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Effect of carbon nanotube damage on the mechanical properties of aluminium–carbon nanotube composites

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ABSTRACT

The effect of carbon nanotube (CNT) damage on the mechanical properties of aluminium (Al)–CNT composites is investigated using mildly and severely damaged CNTs. Composites prepared with mildly damaged CNTs are found to have 97.5% higher strength and 14.2% higher modulus than pure Al. Increased carbide formation – due to the damage sustained – is observed and is believed to be in the form of isolated secondary particles within the matrix which do not contribute to enhancing the Al–CNT bonds. The strength and modulus of composites with severely damaged CNTs are found to be higher by 71% and 3.3% than pure Al, suggesting that even fragmented CNT particles can contribute to enhancing the strength and modulus of the Al matrix. The results are analyzed in light of strengthening mechanisms expected to be playing different roles in Al–CNT composites. The enhancement in strength is believed to be mainly due to matrix strengthening mechanisms and is not affected by CNT damage whereas the gain in Young's modulus is due to load transfer to the CNTs and accordingly is more significant in the case of the mildly damaged CNTs which have retained their tubular structure and high aspect ratio.

1. Introduction

Since the publication of the landmark paper by Iijima [1], carbon nanotubes (CNTs) are being considered for various applications. Their remarkable mechanical properties have instigated their use as reinforcements in composite materials. Depending on the type of matrix used, different techniques have been used to introduce and disperse the CNTs within the matrix. Solid-state processing techniques have been used in studies involving metallic matrices (for example, aluminium (Al)) due to the low temperatures involved and the ease of incorporating the CNTs. An effective technique used to disperse the CNTs in the Al powder is high energy ball milling [2–4]. However, there is concern that this technique introduces defects to the CNTs and may cause their total destruction if harsh ball milling conditions are utilized. One notable study in this regard was conducted by Poirier et al. [4] who reported that ball milling CNTs with Al powder destroys most of the CNTs. Other studies, however, presented images of intact CNTs on the fracture surfaces of Al–CNT composites prepared by ball milling. Some studies have claimed that cold welding of the Al matrix particles around the CNTs protects them from damage [2].

Studying the effect of ball milling on the structure of CNTs has received attention from researchers. Studies of the effect of milling time show that ball milling shortens the CNTs and opens their ends and that milling for longer periods may cause their complete destruction [5–8]. Such studies were conducted with the objective of investigating the milling conditions (mainly time) that lead to maximizing the CNTs' specific surface area for potential applications in hydrogen storage and as molecular sieves – both requiring shorter CNTs with open ends.

Several researchers developing Al–CNT composites have reported poor interfacial bonding between the CNTs and the Al matrix which affected the attained properties. It is widely believed that when high quality, low-defect CNTs are used (e.g. arc-evaporated CNTs) their smooth walls and perfect cylindrical structures make attaining a strong interfacial bond with the matrix difficult. Functionalization has been used in many studies, especially ones focusing on polymeric matrices, to enhance the bond chemically. Previous research has shown that a better bond could also be reached by increasing the surface roughness of the nanotubes and/or by increasing their surface reactivity [9]. Many researchers reported the formation of Al_4C_3 – as an adverse reaction likely to negatively influence the mechanical behavior – when processing Al–CNT composites with high CNT volume fractions at temperatures above 450 °C [3,4]. Conversely, the in-depth investigation

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by Ci et al. [10], in which HRTEM was used to provide detailed interface structure, reported nanoscale Al_4C_3 at defect sites on the CNT surfaces and on CNT tips. Based on their observations, the authors argued that the Al_4C_3 helps lock the CNTs in place and thus can contribute to enhancing the mechanical properties of the composite.

The focus of the current work is to investigate the effect of intentionally damaging the CNTs before mixing them with the Al powders on the mechanical behavior of the composites. To this end, in addition to as-received CNTs, two levels of damaged CNTs were used: (1) mildly damaged but retaining their tubular structure and (2) completely damaged CNTs in the form of fragments.

2. Experimental procedure

This work is divided into two parts: (a) pre-milling of CNTs and (b) fabricating Al–CNT composites. The CNTs used in this study were supplied by the MER Corporation, USA. They are catalytic multiwall carbon nanotubes (MWCNTs) with an outer diameter of 140 ± 30 nm, an approximate length of 7 ± 2 μm and a purity of >90%.

2.1. Milling of CNTs alone

The CNTs were milled with 10 mm diameter stainless steel balls in stainless steel jars using a Retsch PM 400 MA planetary ball mill. Several milling conditions were investigated in order to select a condition which introduces damage without affecting the tubular structure of the CNTs. Milling time was limited to 10 min in order to restrict the damage to the CNTs particularly at high RPM and ball-to-powder (BPR) weight ratios. The milling conditions were: 100 RPM (BPR 4:1 and BPR 300:1) and 400 RPM (BPR 4:1 and BPR 300:1). Additional CNT samples were milled using the harshest conditions of 400 RPM with a BPR of 300:1 for up to 30 min; expected to lead to total destruction of the tubular structure of the CNTs.

2.2. Composite fabrication

Al powder (99.7% pure, average particle size = 75 μm) was mixed with 2 wt.% CNT. Three sets of samples were prepared with: (1) as-received CNTs, (2) mildly damaged CNTs, and (3) severely damaged CNTs. Composite samples were prepared by ball milling the Al–CNT powder mixtures in the planetary ball mill at 400 rpm using a BPR of 10:1 for 30 min. 300 μl of methanol were added as a process control agent. The milling was conducted under an argon atmosphere. Similar milling conditions were reported previously by the current authors to lead to well dispersed CNTs [11]. In addition, pure Al powders were milled under the same conditions to provide control samples.

The milled powders were cold compacted for 30 min at 475 MPa and then homogenized for another 30 min at 500 °C before being extruded. A die with an extrusion ratio of 4:1 was used to produce 10 mm diameter extrudates which were then machined into dog-bone shaped tension test specimens with gauge lengths of 20 mm and gauge diameters of 4 mm. The shoulder diameter was 8 mm, the shoulder length was 10 mm and the fillet radius was 2 mm. Finally, the specimens were annealed for 10 h at 500 °C to relieve the stresses from the extrusion and machining processes, and to promote carbide formation at the introduced defect sites since according to literature [3,4,10], Al_4C_3 is expected to form at defect sites at temperatures above 450 °C.

2.3. Testing and analysis

The densities of the composites were measured using Mettler Toledo XS 205 digital densitometer. Tension tests were conducted using an Instron 50 KN capacity universal testing machine using 1 mm/min crosshead speed. A LEO Supra 55 field emission scanning electron microscope (FESEM) was used to image the pre-milled CNTs as well as the fractured surfaces of the composites after the tension tests. Transmission electron microscopy (TEM) images of the pre-milled CNTs were collected using JEOL 2010 TEM at 200 kV. Samples were prepared by mixing the pre-milled CNT powders in alcohol, sonicating to disperse them and then placing a drop of the liquid on a holey carbon TEM support grid. A Scintag XDS 2000 powder X-ray diffractometer was used to collect X-ray diffraction (XRD) patterns of as-received CNTs using Cu Kα radiation. For Al–CNT bulk samples, diffraction patterns were collected using Philips XPERT multi-purpose X-ray diffractometer (MPD) using wavelength $\lambda = 0.154$ nm. Raman spectra were recorded with Enwave Optronics Raman spectrometer using a laser with an excitation wavelength of 523 nm. The nanoindentation technique was used to measure the indentation modulus of the composite samples. MTS Nanoindenter XP (MTS systems Co.) employing a Berkovich tip was used for the test. The test was conducted by means of the continuous stiffness module (CSM) which allows dynamic measurements throughout the indentation depth. The maximum indentation depth was set to 5 μm. The measurements were averaged for depths between 2 and 4 μm. Indentations were applied in a 6 × 6 array (36 indentations) on each sample.

3. Results and discussion

The CNTs used in the current study are straight and stiff, as shown in Fig. 1(a) and (b). It is also noticeable that their diameters are not uniform and that they have large end caps. TEM analysis showed that they have a large number of walls with a small inner core, as noticeable from Fig. 1(c). They have some topological and crystallographic defects as is commonly present in catalytic CNTs. Their outer walls appear rough and they have an irregular graphitic structure which is attributed to their Chemical Vapour Deposition (CVD) synthesis process. Though their walls appear straight, what is also noticeable is that their shell structure is not well-defined. It is only at high magnifications that their individual layers of graphitic carbon and their small hollow cores can be recognized. Further analysis by XRD showed a significant peak at around $2\theta = 26°$ (representing the inter-layer spacing of the CNTs) which confirms their ordered and parallel graphene sheets. They were chosen because of their availability and high usage having been reported in a number of earlier studies.

3.1. Milling of CNTs alone

FESEM images – Fig. 2(a–d) – of the CNTs milled using the various milling speeds and BPRs show that the CNTs milled at 100 rpm using a BPR of 4:1 do not appear to have experienced any change in their structure (Fig. 2a). Similarly, it is noticeable that increasing the milling speed to 400 rpm, while keeping the BPR at 4:1, had no apparent effect (Fig. 2c). On the other hand, milling using a BPR of 300:1 was found to affect the CNTs' structure. Milling at 100 rpm was found to introduce limited damage and to open some CNT caps whilst preserving the CNT tubular structure, as apparent in the FESEM images (Fig. 2b). Increasing the milling speed to 400 rpm at this high BPR appeared to fragment the CNTs (Fig. 2d). Cleavage of the CNTs is believed to have taken place at the sites of existing structural defects. These results were confirmed by TEM analysis (Fig. 3). Although it is believed that wall defects have been introduced in the CNT structures upon milling, it is difficult to ascertain their amounts using SEM or TEM. Raman spectroscopy was used, as will be discussed later, to confirm the changes in the overall defect density under the different milling conditions.

FESEM images of CNTs milled using the harshest investigated conditions (BPR of 300:1 for 30 min at 400 rpm) show the damage sustained by the nanotubes as a function of milling time. The images are presented in Fig. 4(a–d). After 5 min of milling the CNTs are partially destroyed and fragments of graphene appear to agglomerate to form particles. The formation of these particles increases after 10 and 15 min of milling after which CNTs are hardly seen. Images of CNTs milled for 30 min show the particles with no trace of the CNT tubular structure (Fig. 4d). TEM images of these particles (Fig. 5) show that they are agglomerates of nano-sized fragments which have a similar crystalline structure (lattice fringes) to CNTs.

The observations made by SEM and TEM were further confirmed by the results of the Raman analysis shown in Fig. 6. The D and G bands are commonly used to characterize the quality of the nanotubes. The G band, which represents the graphitic structure of the CNTs, is observed around wavenumber 1600 cm^{-1}. It will decrease and broaden with increasing number of defects in the nanotubes [4]. The D band, which originates from defects in the graphitic structure, is found around wavenumber 1300 cm^{-1}. It will increase with increasing number of defects in the nanotubes [4]. The Raman spectra of all milled CNT samples can be divided