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Study of the structural defects on carbon nanotubes in metal matrix composites processed by severe plastic deformation

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ABSTRACT

Carbon nanotubes (CNT) have been recently proposed as stabilizers against grain growth that can happen even at low temperature inputs in nano-crystalline and ultrafine-grained materials obtained by severe plastic deformation. In this study, we analyzed the evolution of the structural defects on the nanotubes in CNT-reinforced nickel matrix composites with different reinforcement weight fractions. The composites were processed by high pressure torsion, and we used Raman spectroscopy as the main characterization technique. The results indicate that for CNT subjected to highly energetic processing, it is not sufficient to analyze only the I_D/I_G ratio (as proposed in the available literature), but it is also necessary to evaluate the shifting of the G band, which traces the amorphization trajectory undergone by the CNT. Furthermore, we observed that the deformation suffered by the CNT is related to the accumulated strain and varies with the partial CNT fractions of these composites. This is related to their capacity to withstand the plastic strain that occurs during deformation. In addition, the defective state reaches a saturation before achieving the saturation in the microstructural refinement. These results will help to efficiently optimize the processing of this type of engineering composites.

1. Introduction

Carbon nanotubes (CNT) possess superior characteristics (outstanding physical properties, low weight and high aspect ratio), which render them as suitable candidates to be used as reinforcement in composite materials. In the past years, there have been several reports where they are used as reinforcements in metal matrix composites (MMC) with different metallic matrices, aiming mainly to improve the electrical and mechanical properties. An improvement in the mechanical properties has been observed by adding different volume fractions of CNT to different metallic matrices (e.g. Al [1–8], Cu [9–11] and Ni [12–14]). Nevertheless, the processing route also dictates to what extent the properties are improved, where the agglomerates and a weak interface can lead to a lower improvement [15] or even to a deterioration thereof [16]. CNT have been also used in MMC as stabilizing phases against grain growth in materials subjected to severe plastic deformation (SPD) [17,18]. This was based on their ability to pin the grain boundaries in coarse-grained materials under thermal inputs, enabling the control of the final microstructure [19] and subsequently, the tailoring of their mechanical properties [12]. Particularly, the boundary drag effect becomes more evident in composites manufactured by solid-state routes (e.g. powder metallurgy), since the reinforcement can only be placed on grain boundaries, as opposed to other chemical synthesis routes (e.g. molecular-level mixing). A thorough literature review about the use of CNT in MMCs is beyond the scope of this manuscript and can be found in Ref. [20] and the references therein.

As previously demonstrated [21], the particle distribution homogenization in MMCs is achievable using high pressure torsion (HPT), which is essential in the case of CNT, given their predisposition to form agglomerates due to van der Waals interactions. The homogeneous distribution of the particles within the matrix in MMCs is very important to avoid anisotropic behavior during mechanical loading. Additionally, in the case of CNT-reinforced composites, it is also of paramount importance that the CNT keep their microstructural features as unaltered as possible after processing. This would ensure to some extent that the CNT will retain their

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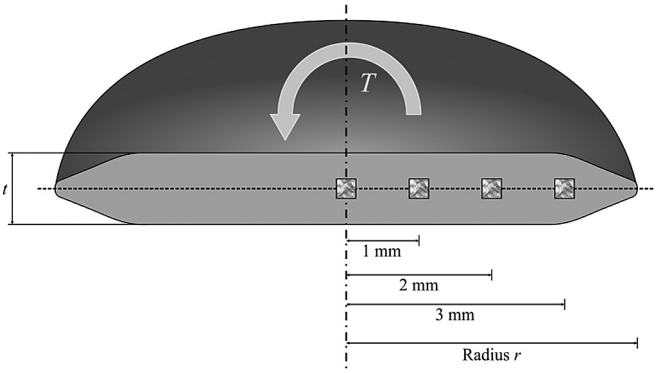

Fig. 1. Schematic view of the measurement positions in the cross section of the composites.

physical properties and could avoid chemical interactions with the metallic matrix. These chemical interactions are detrimental to the mechanical performance, since they generate brittle phases (i.e. carbides) which stem from the degradation of the C-containing phase. Even though some authors correctly state that the presence of carbides enhance the interface in composites, this would be a detrimental feature in two ways. First, the aforementioned brittle interface might crack after applying a certain stress, thus rendering the load transfer negligible. Second, by degrading the CNT, their intrinsic physical properties are severely compromised. Therefore, a processing route in which the structural state of the CNT is retained and a seamless interface with the matrix is achieved becomes extremely important.

Different kind of defects (e.g. point defects or dangling bonds) can be present in CNT after highly energetic processes such as ball milling [22–24], which can lead to interaction between the CNT and the matrix. In the same way, seeking the refinement of the microstructure by means of HPT, the samples can be subjected simultaneously to high pressures and high strains, and although the CNT are surrounded by the softer matrix and can –to some extent– be protected by it, they might be degraded during the processing. It is widely recognized that Raman spectroscopy is a very powerful and versatile technique for the characterization of carbon-based materials. By analyzing the change of certain characteristic bands of sp^2 carbons (D, G and G′ bands and their intensity ratios) and certain descriptive features (peak central position and full width at half maximum – FWHM, Γ – of the G band), it is possible to obtain a fairly accurate picture of the structural state of the carbonaceous phase. To the best of our understanding, there are no thorough studies of the damage suffered by CNT after SPD using Raman Spectroscopy. Though certain reports present Raman spectra of deformed composites, the analysis is extended (in the best cases) to an observation of the so-called defect index (I_D/I_G) [17,25,26], which would not present a full overview of the structural state. Specifically, Tokunaga and co-workers [25] studied the HPT deformation of CNT-reinforced Al composites at 2.5 GPa and 30 turns. They report that there is an increased D-band intensity due to structural damage generated by bending and/or breaking of the CNT. However, by analyzing the presented Raman spectra, an increase in the G-band width and a strong upshifting is clearly noticeable. This might indicate a possible amorphization of the graphitic structure. This was also observed in Ref. [26], even after the pre-processing, but was not discussed. In this case, the authors only focus on a brief analysis of the I_D/I_G ratio. Thus, in light of the available literature, a thorough study of the influence of HPT on the CNT structure becomes very important.

In the present work, we obtained CNT-reinforced nickel matrix composites via HPT, and evaluated the influence of the processing parameters on the nanotubes structural state for different CNT weight fractions. These composites were sintered by means of hot uniaxial pressing (HUP) and afterwards subjected to HPT at room temperature using different number of turns (T) applying a pressure of 4 GPa.

2. Experimental

2.1. Manufacturing and HPT processing of CNT/Ni composites

Different CNT weight fractions were analyzed, namely: 0.5 wt.% (2.4 vol.%), 1 wt.% (4.7 vol.%), and 2 wt.% (9 vol.%), the latter being the maximum reasonable amount of CNT to be used in CNT/Ni composites as determined in previous studies [12]. The manufacturing of the composites started with the dispersion of multi-wall carbon nanotubes (MWCNT) (CCVD grown, Graphene Supermarket, USA. Density 1.84 g/cm^3, diameter: 50–85 nm, length: 10–15 μm, carbon purity: >94%) in ethylene glycol EG (MWCNT/EG concentration ratio at 0.2 mg/ml). Afterwards, a mixture with nickel dendritic powder (Alfa Aesar, Mesh 325 (45 μm), density 8.91 g/cm^3) was produced by means of a homogenizer (WiseTis, Witeg) to disperse the larger agglomerates, and an ultrasonic bath (Sonorex Super RK 514 BH, Bandelin, 860 W, 35 kHz) to disperse the smaller ones. The dispersion was performed following the process described in Ref. [27]. The solvent was evaporated in a ventilated furnace at 150 °C and the powder was carefully grinded using an agate mortar to obtain more uniformly distributed particles and therefore to ease the compaction of the green pellets (990 MPa). After the densification process at 750 °C in vacuum (2×10^{-6} mbar) for 2.5 h, using a hot uniaxial press (264 MPa), the resulting samples with different compositions were subjected to HPT at room temperature using different number of

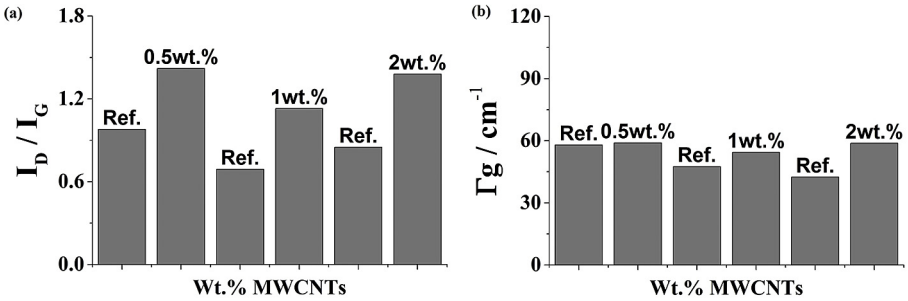

Fig. 2. Effect of the applied Pressure during HPT (taken at the center of the sample, $\varepsilon_{vM} = 0$) after 1 turn. (a) Defect index I_D/I_G and, (b) full width at half maximum (FWHM) of the G band.