One-Step Synthesis and Characterization of a Nanocomposite Based on Carbon Nanotubes/Aluminum and Its Reinforcement Effect on the Metal Matrix

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Abstract: The nanocomposite based on carbon nanotubes/aluminum (CNT/Al) was one-step prepared by the DC arc discharge method under an argon/acetone mixed atmosphere. Synthesis was performed by arc plasma on a pure graphite rod, filled by aluminum powder as an anode and aluminum plate as a cathode. Discharge conditions of 85 A and 20 V were used at a pressure range of 375 to 750 Torr. The CNT/Al was characterized by Scanning Electron Microscopy with Energy Dispersive Spectroscopy; Transmission Electron Microscopy; Laser Diffraction Particle Size Analysis; X-Ray Diffraction; Raman Spectroscopy; Thermogravimetric Analysis; and, its reinforcement effect of the CNTs on the aluminum matrix was measured by Vickers microhardness test. This nanocomposite shows agglomerates of multiwalled carbon nanotubes filled with Al_4C_3 and blended with aluminum particles; moreover, in the nanocomposites was found a hardness increase of 40% for nanocomposites with 1.0 wt.% of CNT/Al.

Key words: One-step synthesis, CNT/Al nanocomposite, reinforcement effect.

1. Introduction

The DC arc discharge method under several atmospheres in order to produce CNTs (Carbon nanotubes) has been researched because it involves a very simple and efficient apparatus, low cost and potential industrial applications [1-5]. In 1997, Journet C. et al. produced SWCNTs (Single-walled carbon nanotubes) in a large scale, by arc discharge under inert gas [1]. Afterward, Antisari M. V. et al. [2] successfully synthesized MWCNTs (Multi-walled carbon nanotubes) in liquid nitrogen and deionized water and Kim H. H. et al. [3] produced MWCNTs in an air atmosphere with a low quantity of amorphous carbon. Their experimental results showed that CNTs

could be synthesized by a simple optimization of the pressure in the chamber. Furthermore, Li Z. et al. [4] improved the methodology by preheating the metal catalysts and Shimotani K. et al. [5] increased yields of MWCNTs by up to five times using DC arc discharge under atmospheres of helium or several organic molecular vapors, e.g., acetone (CH_3COCH_3) or hexane (C_6H_{14}).

Nowadays, many researchers have been developing alternative routes to produce CNTs by arc discharge for industrial applications, as in composite materials because of its extraordinary thermal, electric and mechanic properties [6-8]. In general, several studies have related the synthesis of CNTs with the posterior goal of attempting the mixture of another material as metallic matrix [9-11]. Recently, Keshri A. K. et al. [12] showed a growth of CNTs onto aluminum oxide

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powders by chemical vapor deposition. This is an alternative way, since it increases the density and dispersion of CNTs inside a metal composite, but the nanoparticles showed a poor graphitization of the walls in comparison to CNTs produced by arc discharge synthesis, which does not lead to a good reinforcement in CNT-based composites [13].

In this work, the main goal was to perform a one-step CNT/Al nanocomposites synthesis by DC arc discharge under a mixed argon/acetone atmosphere in order to obtain a fast, efficient and low-cost route of producing metal composites with CNTs as nanomaterial. Therefore, through this synthesis, a CNT agglomerates filled with aluminum carbide was obtained. After that, these nanocomposites were applied in an aluminum matrix using powder metallurgy showed by these authors in previous works [14, 15].

2. Experimental Details

The nanocomposite based on CNT/Al was one-step synthesized by a DC arc discharge apparatus using a pure graphite rod (99.99%) as an anode with dimensions of $\varnothing 12 \text{ mm} \times 100 \text{ mm}$ (length) and filled with Al-Si powder, i.e., Al (with a purity of 99.94% wt.), while an Al-plate with $\varnothing 30 \text{ mm} \times 15 \text{ mm}$ (thickness) was used as a cathode, with the same amount of Al-Si powder. The arc plasma was maintained constant by a voltage of 20 V and a current of 85 A, under a mixed argon/acetone atmosphere and pressure conditions of 375 to 750 Torr. This mixed atmosphere was obtained after three purge steps by a continuous argon flow through a bubbler containing 200 mL of acetone. Finally, the sample was collected from the cylindrical wall and the cathode parts of the chamber.

In order to increase the yield of the sample, it was calcined at 575°C in a furnace for 60 min in air, where the most favorable combustion temperature of amorphous carbon was expected [16]. Hereafter, the sample was characterized by SEM (Scanning electron microscopy) with EDS (Energy dispersive

spectrometry) (SEM/EDS, FEI Quanta 400 FEG) at an accelerating voltage of 15 KeV and TEM (Transmission electron microscopy) (JEM-2200 FS-200 kV), using SAD (Selected-area diffraction) patterns for phase identification. XRD (X-ray diffraction) (X'Pert Pro – PANalytical) with $\text{CuK}\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation and micro-Raman Spectroscopy (Horiba Jobin Yvon LabRam HR system with an excitation wavelength of 633 nm) were also used to phase identification and to evaluated the structure features as damage and/or defects in the CNTs. The yield of one-step synthesis was obtained by thermogravimetric analysis (TGA, Seteram Labsys) that was performed at 900°C with a heating rate of $5^\circ\text{C}/\text{min}$ in synthetic air. Particle sizes were measured by laser diffraction using Malvern Mastersizer 2000 equipment.

For the production of the metal matrix samples, the CNT/Al (synthesized) and pure CNTs (from FIBERMAX, synthesized by Chemical Vapor Deposition – CVD) were mixed with Al powders with a maximum particle size of $50 \mu\text{m}$ and a purity of 99.5% (from Goodfellow) in a Turbula during 1h and then uniaxial pressed with 100 MPa. The compacts were produced at 0.5 and 1 wt.% and sintered at 625°C during 1 h under a vacuum better than 10^{-2} Pa . The reinforcement effect of the nanocomposite was evaluated by microhardness and tensile tests. The hardness was evaluated by Vickers microhardness using a 98 mN load; ten tests were performed on each sample: with CNT/Al nanocomposite; with pure CNT; and on an aluminum sample produced under the same processing conditions, for comparison. The tensile tests were performed at a rate of 0.2 mm/s ; five specimens were tested for each condition. The geometry of the specimens is described elsewhere [14, 15].

3. Results and Discussion

3.1 Microstructural Characterization of CNT/Al Nanocomposites

SEM images of nanocomposites indicated cushion

structures of CNTs, as shown in Fig. 1a. These SEM images using electron backscattering showed agglomerated structures of CNTs nucleated by a metal cluster, indicating extrusion or base growth mechanism for CNTs, as shown in Fig. 1b. Details could be seen in the magnification of the SEM images of Figs. 1c and 1d. These images indicated high density of CNT nets into cushion structures. In this synthesis it was not possible to have control over the lengths of CNT as was also related by Balani et al. [17]. Similar results were obtained by other methodologies and were previously reported in literature. Liu et al. [18] related large-scale production of CNTs by the fluidized-bed method, which had some advantages when compared with other

methods, e.g., it was not dependent on a substrate and the agglomerates can be controlled from microscale to macroscale dimensions. However, unlike our nanocomposites, their material showed metal-free CNT cushions; on the other hand, our nanocomposites showed several metal particles with the same composition as the aluminum metal matrix.

TEM images of agglomerated CNT/Al nanocomposites showed the presence of MWCNT. These CNTs were characterized by a inner diameters of 10 to 25 nm, open and close tips and polygonal carbon nano-onion. Furthermore, as it was possible to see in Figs. 2a and 2b, the nanoparticles were filled with aluminum. The carbon nano-onion showed a polygonal

Fig. 1 SEM images show (a) an uniform dispersion of agglomerated CNTs, (b) growing mechanism by metallic nucleation (red arrow), (c) low magnification image of agglomerate and (d) high magnification of MWCNTs bundle.

Fig. 2 TEM images of (a) CNTs showing 5 ± 2 walls and (b) polygonal carbon nano-onion filled by aluminum, which can be seen some of its vertices (red arrows), (c) MWCNT linked at aluminum particle (white arrow), and high magnification of CNT filled by Al_4C_3 with lattice spacing of 2.49 Å. Inset image shows the typical SAED pattern of aluminum carbide and CNT sheets.

shape, because of deformation forces caused by metal solidification, i.e., the CNTs and carbon nano-onions were formed before the aluminum solidification. This explained the capillary effect of the nanotubes, as shown in Fig. 2c. The filling of the nanotube could be seen with more detail in Fig. 2d, where it showed a SAED (Selected area electron diffraction) pattern of the Al_4C_3 phase with direction at $\{1\bar{1}00\}$ planes. A similar growth

direction of aluminum carbide was related by Zhang et al. [19], but using lithium as a catalyst. The aluminum carbide and aluminum oxide were commonly found at the interface of CNT/Al nanocomposites [20-25].

3.2 Additional Characterizations

The Gaussian distribution of particle sizes made of CNT/Al agglomerates was measured by Laser diffraction of 4.85 to 10.71 μm , with a mean of 7.37 μm ,

where one of the samples was analyzed by SEM/EDS to obtain the chemical composition of the CNT agglomerates (Fig. 3a). It was possible to see that these agglomerates were composed by carbon (C), oxygen (O), aluminum (Al) and silicon (Si) elements. Moreover, the XRD spectrum of these particles was characteristic of the graphite sheets of MWCNTs (Fig. 3b). This same results was related in literature [23-26], which showed a high intensity and sharp “C (002)” peak at $2\theta \approx 26.6^\circ$, a

low intensity peak of aluminum at $2\theta \approx 44.7^\circ$ [25] and an aluminum carbide peak at $2\theta \approx 35.7^\circ$ [26]. These values were in agreement with the TEM images, where interlayer spacing of the graphite sheet was found in $3.44 \text{ \AA}$ for MWCNTs. Additionally, the XRD spectrum indicated that, after the sample purification at 575°C under air atmosphere, there was no evidence of structural damage in the CNTs.

The structural features were also investigated by

Fig. 3 (a) X-ray microanalysis of agglomerated CNTs (Z1 region) showing the chemical composition. (b) XRD plots for sample before and after of the calcinations, where the reflection for Al_4C_3 (★) and Al (◆) observed in inset with more detail.

Fig. 4 (a) Raman spectrum of CNTs/Al powder suggesting a good I_D/I_G ratio and presence of SWCNTs and (b) TGA spectrum of the nanocomposite.

Raman spectroscopy with excitation lasers at 633 nm, as shown in Fig. 4a. Raman spectra shows two typical modes for CNTs, where the first mode is separated in two bands: the G-band and D-band at 1,630 cm⁻¹ and 1,380 cm⁻¹, respectively; and the second mode is the low wave number region, called RBM (Radial breathing mode), showing two distinct peaks at 215 cm⁻¹ and 206 cm⁻¹, that correspond to the SWCNTs diameters of 1.08 nm and 1.13 nm, respectively. These

diameters can be obtained by the following equation: $\omega_{RBM} = (223/\phi_d) + 10$, where ω_{RBM} is the RBM frequency (cm⁻¹) and ϕ_d is the SWCNT diameter (nm) [27]; in addition, I_D/I_G ratio was also calculated for this sample at 0.84 and indicates a high degree of graphitization of CNTs in the nanocomposite. Our procedure achieved a better graphitization when compared with the plasma spraying process of CNTs/Al₂O₃ powders shown in Ref. [12].

The yield of one-step synthesis was obtained by TGA and its derivatives. In Fig. 4b, it is possible to observe an overlap between the first and second peaks around 345 °C and 434 °C, corresponding to the oxidation temperature of amorphous carbon and SWCNTs [4], respectively. The MWCNTs combustion has a maximum peak at 637 °C and finishes around 750 °C [3], resulting in only residual aluminum. The total yield of the nanocomposite obtained was over 95% wt (the sum of 6.8% SWCNTs, 55.55% MWCNTs and 33.45% Al), and the remainder from calcinations of amorphous carbon was estimated around 4.2%.

3.3 Mechanical Characterization of CNT/Al Nanocomposites

The reinforcement effect on the metal matrix samples sintered with pure CNTs and CNT/Al nanocomposites was evaluated by Vickers microhardness and tensile tests. The highest hardness values of 44 ± 3.27 HV0.01 and 42 ± 4 HV0.01 were

observed in samples produced with pure CNTs and CNT/Al (Fig. 5), respectively; these composites are 40% harder than pure Al, yet pure CNTs shows saturation for HV at 0.5 wt.%; on the other hand, the CNT/Al tends to rise over 1.0 wt.% for HV. This behavior can be attributed to graphitized sheets of CNT/Al synthesized by arc plasma and aluminum carbide inside them.

The results obtained in the tensile tests for pure Al and for CNT/Al nanocomposites can be observed in the Table 1. The introduction of CNT/Al nanocomposites into the Al matrix leads an increase of 33% of yield strength with a decrease in elongation from 27.6% to 10.7%. SEM image of Fig. 6 shows the fracture images of tensile test specimens for the CNT/Al composite. There is clear evidence of a brittle fracture which is consistent with increased strength and decreased in ductility. This may be associated with CNT/Al clusters that are present at the grain boundaries and the effect of reinforcing the matrix by the nanocomposites.

Fig. 5 Vickers microhardness evolution of metal matrix samples made of pure Al, Al with pure CNT and Al with CNT/Al nanocomposite. Inset shows some samples used in this microhardness test.

Table 1 Tensile strength values of pure Al and Al with CNT/Al nanocomposite.

	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
Al	23	66	27,6
Al + CNT/Al 1.0 wt.%	50	88	10,7

Fig. 6 SEM images of the fracture of tensile test specimens for 1.0 wt.% of CNT/Al composite: (a) Carbon deposits by Z mode operation; (b) The characteristics of brittle fracture.

4. Conclusions

The CNT/Al nanocomposites was successfully one-step synthesized by a DC arc discharge process under a mixed argon/acetone atmosphere, producing agglomerated particles with a size of 7.37 μm. Agglomerates showed a high density and uniform distribution of MWCNTs around aluminum particles; moreover, the polygonal carbon nano-onion and residual amorphous carbon were also observed after the calcinations at 4.2% wt. The CNTs presented a high graphitization level and were filled with Al and Al₄C₃, forming an overall yield higher than 95% wt. Finally, the reinforcement effect of the nanocomposite was evaluated by Vickers microhardness, and compared with pure Al and pure CNTs synthesized by CVD process; hence, the CNT/Al showed an increase of 40% in hardness without a saturation trend and of 33% in tensile strength. This nanocomposite is very promissory for cushion applications and the modified arc discharge method could be used to produce several metal matrix composites based on CNTs.

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