Materials Letters 215 (2018) 144–147

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Electrical conduction in aluminum nitride-single-walled carbon nanotube nanocomposites

R. Singh [a], A. Chakravarty [b], U. Chowdhury [b], D. Bhattacharya [b], S.K. Biswas [a,*]

[a] *Malaviya National Institute of Technology, JLN Marg, 302017 Jaipur, India*
[b] *CSIR-Central Glass and Ceramic Research Institute, Jadavpur, 700032 Kolkata, India*

ARTICLE INFO

Article history:
Received 10 June 2017
Received in revised form 6 December 2017
Accepted 17 December 2017
Available online 18 December 2017

Keywords:
Ceramics
Carbon nanotubes

ABSTRACT

Analysis of the temperature dependence of electrical conductivities of aluminum nitride (AlN)-single walled carbon nanotube (SWCNT) ceramic nanocomposite containing 1, 3 and 6 vol% SWCNT has been reported in this communication. A conductivity as high as 200 Sm^{-1} in the composite containing 6 vol% SWCNT has been explained with the low hopping parameter and high metallic conduction in three dimensions due to the presence of large quantity of metallic SWCNTs in the composite. Microstructure analyses of the composites reveal the presence of nets containing SWCNT ropes oriented in different directions and forming highly connected 3D networks in the grain boundaries.

1. Introduction

Ceramic-CNT composites are gaining importance over the last two decades due to improved properties over their monolithic matrix for multifunctional applications like smart structures, heaters, electromagnetic shields and supercapacitors and ease of machining by electrodischarge machining (EDM) [1–3]. EDM machining of any material demands the conductivity should be at least in the semiconducting region [4]. Properties of ceramic-CNT composites could be tailored by choosing the types of SWCNT (metallic or semiconducting) [5]. No report could yet be noticed highlighting the development and properties of the ceramic nanocomposites containing a particular electrical variety of the SWCNT.

Special approaches like electrophoretic deposition could lead to designed microstructure of ceramic-CNT composite and overcome the processing challenges to prepare ceramic/SWCNT nanocomposites with uniform dispersions [6]. Understanding the functional properties of these composites is very important and very little work could be observed in the literature [7–12].

The present communication reports the electrical properties in AlN-SWCNT, a new nanocomposite which has been prepared by conventional hot pressing from commercial AlN powder and SWCNTs enriched with metallic variety tubes. The combination of AlN and SWCNT is chosen since both of these materials have high thermal conductivity and improvement in electrical conductivity could lead to several applications where heat dissipation is a great concern. Analyses of the temperature dependences of the dc-electrical conductivities and the microstructure of the composites are presented to explore the mechanism of transport in the composite.

2. Experiments

Procedure for the preparation of the composite is similar to that communicated recently [13]. The ingredients for the composite consisted of AlN powder (H.C. Starck – Grade C), SWCNT (processed from Elicarb, Thomas Swan, UK) and sintering additive Y_2O_3 (Indian Rare Earths Ltd., India) were taken in ethanol sols separately and mixed slowly with continuous stirring and sonication at room temperature. SWCNTs were enriched with metallic tubes (68%) simultaneously with the removal of amorphous carbon, metal and ceramic impurities [14]. Hot pressing was carried out at 2123 K with a hold time of 40 mins in a graphite die (36 mm dia) and plunger with a pressure of 35 MPa under nitrogen atmosphere (FCT systems). Bulk densities of the samples were measured by Archimedes' method. DC resistivities of the polished samples (10 × 5 × 3 mm) were measured by 4 probe technique using a precision current source (Keithley 6220) and a voltage measuring multimeter (HP3458A) connected with a cryostat. Thin foil specimens for the Transmission Electron Microscope (TEM) (Tecnai G2 F30 ST 300 kV, FEI) images were prepared by standard techniques involving grinding, ultrasonic cutting, dimpling and ion beam etching of the samples. Fracture surface topography of the composites have been analyzed by Field Emission Scanning Electron micro-

---

* Corresponding author.
E-mail address: sbiswas.meta@mnit.ac.in (S.K. Biswas).

https://doi.org/10.1016/j.matlet.2017.12.071
0167-577X/

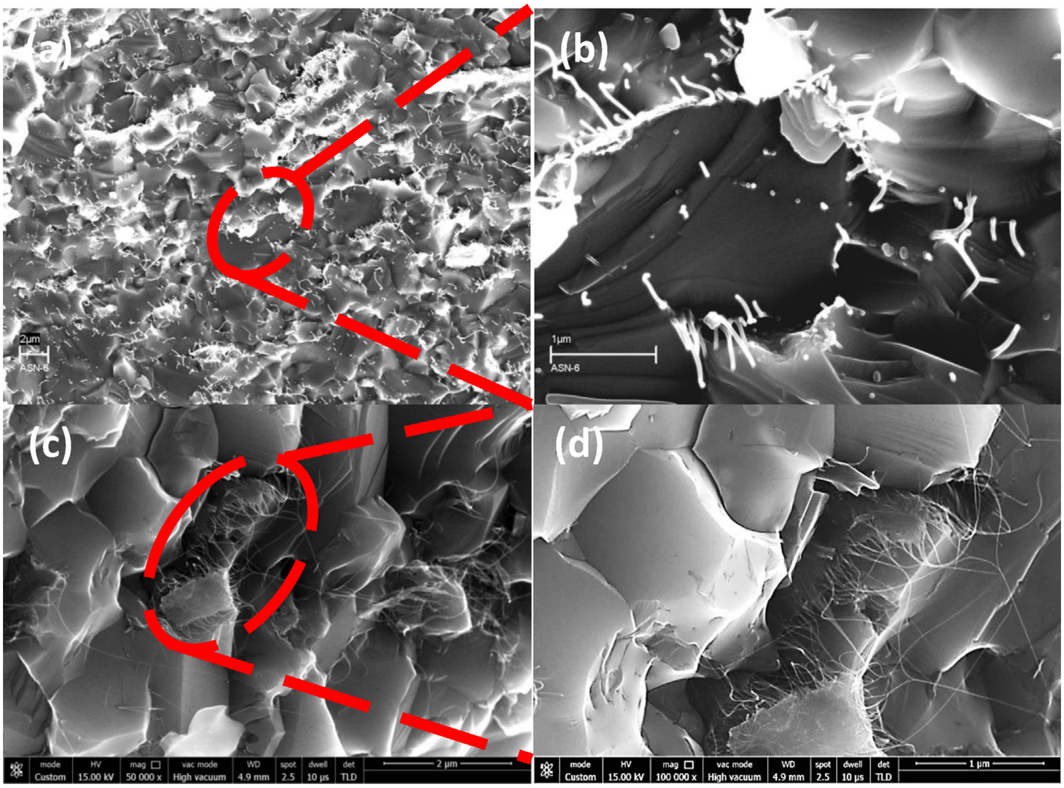

Fig. 1. FESEM micrograph of the fracture surface of ASN-6 showing formation of nanotube nets around grains of AlN. Micrographs taken from (a) ETD detector at 20 kV and (c) from TLD detector at 15 kV. Red circles indicate the positions of enlargements for higher magnification micrographs (b) and (d).

graphs (Zeiss Supra 35VP and Nova Nanosem 450 instruments). Both Everhardt-Thornley (ETD) and In-Lens (TLD) secondary electron detectors were used for the voltage optimization (5–15 kV) and contrast studies. Raman spectra of solid samples were analyzed (Renishaw-in Via Raman microscope) with a laser frequency of 785 nm.

3. Results and discussion

Relative densities achieved by hot pressing the powder mix consisting of AlN, 0, 1, 3 and 6 vol% SWCNTS labelled as ASN-0, ASN-1, ASN-3 and ASN-6 respectively are very high (~99%). Retention of the diameter distribution and prevalence of metallic SWCNTs in the starting feedstock and the composites have been confirmed from RBM Raman spectra in the Supporting information (S1) and optical spectra reported earlier [14]. Ropes of SWCNTs form 2D architecture in the form of nets or mesh which surround the grains of polycrystalline ceramics building a 3D network [15]. The presence of nanotube nets at grain boundaries of AlN in the composite samples could be confirmed from the FESEM fractographs (Fig. 1). Voltage optimization has been carried out to look at the grain boundaries of the polycrystalline ceramic composite similar to the procedures adopted earlier [16,17] for better visibility of the nanotubes and their structures in the material.

TEM images of thin foils of the composite samples in Fig. 2 show that SWCNT ropes are present along the grain boundaries of AlN. 3D connectivity of the ropes could be established from the images taken both in parallel and perpendicular to the hot pressing direction [Fig. 2(a), (b) and (c)]. Higher magnification image and selected area diffraction (SAED) of grain boundary [Fig. 2(d) and (e)] confirm the presence of SWCNT tubes (PDF Card No. 00-058-1638). HRTEM of SWCNT nets at grain boundary [Fig. 2(f)] show the different orientations and bending of the nanotubes in the net.

Comparison of the microstructures presented above with the TEM images of the starting SWCNTs (Supplementary information, S2) prove the retention of the structure of the nanotubes in the composite. Thus, the electrical conduction in these composites originated from the conducting pathways with 3D connectivities made by SWCNTs along the boundaries of AlN grains [Figs. 1 and 2]. The ropes orient themselves in different directions and often bend to form nets. A percolating level below 1 vol% SWCNT content in the composite has been observed earlier [13]. Dc electrical conductivity (200 $\mathrm{Sm^{-1}}$) in ASN-6 sample is the highest among the published results for non-oxide ceramic-SWCNT composites containing 6 vol% SWCNT [13 and Supplementary information, S3]. Conductivity increase with nanotube contents in the composite could be explained by the reduction of intertube spacing, higher connectivity of the network and increased intertube tunnelling of electrons as proposed earlier for a percolative behaviour [10,11]. The temperature dependences of the electrical conductivities have been analysed to gain better insight of the mechanism of the electrical conduction in our samples. Fig. 3(a) shows that the dependence of electrical resistivities of the samples with temperature diminishes with the increase in nanotube content. The normalized conductivity values (lnG) of all the samples were plotted with $T^{-1/4}$ in Fig. 3(b) for further analyses on the compliance of the mechanisms of transport in the composites with the 3D variable range hopping (VRH) model. Interestingly, the conductivities of all the composites could be extrapolated to non-zero values at 0 K indicating free charge carriers requiring no thermal activation. This is a signature of the metallic behaviour of the composites. It could also be observed that the hopping mechanism is followed in ASN-1 and 3 samples and not followed entirely over the whole temperature range studied in ASN-6. The variation in ASN-6 could be approximated to an equation of the form suggested earlier [18,19],