiO_3$ powder with a Ba/Ti mol ratio of 1.001, were provided by Nantong Ao Xin Electronic Technology Co., Ltd., JiangSu, China. The values of d_{10}, d_{50} and d_{90} of the $BaTiO_3$ powder are 50 nm, 250 nm and 450 nm, respectively, and these were obtained from the manufacturer. Silica colloid with about 30 wt% silica (particle size is about 20 nm) used as binder were provided by Xi'an Chemical Reagent Co., Ltd., Shaanxi, China. The sodium dodecyl benzene sulfonate (SDS) (Sinopharm Chemical Reagent. Co., Ltd., China), employed to obtain better dispersion of the MWCNTs, was used as a surfactant for all of the composites.

2.2. Sample preparation

Samples with a fixed content of $BaTiO_3$ powder (50 wt%) and different content of MWCNTs (2, 4, 6 and 8 wt%) in the final composite were prepared. In order to prevent the entanglement of MWCNTs, SDS with a concentration of 0.5 wt% was employed as a surfactant for all of the samples. Firstly, the MWCNTs were dispersed in ethanol by an ultrasonic bath at room temperature for 1 h. After adding the $BaTiO_3$ powder into the ethanol-based solution, the mixtures were stirred at 2000 rpm for 10 min and then sonicated at room temperature for 1 h. Subsequently, the mixtures were placed in an oven at 80 °C until the ethanol evaporated completely. Then the silica colloid was added into the mixtures, followed by stirring at 2000 rpm for 30 min. After the mixtures were dried at 100 °C in oven, the dried mixtures were compacted into disks with 50 mm diameter and 3 mm thickness under a pressure of 100 MPa. According to the sintering condition applied to fabricated CNTs/silica composite,[7] the green compact was sintered at a temperature of 600 °C for 1 h in a nitrogen atmosphere, and the heating rate was set at 5 °C min^{-1}.

2.3. Measurements

The composite ceramic was machined into specimens with two kinds of dimensions for flexural strength and dielectric property measurement. The transmission and reflection scattering parameters (S_{11}/S_{22} and S_{21}/S_{12}), the complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) of the composites were measured by a network analyzer (Agilent technologies E8362B: 10 MHz to 20 GHz) between 25 and 600 °C in the frequency range of 12.4–18 GHz using the wave-guide method. The apparatus for high temperature test was similar to Ref. 7. During the high temperature measurement, a period of 30 min for the system to stabilize at each selected temperature was achieved to ensure the accuracy of the measurement. From S_{11} (S_{22}) and S_{21} (S_{12}) measurements, reflected coefficient (R) and transmitted coefficient (T) are given by: $R = |E_R/E_I|^2 = |S_{11}|^2 = |S_{22}|^2$ and $T = |E_T/E_I|^2 = |S_{21}|^2 = |S_{12}|^2$. The absorbed coefficient (A) can be obtained by $A = 1 - R - T$. The EMI SE of a material is defined as the ratio between the incident power (P_i) and outgoing power (P_t) of an EM wave. The EMI SE is expressed in dB and given by,[8]

$$\text{EMI SE (dB)} = -10 \log \left(\frac{P_t}{P_i} \right) \quad (1)$$

The morphology of the MWCNT–$BaTiO_3$/silica composites was observed using field emission scanning electron microscopy (FE-SEM) (Model JSM-6700F, Tokyo, Japan). The electrical resistivity was measured by two-wire method using a current source (6220 DC Keithley, OH, USA). The theoretical density of the MWCNT–$BaTiO_3$/silica composites calculated based on the density of $BaTiO_3$ (6.02 g cm^3, claimed by the manufacturer), that of SiO_2 (2. 36 g cm^3, claimed by the manufacturer) and that of MWCNTs (2.1 g cm^3, claimed by the manufacturer) was used to calculate the relative density of products.

3. Results and discussion

3.1. The microstructures and mechanical properties of MWCNT–$BaTiO_3$/silica composites

In order to obtain the full reinforcement potential of MWCNTs and $BaTiO_3$ powder, a highly homogenized dispersion of the fillers is required. Unfortunately, MWCNT materials produced by large-scale chemical vapor deposition processes tend to form strong agglomerates due to high van der Waals forces and physical entanglements.[17,18] Commonly, one approach for improving the dispersion of CNTs is introducing surfactants such as SDS in a water or organic base solution. Previous works have shown that the SDS can stabilize the aqueous solutions of CNTs, which attributed to high electrostatic repulsive forces provided by the adsorbed surfactant.[19,20] Another approach most commonly adopted is exposure of CNTs to ultrasound in ethanol based solution followed by intense stirring the subsequent material, leads to a dramatic improvement of the CNTs dispersion in the matrix. [21,22] Furthermore, the addition of $BaTiO_3$ powder can hinder the aggregation of CNTs during the ultrasonic procedure, which also resulted in the uniform dispersion of CNTs

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