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Improving sintering behavior of MWCNT/$BaTiO_3$ ceramic nanocomposite with Bi_2O_3-B_2O_3 addition

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ABSTRACT

The present research systematically investigated the novel low-temperature fabrication of a multi-walled carbon nanotube (MWCNT)/barium titanate nanocomposite using a two-step mixing technique. The synthesis was conducted using different amounts of MWCNT (0.25%, 0.5%, 1%, 2%, 4%, and 8% wt) with different compositions of (Bi_2O_3 + B_2O_3) as a sintering aid. Scanning and transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, three-point bending strength, Vickers hardness indentation and Archimedean technique were used to characterize the as-synthesized specimens. It was found that the appropriate content of sintering aid (Bi_2O_3+B_2O_3) strongly decreased the sintering temperature from 1200 °C to 950 °C. The results also revealed that any sintering aid with the optimum composition that included 30% (mol) Bi_2O_3 was optimal for a sintering aid content of 6% (wt). Consequently, the highest values of the flexural strength and fracture toughness were achieved by applying the optimal amounts of MWCNT (1% wt) and sintering aid (6% wt).

1. Introduction

Carbon nanotubes (CNTs) are applied as mechanically reinforcing fillers, nanoscale semiconductor devices, hydrogen storage materials, and smart sensors [1–5]. Hybrid materials such as CNT ceramic composites have attracted attention because they feature exclusive characteristics that enable the mechanical, electrical, thermal, and chemical improvement of fabricated composites [5–10].

The high dielectric constant of multi-walled carbon nanotube in the (MWCNT)/$BaTiO_3$ nanocomposite make it a promising candidate for improving microwave-absorbing and electromagnetic interference (EMI) shielding material with outstanding microwave attenuation characteristics [11]. Controlling nanocomposite sintering behavior (porosity and densification) is critical to attaining these dielectric properties.

Huang et al. [12] prepared an MWCNT/$BaTiO_3$ nanocomposite ceramic by applying hot-press sintering, and reported that the high sintering temperature (1200 °C) was a major technical challenge for the economical fabrication of this nanocomposite. Decreasing the sintering temperature is essential to commercial production of this nanocomposite. Practical techniques for decreasing the sintering temperature of ceramics densified at high temperatures include the use of materials having a finer particle size, a chemical process or doping of low-melting temperature constituents [13–16]. It appears that the latter technique, in which liquid phase-assisted contact is the predominant densification mechanism, efficiently improves sintering behavior. It also features a simple procedure that is low cost, and requires comparatively little time.

In the present research, the sintering behavior of MWCNT/$BaTiO_3$ nanocomposite was systematically studied by applying a mixture of Bi_2O_3 and B_2O_3 as the sintering aid. A Bi-liquid phase aids densification of oxides [16–21], and B_2O_3 is commonly employed as a flux former [22–26]. The effect of content and mixture composition of the sintering aid (Bi_2O_3+B_2O_3) on the sintering temperature of the nanocomposite was also investigated. The relative density and flexural strength of the nanocomposite were determined, and an appropriate sintering temperature was obtained with the assistance of the micrographs from scanning electron microscopy (SEM).

2. Experimental procedure

The MWCNT/$BaTiO_3$ nanocomposite was synthesized using reagent-grade barium titanate (Merck), bismuth trioxide (Merck), boron trioxide (Merck), sodium dodecyl sulfate (SDS; Merck), and MWCNTs (US Research Nanomaterials; USA) functionalized by a COOH agent. The purity of the MWCNTs was > 98%, the external diameter was 20–30 nm, the internal diameter was 5–10 nm, and the length was 10–30 nm. Ethanol (Merck) was applied as a chemical mixture medium.

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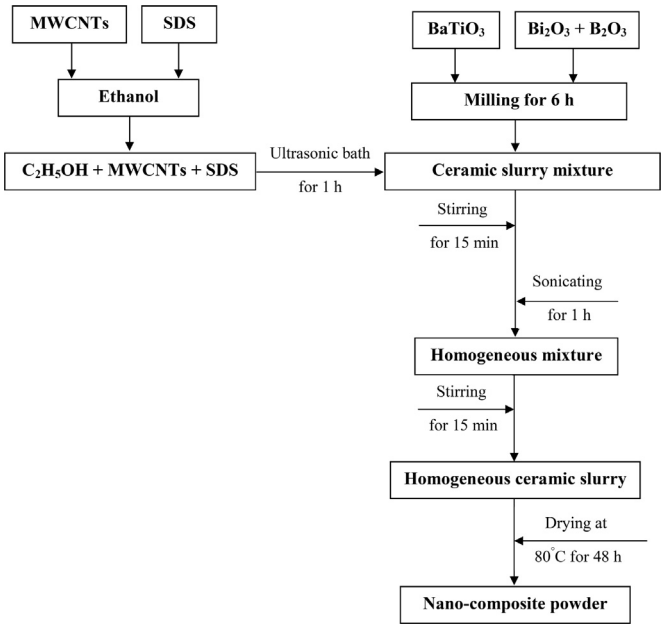

Fig. 1. Flowchart of synthesis of MWCNT/$BaTiO_3$ nanocomposite.

The nanocomposite was synthesized by mixing the aforesaid chemicals with various percentages of MWCNT (0.25%, 0.5%, 1%, 2%, 4%, and 8% wt) as a composite filler. A two-step mixing technique in ethanol medium was employed to fabricate the nanocomposite. Fig. 1 shows the flowchart of nanocomposite synthesis. First, the calculated amount of MWCNT was added to ethyl alcohol (C_2H_5OH), and a small amount of SDS was added to the mixture as a surfactant agent to prohibit the entanglement of the CNTs. The system was then put in an ultrasonic bath for 1 h at room temperature. A defined quantity of barium titanate (as a matrix for the nanocomposite) and 2%, 4%, 6% or 8% (wt) sintering aid ($Bi_2O_3 + B_2O_3$) containing 10%, 30%, 50%, 70% or 90% (mol) Bi_2O_3 were ball-milled for 6 h, and the mixture was added to the slurry.

The system was stirred at 1000 rpm for 15 min and again sonicated for about 1 h. The resulting homogeneous mixture was stirred for the last time at 1000 rpm for 15 min. Thereafter, the prepared slurry was poured into a glass beaker covered with aluminum foil; the beaker was transferred to an 80 °C oven and kept there for 48 h. The dried composite powders were sieved through # 200 mesh, and pressed into disks 32 ± 0.5 mm in diameter and 3 ± 0.5 mm in thickness under a pressure of 400 MPa. The green compacted products were sintered at 800–950 °C for a holding time of 1 h in an argon-controlled atmosphere at a heating rate of 10 °C/min.

Densities of the products were measured by Archimedes technique using distilled water. To evaluate the sintering progress, relative density of the samples was calculated by dividing the measured densities into the theoretical densities. For this purpose, theoretical density of the composites was measured using helium pycnometer.

The sintered nanocomposites were ground flat using a diamond grinding wheel and then well polished with finer diamond pastes. The flexural strength was determined using the three-point bending method (Instron Universal Testing Machine 1196) at a bending span and crosshead speed of 20 mm and 0.5 mm/min respectively. The size of specimens was 25 ± 1 mm (length) × 2 ± 0.1 mm (breadth) × 2.5 ± 0.2 mm (height). The fracture toughness (K_{IC}) of the specimens was measured based on indent crack measurement using Vickers micro-hardness indentation in which a fine indent was created on the polished surface under loading of 9.8 N for 15 s by means of a Vickers micro-hardness tester (Buehler-micromet 5114). Fig. 2 shows the image of the Vickers's hardness indent for fracture toughness estimation. The cracks generated through indentation process were clearly observed. The lengths of the

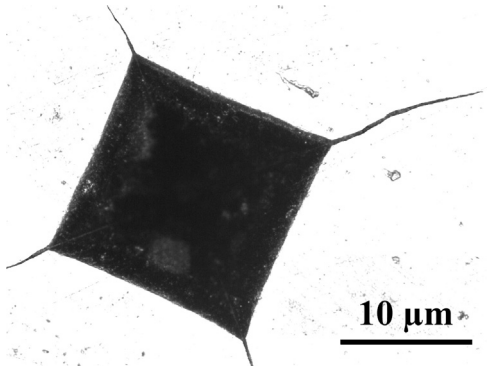

Fig. 2. The Vickers's hardness indent under loading of 9.8 N for fracture toughness estimation.

resultant crack during indentation were precisely estimated under an optical microscope (Olympus GX71) equipped with image processing and analysis software. The K_{IC} values were then calculated using the following equation [27]:

$$K_{IC} = 0.016\left(\frac{E}{H}\right)^{\frac{1}{2}}\left(\frac{P}{C^{\frac{3}{2}}}\right) \quad (1)$$

where E is the Young's modulus, H is the micro-hardness, and C is the radial crack length result after indentation. More than 10 indentations were used to obtain a mean value with which to calculate K_{IC}. The Young's modulus of the specimens was measured on samples 32 ± 0.5 mm in diameter with a thickness of 3 ± 0.5 mm using the resonance technique based on ASTM C 1259-01 using a Gindosonic Mk5I.

A KYKY-SEM3200 scanning electron microscope along with an energy dispersive X-ray spectroscope (EDX) spectra equipment was employed to investigate the phase distribution of the sintered nanocomposites, and chemical composition. Morphology and chemical microanalysis was carried out by transmission electron microscopy (TEM) using a JEOL JEM-3010 microscope operated at 300 kV and equipped with an energy dispersive X-ray spectroscope.

X-ray diffraction (XRD) was employed for the phase analysis of the sintered nanocomposite using a Philips X-pert diffractometer using Co Kα radiation. The average crystallite size of the specimens was calculated using the Scherrer formula [28,29]. Fourier transformation infrared spectroscopy (FTIR) of a prepared nanocomposite was performed to determine the bonding information in a Nicolet Nexus 6700 apparatus at 500–4000 cm^{-1}.

3. Results and discussion

The phase diagram of a Bi_2O_3-B_2O_3 binary system (used here as sintering aid) which was reported by Kargin et al. [30] is shown in Fig. 3. The diagram clearly reveals that the predominant phase at sintering temperatures of (800–950 °C) and a chemical composition of 10–90% (mol) Bi_2O_3 is liquid; hence, the implementation of this sintering aid as a liquid phase has been confirmed.

The dependence of the relative density of the nanocomposites on sintering temperature in the presence of various amounts of ($Bi_2O_3 + B_2O_3$) sintering aid at a constant Bi_2O_3 content (50% mol), and 1% (wt) MWCNT is shown in Fig. 4. Densifications of the nanocomposites increased as the sintering temperature increased because of the faster diffusion kinetics. In addition, at a constant sintering temperature, an increase in the dopant content of ($Bi_2O_3 + B_2O_3$) produced high relative density in the nanocomposites. This can be attributed to the presence of the low-melting temperature phase (Bi_2O_3 + B_2O_3). An increase in additive produced liquid-phase flux in which a tight interface bonding between the MWCNTs and $BaTiO_3$ particles can be concluded by presence of the sintering aid.