Solid-state fabrication of Al/CNTs nanocomposites

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Abstract. In the present work, synthesis of Al-based composites reinforced with carbon nanotubes has been carried out using solid–state manufacturing routes exclusively to consolidate Al–1100/CNTs laminates. Preliminary results regarding consolidation of Al/CNTs nanocomposites in which pressure and temperature are combined in a single step are presented. Preliminary Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) characterization allow us to conclude that CNTs were effectively set on the Al matrix.

1. Introduction

In recent years, there has been an increase in the development of composite materials that surpass the properties of traditional metallic, polymeric and ceramic composites, using carbon nanotubes (CNTs) as reinforcement due to their excellent properties [1], such as an average elastic modulus in the range of 1 to 2TPa and a tensile strength from 11 to 63 GPa [2].

Currently, incorporation of CNTs on aluminium-based metal matrix nanocomposites (Al-MMCs) has become one of the most active fields of research in order to obtain thermal stability, high strength and stiffness or higher electrical conductivity. Challenges in this area still include poor dispersion of reinforcements in matrices due to agglomeration [3], Van der Waals forces between nanotubes and poor wettability between Al surface and CNTs [4].

Due to chemical incompatibility between CNTs and aluminium matrices, surface modification strategies and complementary routes must be applied in order to guarantee homogenous dispersion and densification of the composite material. In this study, forging of Al/CNTs laminated nanocomposites is proposed. Surface-modified multi-walled carbon nanotubes (m-CNTs) and three different strategies for dispersion and mixing are implemented, including: (I) surfactants, (II) Electro-hydro-dynamic-atomization (EHDA) and (III) dispersion through gas currents.

2. Experimental

Multi-walled carbon nanotubes (MWCNTs) were synthetized via carbon vapour deposition (CVD) following a process previously reported by Hoyos Palacio et al. [5]. With the aim of improving wettability of CNTs on aluminium, a surface modification step was carried out during the growth of CNTs in the CVD process. An ultrasonic nebulizer coupled to a quartz tube was implemented, and liquid aluminium nitrate [(Al(NO₃)₃] was introduced into the nebulizer as aluminium precursor, being posteriorly supplied through pulses to the CVD tube. The nebulized precursor was dragged to the reaction zone using nitrogen (80cc/min).
2.1. Dispersion of m-MWCNTs
Dispersion of the nanometric reinforcement plays an important role in the fabrication of Al-MMCs. Three kinds of dispersions were carried out as explained below.

2.1.1. Surfactants. For this project purpose, Sodium Dodecyl Sulphate (SDS) was selected, an anionic analytical grade surfactant. According to different authors [6,7], sodium dodecylbenzene sulfonate (NaDDBS) yields the best results for dispersion of MWCNTs. NaDDBS is useful to produce stable dispersions, without any need for chemical modification of CNTs or any sort of polymeric coating application [6]. Nevertheless, among all surfactants, anionic are the most common in terms of industrial volumes. Besides, due to their effectiveness/price ratio, they are also the best qualified [8].

1g of modified MWCNTs (m-MWCNTs) was dispersed in 100ml of deionized water, with a ratio of 1:1 (H₂O: SDS). The solution was sonicated at 32Hz during 30min at room temperature and completely dried in a convection oven at 100°C (Figure 1(a)). Finally, the container was cooled down at room temperature and the nanotubes were extracted from the bottom of the beaker (Figure 1(b)).

2.1.2. EHDA. In this case, a dispersion of 0.01g of m-MWCNTs in 1ml of an aqueous solution with 0.01g of SDS was prepared (Figure 2(a)). Ideal conditions were obtained for a cone-jet mode (7.5kV, 5cm of distance and a flux of 0.6ml/h). However, after several tests, the nozzle started to show signs of clogging, indicating that the process wouldn’t be easily scalable despite reaching minimum dispersions in a matter of hours (Figure 2(b)).

Figure 1. (a) m-MWCNTs dispersed in deionized water and SDS, (b) dry CNTs.

Figure 2. (a) m-MWCNTs dispersed in SDS, (b) detail of aluminium substrate after 50min of EHDA.

2.1.3. Compressed air dispersion. This process was designed in order to disperse great quantities of m-MWCNTs over the Al sheets. This method uses a “cloud” of m-MWCNTs (0.15g) previously dispersed in SDS and completely dried at 100°C inside a tight-lid container with the aid of compressed air at a
The pressure of 0.5Psi (Figure 3(a)). The appearance of the aluminium sheets after dispersion is presented in Figure 3(b).

Figure 3. (a) Al sheet in the bottom with cloud of m-MWCNTs on top, (b) Al sheet after dispersion.

2.2. Fabrication of Al/MWCNTs laminated nanocomposite
Aluminium 1100 sheets were used for the consolidation of nanocomposites. At first, the sheets were immersed in a solution of nitric acid (5%vol.), washed and cleaned with ethanol and subsequently dried. Then, an aqueous solution of polyvinylpyrrolidone (PVP) was sprayed to mitigate slippage between m-MWCNTs and the supporting matrix. Finally, m-MWCNTs were dispersed over the sheets using compressed air dispersion as explained in section 2.1.3.

The fabrication of the laminated nanocomposite was carried out in a press under 38Ton-force at 500°C during 600s (Figure 4(a)) and then thermally treated at 560°C during 3h. In total, 10 Aluminium 1100 sheets containing 0.25%wt of m-MWCNTs were stacked and then consolidated to obtain the MMC showed in Figure 4(b).

Figure 4. (a) Process of consolidation (time vs. force at 500°C) and (b) Laminated nanocomposite of 10 Al sheets (23×23cm).

3. Materials characterization
Characterization of MWCNTs was carried out using Raman spectroscopy and TEM. Comparison of m-MWCNTs with pristine MWCNTs (p-MWCNTs) from the same CVD furnace was performed in order to identify morphological differences. The consolidated nanocomposite was characterized using SEM and TEM.
3.1. Raman spectroscopy
Raman spectroscopy was carried out in a Horiba Jobin Yvon®, Labram HR Raman spectrometer. Figure 5 shows the spectra correspondent to the m-MWCNTs and the p-MWCNTs. In the spectra, D, G and G’ bands appear at 1328, 1580 and 2650cm⁻¹ respectively, corresponding with the typical theoretical values, which are 1350cm⁻¹ for the D band and 1582cm⁻¹ for the G band [9,10].

![Raman spectra of p-MWCNTs and m-MWCNTs.](image)

**Figure 5.** Raman spectra of p-MWCNTs and m-MWCNTs.

The \( \text{I}_D/\text{I}_G \) was obtained by adjusting the acquired data to a Gaussian approximation of eight-order through Matlab®’s cftool toolbox (Figure 6). According to S. Liang et al. [11], a higher \( \text{I}_D/\text{I}_G \) indicates the presence of defects or functional groups on the surface of MWCNTs. In this regard, for m-MWCNTs the \( \text{I}_D/\text{I}_G \) ratio is 0.954, which is relatively high. In addition, when compared to the spectra obtained for p-MWCNTs, it can be noted that the potential modification of MWCNTs contributed to the increment in the material structural order, to the extent that the \( \text{I}_D/\text{I}_G \) ratio acquired a value of 1.22 for p-MWCNTs.

3.2. TEM of MWCNTs
A TEM microscope (FEI TF20) operated at 200Kv was used to obtain TEM images. The samples of p-MWCNTs and m-MWCNTs were dispersed in ethanol and sonicated during 30min. For each case, a drop was extracted and dried over a cooper grid before being analysed with the microscope. Figures 7(a)
and 7(b) correspond to p-MWCNTs and m-MWCNTs respectively. The average inner diameter for both p-MWCNTs and m-MWCNTs was found to be 9.12nm. Meanwhile, the external diameter was within a range from 30.8 to 46nm. These values confirm that MWCNTs have large diameters, while explaining why the Radial Breathing Mode (RBM) wasn’t observed in the samples Raman spectra.

Theoretically, interplanar distance between CNTs averages an estimate of 0.34nm [12], thus the approximate number of concentric nanotubes used varies from 17 to 55.

Figure 7. (a) TEM image of p-MWCNTs and (b) m-MWCNTs.

In Figure 7(b), correspondent to the m-MWCNTs TEM, there are no noticeable modifications, probably because the differences in the Raman spectra showed above correspond only to Al atoms embedded in the m-MWCNTs’ walls.

3.3. SEM of Al/m-MWCNTs nanocomposite

A SEM microscope (JEOL JSM 5910 LV) with a 3nm resolution was operated at an acceleration voltage of 30kV. Figure 8 shows a laminated nanocomposite consolidated at 500°C with a compressing load of 38Ton-force during 10min, with a previous thermal treatment at 560°C during 3h.

Figure 8. SEM image of the Al/m-MWCNTs laminated nanocomposite.

Homogeneously dispersed MWCNTs can be observed in the matrix, and results are comparable to previous information found for Al/MWCNTs [13] and CNTs/Al-Cu [14] nanocomposites.
3.4. TEM of Al/m-MWCNTs nanocomposite

TEM observation was carried out using a TECNAI F20 SUPER TWIN TMP microscope with a 0.1nm resolution and an acceleration voltage of 200kV. The laminated nanocomposite sample was prepared according to the procedure developed by Yan Liu et al. [15] for transversally observing films deposited on metallic substrates.

Xudong et al. [16] characterized an Al/CNTs composite manufactured by powder metallurgy. In their results, the interface between Al and CNTs had no interfacial sub products, like the Al4C3 observed by Z. Y. Liu et al. [17] at higher processing temperatures. Figure 9 shows the interface between the m-MWCNTs and the Al matrix obtained in this study. As can be seen on the image the interface does not exhibit any signs of interfacial sub products and a reinforcement layer of approximately 33.4 nm can be noticed.

![Figure 9. Interface between the m-MWCNTs and the Al matrix.](image)

4. Conclusions

The CNTs used in this study have typical characteristics of CNTs fabricated via CVD. The differences between pristine and modified CNTs may likely be due to weak bonding related to physical adsorption of aluminium on the surface of the nanotubes.

Infiltration of CNTs into the matrix was lower than expected, mainly because of the temperature used during the consolidation process, which was selected within a range suitable to avoid formation of Al4C3 intermetallic compounds at higher temperatures.

In contrast to EHDA, mechanical dispersion through compressed air proved to be a technique useful for the deposition of greater quantities of MWCTNs on Al sheet surfaces.

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