Synthesis and characterization of mechanically milled nanocomposites—carbon nanotube-reinforced aluminium

M. Tayyab,* M. Mutahir, M. Sajid and A. Ali

Department of Materials Engineering, N.E.D. University of Engineering & Technology, Karachi, Pakistan

Ever since the discovery of carbon nanotubes (CNTs), their interesting properties have captured the interest of researchers for commercial applications. Exceptional mechanical properties, with an average elastic modulus of 1–2 TPa and fracture strength of 200 GPa, provide the motivation for CNTs to be used in service conditions requiring high strength-to-weight ratios. The present research aims at the incorporation and characterization of CNT-reinforced aluminium nanocomposites. High energy ball milling was used to embed CNTs in a soft and ductile aluminium matrix. Milled powders having CNTs sandwiched in between aluminium grains were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results revealed the presence of CNTs at the aluminium powder cold weld interfaces, which was further confirmed by diffraction analysis.

Keywords: carbon nanotubes, nanocomposites, scanning electron microscopy, X-ray diffraction

1. Introduction

Carbon nanotubes are the toughest known material to date, and are a potential material of choice for realizing the space elevator. High stiffness and strength make them a viable material for the many applications requiring a high strength-to-weight ratio. For this reason, incorporation of CNTs in composites as reinforcement is of major significance. Nanotubes are the stiffest known fibre, with a measured Young's modulus of 1.4 TPa.[1] They have an expected elongation to failure of 20–30% which, combined with the stiffness, gives a tensile strength well above 100 GPa

* Corresponding author. E-mail: mallicktayyab@gmail.com

[1] M.F. Yu. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. *Phys. Rev. Lett.* **84** (2000) 5552–5555.

(possibly higher), and so far the highest known.[2] For comparison, the Young's modulus of high-strength steel is around 200 GPa, and its tensile strength is 1–2 GPa.[3] Considerable research has already been conducted on CNT-reinforced polymer matrix composites, but the evolution of carbon nanotube-reinforced metal matrix (CNT–MM) composites is at an earlier stage. Progress has, however, been rather slow, primarily due to the challenges associated with CNT dispersion and the high temperature processing used in the synthesis of metal composites.[4] Some of the processing techniques used in the fabrication of CNT-reinforced MMC are conventional powder metallurgy techniques, electroplating and electroless plating from CNT-containing electrolytic baths, spark plasma sintering, mechanical alloying and thermal spraying. Uniform dispersion and alignment of nanotubes within the metal matrix composites is still difficult. Many problems hinder the achievement of optimum conditions during fabrication of CNT-MM nanocomposites. Neubauer et al. described the challenges associated with nanocomposite fabrication as "selection of suitable raw materials, dispersion of reinforcement in the matrix material, densification of the composite, processing/reactivity with the matrix, alignment/orientation/anisotropy, the external interface, and their applications".[5] Several fabrication routes, namely ball milling, extrusion, hot pressing, equal channel angular pressing, spark plasma sintering, electrodeposition, electroless deposition and thermal spraying have been used to synthesize metal matrix composites with CNTs.[6] Powder metallurgy is the most popular and widely used technique for preparing CNT–MM composites. Electrodeposition and electroless deposition are the second most important techniques, used for deposition of thin coatings of CNT–MM composites as well as for deposition of metals onto CNTs.[7]

In this study, CNTs were mechanically milled in aluminium powder via ball milling. The milled powder was characterized by various analytical techniques to probe the distribution of CNTs in the ductile aluminium matrix. The results from scanning electron microscopy (SEM) and X-ray diffraction (XRD) showed the distribution pattern and the effect of milling time.

2. Materials and methods

2.1 Materials

Pure 99.9% aluminium was used in this study together with CNTs produced by chemical vapour deposition (CVD) by Shenzhen Nanotech (China) or produced in our laboratory by spark ablation (arc discharge) techniques. The diameter of the (multiwalled) nanotubes produced by CVD was

[2] A.R. Ranjbartoreh, G.X. Wang, A. Ghorbanpour Arani and A. Loghman. Comparative consideration of axial stability of single- and double-walled carbon nanotube and its inner and outer tubes. *Physica* E **41** (2008) 202–208.

[3] B.I. Yakobson, C.J. Brabec and J. Bernholc. Nanomechanics of carbon tubes: instabilities beyond linear response. *Phys. Rev. Lett.* **76** (1996) 2511–2514.

[4] Y. Wu and G.-Y. Kim. Carbon nanotube reinforced aluminium composite fabricated by semi-solid powder processing. *J. Mater. Processing Technol.* **211** (2011) 1341–1347.

[5] E. Neubauer, M. Kitzmantel, M. Hulman and P. Angerer. Potential and challenges of metal-matrix-composites reinforced with carbon nanofibers and carbon nanotubes. *Composites Sci. Tech.* **70** (2010) 2228–2236.

[6] S.R. Bakshi, V. Singh, S. Seal and A. Agarwal. Aluminum composite reinforced with multiwalled carbon nanotubes from plasma spraying of spray dried powders. *Surface Coatings Tech.* **203** (2009) 1544–1554.

[7] S. R. Bakshi, D. Lahiri and A. Agarwal. Carbon nanotube reinforced metal matrix composites. *Int. Mater. Rev.* **55** (2010) 41–64.

of the order of 30 to 40 nm and the length 5 to 15 μm with a purity level of 97% (3% ash). Different proportions of Al and CNT were milled for predetermined intervals. SEM micrographs of precursors are shown in Fig 1.

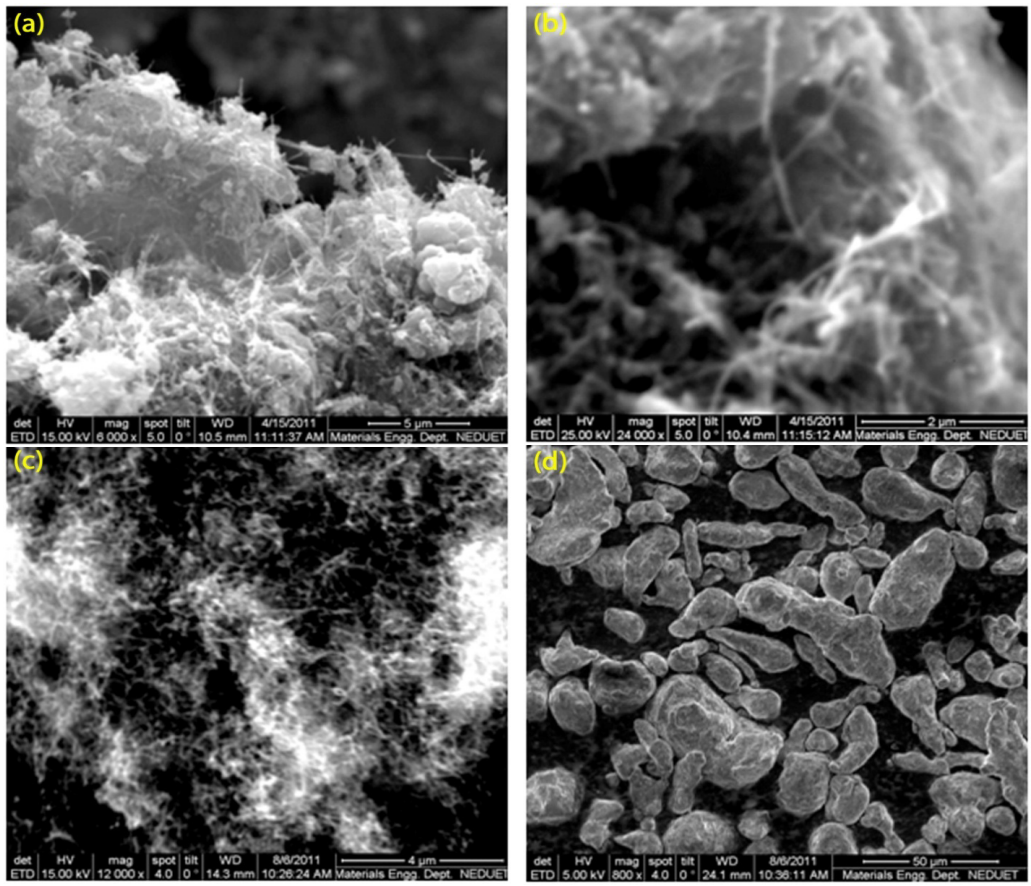

Figure 1. SEM images. (a, b) CNTs produced by the arc discharge process; (c) as-received CNTs (produced by CVD); (d) as-received aluminium powder.

2.2 Methods

The reactive nature of aluminium powder in the presence of atmospheric oxygen results in a thin passivation layer of alumina upon exposure to the atmosphere. Hence, all powder handling was performed in a glove box in a passive environment of argon to avoid oxygen contamination.

CNTs were disentangled by suspending in ethanol and sonicating at a temperature of 80 °C for one hour. Ball-milling was undertaken with both types of CNTs and with different concentrations (1%, 2% and 5% $^{W}/_{W}$). CNTs with powdered aluminium weighing 5 g in addition to a pure aluminium sample as a reference were milled in a high energy SFM-1 desktop planetary ball mill using stainless steel jars and steel balls weighing 50 g. The ball:powder ratio for milling was 10:1. The machine was set to 200 r.p.m. and the milling time was 3 h. A process control agent had to be added to the mixture once at the beginning of the process—300 μL of ethanol to

the Al–CNT sample—in order to avoid excessive milling. The mill had to be stopped every hour for 15 min to cool down the jars. Milling time has to be optimized in order to achieve a well dispersed mixture of CNTs in Al; it is reported that milling time influences the particle size due to repeated fracturing and cold welding of the Al powder particles.[8]

All the specimen were subjected to uniaxial cold compression in a 100 t hydraulic press to compact specimens at various pressures and time intervals. The compacted samples were then sintered in a box furnace at 540 °C for about half an hour to achieve a consolidated sinter compact.

SEM (FEI 2000 Quanta) and XRD (PANalytical X'pert MPD) techniques were used in order to characterize the powder morphology with the dispersion of CNTs in the matrix and for phase analysis, respectively. Energy dispersive spectroscopy (EDS) was carried out to identify the chemical nature of particles.

3. Results and discussion

3.1 SEM characterization

The CNT dispersion was found to be uniform, the following Figs 2–4 indicate the CNTs in the matrix with the help of arrow heads. Regarding Fig. 2, note that CNT is sandwiched between two deformed Al particles as a result of cold welding of the ductile Al upon milling. Results obtained from the SEM analysis of the powder nanocomposite show that ball milling was effective in dispersing nanotubes in the matrix.

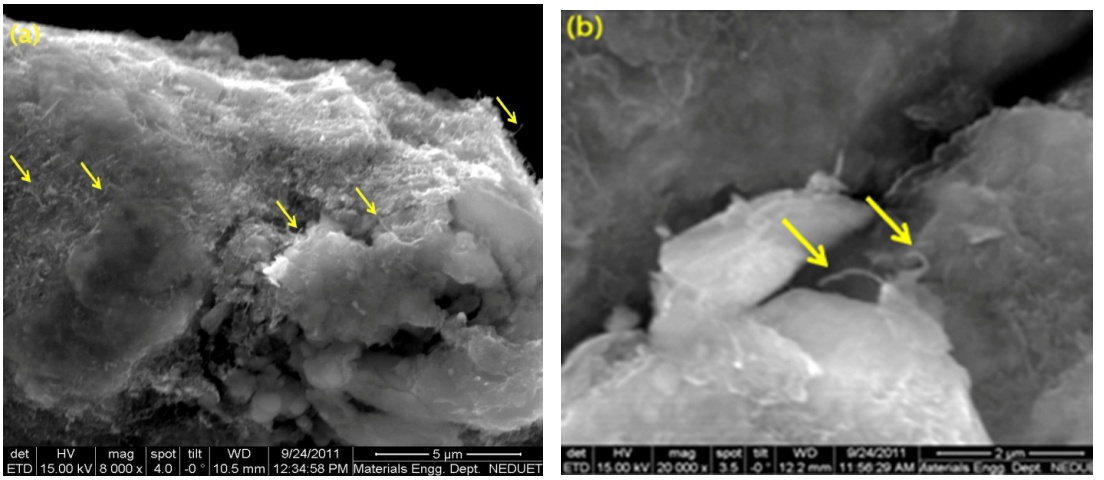

Figure 2. SEM micrographs of milled nanocomposite showing CNTs (arrows) in an aluminium matrix (a) on an as-milled powder surface and (b) CNT capture at a weld interface.

[8] M.J. Rhodes. *Principles of Powder Technology*, pp. 193–225. New York: John Wiley & Sons (1995).

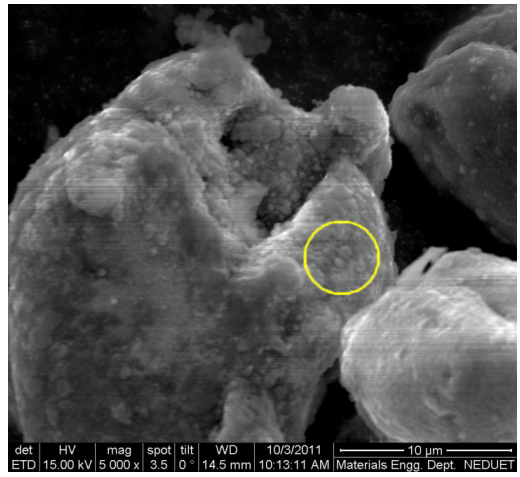

Figure 3. SEM image of a 5% $^{W}/_{W}$ CNTs composite. Finer Al particles deform during ball milling and form weld splats on coarser ones. The circle indicates capture of a CNT at such a weld interface (weld splat).

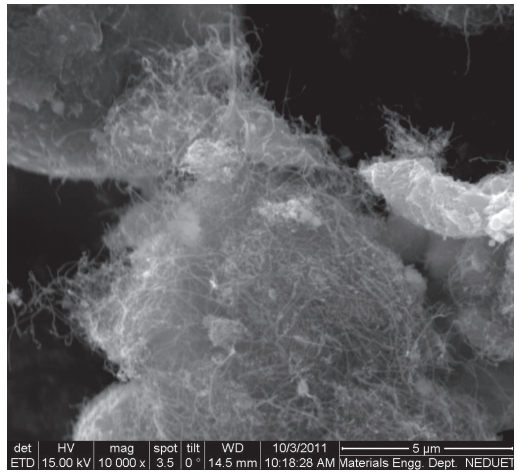

Figure 4. SEM showing a CNT cluster at a weld interface in a nanocomposite sample (cf. Fig. 3).

3.2 X-ray diffraction analysis

XRD was used to investigate the presence of graphite peaks and the formation of any carbide in the nanocomposite sample. The XRD scan of 5% $^{W}/_{W}$ CNT powder presented in Fig. 5 shows a predominant peak at 26° indicating the presence of graphite. Uniformly dispersed CNTs do not support a diffraction peak; clusters of the nanotubes were found to be useful for diffraction analysis.

Peak analysis was further supported with other aids by means of overlapping of individual diffractograms of CNTs and aluminium; as shown in Fig. 5, which made it easy to distinguish the phases in the nanocomposite samples.

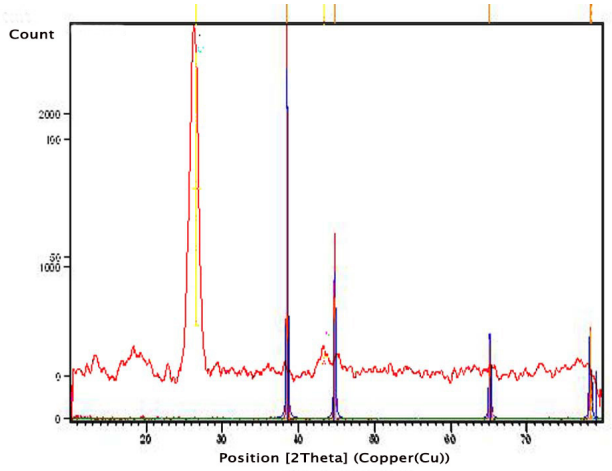

Figure 5. Individual diffractograms (CNT and aluminium) overlapped to distinguish phases as observed in a nanocomposite sample.

From XRD scans for the 5% $^{W}/_{W}$ milled CNT–Al powders milled for 3 hours (Fig. 6), it could be observed that there is a small peak at 26° indicating the presence of graphite (CNT). Nevertheless, some samples containing presumed sufficient proportions of CNT did not reveal any carbon in XRD characterization, a result that is in line with other published work (e.g., George et. al.,[9] where 2% $^{V}/_{V}$ CNT were milled for just 5 min and no carbon peaks were identified). A reasonable explanation for this could be that the carbon peak is only observed when CNTs are clustered (where clusters are well dispersed, the peak diminishes).[10]

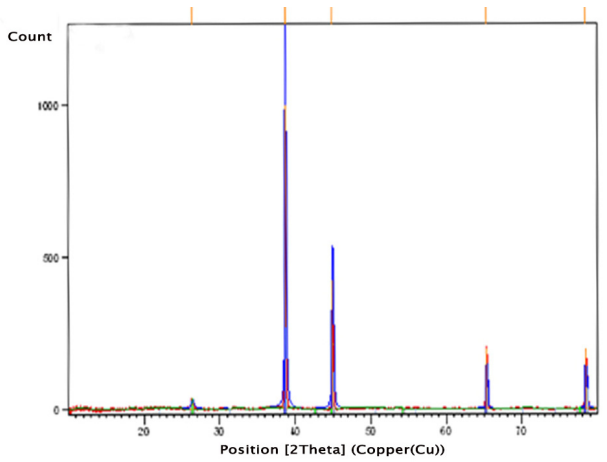

Figure 6. X-ray diffractogram of an Al–CNT sample showing a small peak at 26º originating from the CNTs in the matrix.

[9] R. George, K.T. Kashyap, R. Rahul and S.Yamdagni. Strengthening in carbon nanotube/aluminium (CNT/Al) composites. *Scripta Materialia* **53** (2005) 1159–1163.

[10] A.S.S. Mohamed. *Fabrication and Properties of Carbon Nanotube (CNT)–Reinforced Aluminium Composites*. Thesis, p.77. American University in Cairo (2012).

The entangled CNT clusters in the nanocomposite sample (as observed in Fig. 4) appear to be of great utility for X-ray diffraction analysis since they enable the carbon to be detected. Jinzhi Liao et al. proposed that the clusters exist due to the comparatively large size of the metal powder, which inhibits the even distribution of the CNTs. It is proposed that smaller metal particles would help achieve a more even distribution of the nanoscale tubes.[11]

4. Conclusions

Ball milling is an effective technique to disperse CNTs in an aluminium matrix. The CNTs need to be aligned and disentangled in order to achieve uniform distribution in the matrix; though CNT clusters as observed are beneficial for diffraction analysis. Scanning electron microscopy was helpful for determining the distribution pattern of CNTs in the matrix. The presence of CNTs was found to be at weld interfaces between powder splats and embedded on powder surfaces. The variation in powder morphology and size was found to be useful for capturing CNTs in between two particles of different sizes.

Acknowledgments

The authors gratefully thank Dr Mohammed Tufail, Dean of the Faculty of Chemical Processing, for providing laboratory facilities and Mr Fayyaz Hussain for technical suggestions.

[11] J. Liao and M.-J. Tan. Mixing of carbon nanotubes (CNTs) and aluminium powder for powder metallurgy use. *J. Powder Technol.* **208** (2011) 42–48.