Composites: Part A 40 (2009) 86–93

Contents lists available at ScienceDirect

Composites: Part A

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

Mechanical properties of carbon nanotube–alumina nanocomposites synthesized by chemical vapor deposition and spark plasma sintering

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ARTICLE INFO

Article history:
Received 6 March 2008
Received in revised form 9 October 2008
Accepted 13 October 2008

Keywords:
A. Nano-structures
B. Mechanical properties
D. Electron Microscopy
E. Chemical vapor deposition

ABSTRACT

Carbon nanotubes–alumina (CNT–Al_2O_3) nanocomposites with variable CNT content were directly synthesized by chemical vapor deposition (CVD). The as-grown CNT–Al_2O_3 mixture was densified by spark plasma sintering (SPS) at 1150 and 1450 °C. Vickers hardness of 9.98 GPa and fracture toughness of 4.7 MPam$^{1/2}$ were obtained for 7.39 wt.% CNT–Al_2O_3 nanocomposite. The addition of CNTs gives rise to 8.4% increase in hardness and 21.1% increase in toughness over that of the pure Al_2O_3. The optimum amount of CNTs is considered to be able to significantly enhance the mechanical property of ceramics in composites.

1. Introduction

Carbon nanotubes in the form of single-walled (SWCNTs) or multiwalled (MWCNTs) assemblies have been the focus of considerable scientific research. The unusual mechanical properties of CNTs make them an ideal class of reinforcement for composite materials [1]. CNTs have great potential for use as a toughening agent due to their very large aspect ratio (1000–10,000) [2], low density, high rigidity (Young's modulus of the order of 1 TPa) [3,4], and high tensile strength (up to 60 GPa) [5]. In addition, the excellent electrical conductivity (10^6 S/m at 300 K for SWCNT, >10^5 S/m for MWCNT) [6,7] and thermal conductivity (6600 W/mK for an individual SWCNT and >3000 W/mK for an individual MWCNT) [8,9] make CNTs suitable candidates to synthesize nancomposites with new functional properties. Ceramics can sustain high temperature and high hardness, but the most noted shortcoming of ceramics is the inherent brittleness, which has limited its extensive applications [10]. Thus the incorporation of CNTs with ceramics will provide an unparalleled opportunity to form a new class of CNT–ceramics materials with enhanced mechanical property.

Many attempts have been made to improve the mechanical properties of ceramics through incorporating CNTs in ceramic matrix. Siegel et al. [11] reported that the addition of 10 vol.% MWCNTs to monolithic Al_2O_3 could lead to 24% increase in the fracture toughness. Ma et al. [12] showed that a SiC composite containing 10 vol.% MWNTs had a 10% increase in bending strength and toughness compared with the monolithic SiC. Zhan et al. [13] obtained a fracture toughness of 9.7 MPam$^{1/2}$ from 10 vol.% SWNT–Al_2O_3 composite, which was nearly three times higher than that of pure Al_2O_3. However, Laurent et al. [14] reported a contradictory result in CNT/Fe–Al_2O_3 composites, where the CNT reinforcement did not show any significant effect on the CNT/Fe–Al_2O_3 composites and the fracture toughness of CNT/Fe–Al_2O_3 composites was almost similar to that of carbon-free Fe–Al_2O_3 composites. Earlier work by Wang et al. suggested that the CNT–Al_2O_3 nanocomposites with 10 vol.% CNT are as brittle as bulk Al_2O_3, showing almost the same toughness [15]. Recently, Balani et al. synthesized CNT reinforced Al_2O_3 nanocomposite coating by plasma spray technique and showed an increase in the fracture toughness of 43% [16] and elastic modulus of 200% as compared to pure Al_2O_3 [17]. In the present work, the synthesis and consolidation of as-grown CNT–Al_2O_3 composites are discussed in detail. The Vickers hardness and fracture toughness of the CNT–Al_2O_3 composites as a function of the CNT content and sintering temperatures are investigated.

2. Experimental method

CNT–Al_2O_3 mixture was synthesized by CVD. CNTs are directly grown on Al_2O_3 nanoparticles by using $Co(NO_3)_2{\cdot}6H_2O$ as a catalyst precursor [18]. To upload the catalyst precursor on the Al_2O_3 nanoparticles, $Co(NO_3)_2{\cdot}6H_2O$ (98+%, Sigma–Aldrich) and Al_2O_3 powder

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doi:10.1016/j.compositesa.2008.10.003

(CR30 Al_2O_3 powder, Baikowski Inc., purity 99.99%) were mixed in ethanol, followed by sonication for 15 min. Then, the mixture was dried at 130 °C for overnight followed by grinding into a fine powder. Composites with Co/Al_2O_3 at ratios of 0.5–5.0 wt.% were prepared.

For a large scale synthesis of CNT, the Co/Al_2O_3 powder was loaded directly into a fused quartz tube, whereas for the small scale synthesis, Co/Al_2O_3 powder was dispersed in a Mo boat and inserted in a fused quartz tube which was thereby placed in a horizontal tube furnace. For the large amount synthesis, a fused quartz stirrer was included in the CVD system to stir the powder to achieve a uniform exposure to the reaction gases. In this work, we refer to the composite growth by using Mo boat as 'BM' mode and by stirrer as 'SM' mode. Acetylene (C_2H_2), hydrogen (H_2), and argon (Ar) with ratio of 1:4:6 and a total flow rate of about 1100 sccm were introduced into the reaction chamber through distilled water bubbler for CNT growth. The synthesis of CNTs was carried out at 750 °C for 15 min. After the synthesis, the CNT–Al_2O_3 composite material was placed in 15 mm diameter graphite die and sintered under vacuum in a SPS unit [DR. SINTER spark plasma sintering system, SPS Syntex Inc.]. The following conditions were applied for the SPS treatment: pressure 100 MPa, peak temperatures 1150 or 1450 °C, heating rate 100 °C/min, hold time at peak temperature 10 min, pulse duration 12 ms, and pulse interval 2 ms. For comparison, pure Al_2O_3 was also sintered at the same SPS conditions. In this work, more emphasis is on the mechanical properties of nanocomposites synthesized by SM, as they depict better CNT yield, density, and mechanical properties than that synthesized by BM.

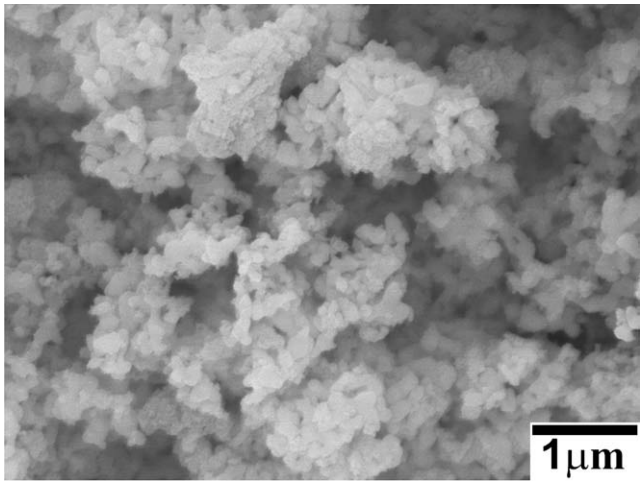

Fig. 1. FESEM image of the original alumina powder used in this experiment. The alumina particle size is about 100–300 nm.

Microstructure analysis was performed by scanning electron microscopy (FESEM, JEOL, JSM-633OF) and high resolution transmission electron microscopy (TEM, JEOL 2010F). The density of the sintered samples was measured by the Archimedes method with deionized water as the immersion medium [13]. The hardness was measured by using a Vickers microhardness tester (HXD-1000TMC, Microhardness Tester, Shanghai Taiming Optical Instrument Co.) under load of 100 g with a dwell time

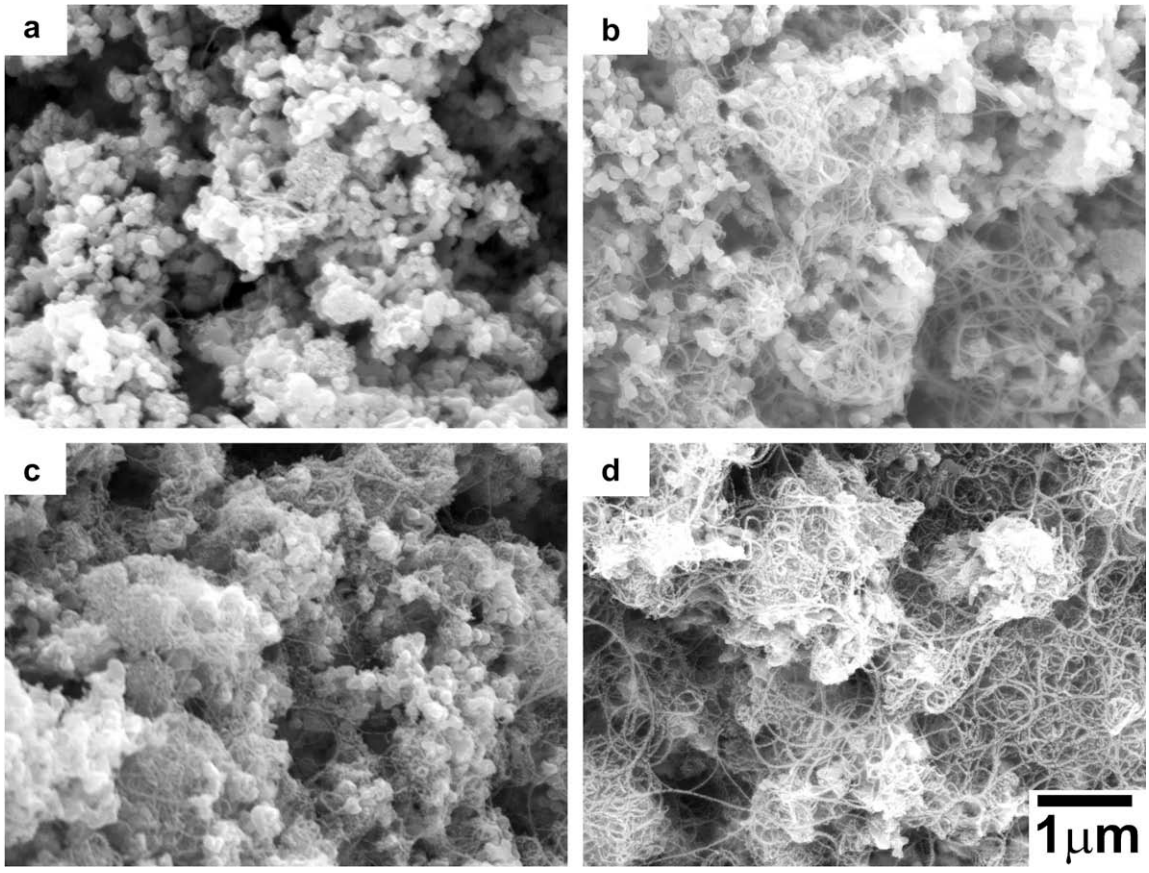

Fig. 2. FESEM images of the CNT–Al_2O_3 nanocomposites (SM) with CNT contents of (a) 3.19 wt.% (on 0.5 wt.% Co/Al_2O_3), (b) 7.39 wt.% (on 1.0 wt.% Co/Al_2O_3), (c) 8.25 wt.% (on 2.0 wt.% Co/Al_2O_3) and (d) 19.10 wt.% (on 4.0 wt.% Co/Al_2O_3). The scale bar for each of these images is 1 μm.