Novel Al-matrix nanocomposites reinforced with multi-walled carbon nanotubes

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Abstract

Novel Al-based nanocomposites reinforced with multi-walled carbon nanotubes were produced by mechanical milling followed by pressure-less sintering at 823Kunder vacuum. The interface between Al matrix and the multi-walled carbon nanotubeswas examined using transmission electron microscopy. These observation showed that the multi-walled carbon nanotubes were not damaged during the preparation of the nanocomposite and that no reaction products were detected after sintering. The mechanical properties of sintered nanocomposites specimens were evaluated by a compression test. The yield stress (σ_y) and the maximum strength (σ_{max}) obtained were considerably higher than those reported in the literature for pure Al prepared by the same route. The values for σ_y and σ_{max} increase as the volume fraction of multi-walled carbon nanotubes increases. The milling time and the concentration of multi-walled carbon nanotubes have an important effect on the mechanical properties of the nanocomposite.

Keywords: Nanostructures; High-energy ball milling; Scanning and transmission electron microscopy.

Introduction

The need to enhance the mechanical properties of aluminum alloys has motivated the study of new materials and innovative processing routes. Aluminum-

based metal matrix composites (MMC) are of great interest because of their low density and high specific stiffness.

These materials can be produced by dispersing oxides, carbides or nitrides into the metallic matrix. Recently, however, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNT) are raising a great interest in the scientific community as a new kind of reinforcement material for the production of novel MMC, because of their excellent mechanical properties. In fact, it has been reported that CNTs possess not only an extremely high elastic modulus but also a high tensile strength [1]. These excellent mechanical properties, concomitant with their chemical stability, suggest that CNTs might be suitable as a novel reinforcement material for MMC. However, so far, the use of CNTs as a reinforcement phase in metal matrix materials has received only a modest attention [2–7]. Furthermore, the use of mechanical milling to produce CNT-reinforcing Al MMC is still very limited [6]. In this regard, the work described herein deals with the production of novel Al-based nanocomposites by combining two immiscible phases, namely aluminum and multi-walled carbon nanotubes (MWCNT), through, mechanical milling and powder metallurgy (PM).

Several concentrations of MWCNT were used in the preparation of Al-based nanocomposites. An analysis of microstructure, yield stress (σ_y) and maximum strength (σ_{max}) is presented and discussed as a function of the MWCNT concentration.

Experimental

Al powder (99.9% pure, −325 mesh in size) and MWCNTs were used to produce Al-based nanocomposites. The MWCNTs used in this work were produced by the spray

pyrolysis method [8]. Different nanocomposite compositions were studied, namely trough MWCNTs additions of 0.25, 0.50 and 0.75 wt.%. For comparison, pure Al was also investigated.

Each mixture was blended in an ultrasonic bath for 5 min and mechanically milled in a high-energy shaker mill (SPEX-8000M) using different milling times.

Table I
Relative densities obtained in pure aluminum and aluminum-based nanocomposites

Milling time [h]	CNT concentration [wt.%]	Theoretical density [g/cm^3]	Measured density [g/cm^3]	Relative density [%]
0*	0.00	2.6989	2.6500	98.1
1	0.00	2.6989	2.5475	94.3
	0.25	2.6987	2.5973	96.2
	0.50	2.6974	2.6328	97.6
	0.75	2.6961	2.6524	98.3
2	0.00	2.6989	2.6001	96.3
	0.25	2.6987	2.6065	96.5
	0.50	2.6974	2.6741	99.1
	0.75	2.6961	2.6574	98.5

* Reference sample.

Argon was used as the inert milling atmosphere. The apparatus and milling media were made of hardened steel. The weight of the samples was set to 5 g, and the milling media-to-powder weight ratio was 5:1. All milling runs were performed with no addition of processing control agents. Consolidated products were obtained by uniaxial load pressing during two minutes at~950MPa. Compacted samples were pressure-less sintered during 3 h at 823K under vacuum (~2 Torr). The pure Al reference samplewas not milled; itwas only consolidated and sintered at the same conditions.

Microstructural observations were performed by scanning electron microscopy (SEM) in a JSM-5800LV and by transmission electron microscopy (TEM) in aCM200, operating at 200 kV, and equipped with an energy dispersive spectrometer (EDS) and a parallel electron energy loss (PEELS) spectrometer. A unique specimen consisting of Al–2%MWCNTwith 2 h of millingwas prepared following the aforementioned

experimental procedure to observe the MWCNT dispersion within the Al matrix. Foils for TEM observations were prepared by electropolishing from milled and sintered samples using a mixture of methanol and 26% nitric acid at about 248K and 20 VDC.

The compressive stress of the nanocomposite specimenswas measured using an Instron testing machine at room temperature and at a constant displacementrate of 0.008 mm/s. The yield stress was measured at the elastic limit and the maximum stress was taken arbitrarily at ε = 0.1. Two height-to-diameter (h:Ø) ratios were used (0.8 and 2.0), in accordance with ASTM E9 standards.

Results and discussion

The densities and relative densities of the nanocomposite specimens prepared are shown in Table I. The density of the reference pure Al sample was very close to the intrinsic density of aluminum (~2.70 g/cm^3). The relative densities of the nanocomposites were 1–5% lower than the theoretical values. Relative densities were closer to 100% than those reported by Yi Feng et al. [7] for silver–MWCNT nanocomposites prepared by the PM technique. In addition to the high relative density values found, specimens with high MWCNT concentration showed the best consolidation, as measured by the Archimedes method.

Fig. 1a shows a secondary electrons SEM micrograph of MWCNTs with lengths of at least 10nm and diameters smaller than 100 nm. Furthermore, bright Fe catalyst nanoparticles used in the synthesis of MWCNT scan also be observed. Fig. 1b shows a high-resolution TEM image of one side of an as-synthesized MWCNT, where approximately 30 walls can be observed.

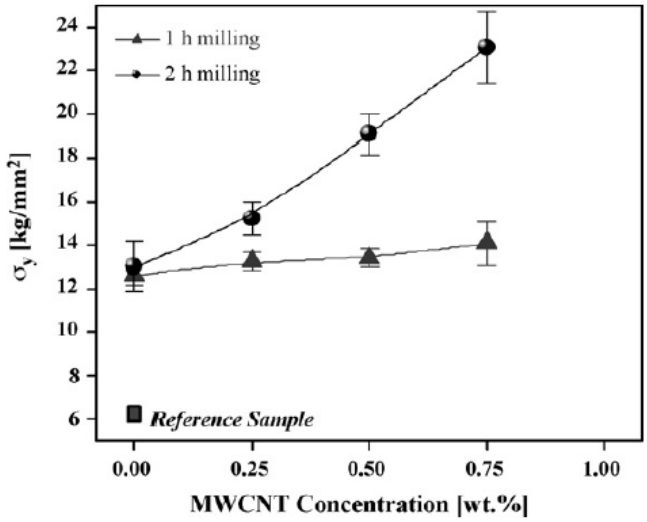

Fig. 2. Yield strength of nanocomposites as a function of CNT concentration.

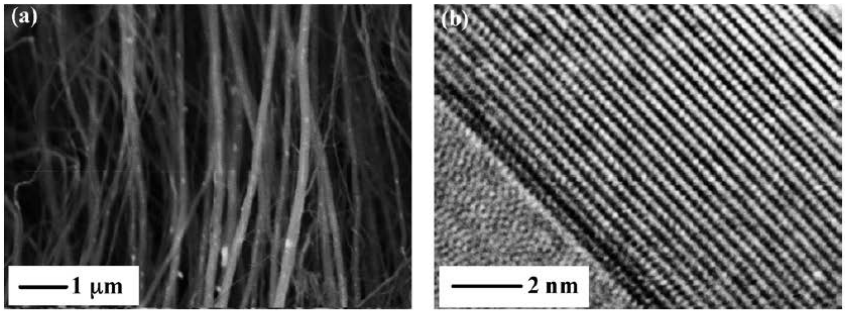

Fig. 1. (a) Secondary electron SEM micrograph of MWCNT bundle. (b) High-resolution TEM micrograph of a MWCNT. Notice that the number of walls in the MWCNT is around ~30.

Table II
Yield strength, maximum strength and Vickers hardness values obtained in pure aluminum and aluminum-based nanocomposites

Milling time [h]	MWCNT concentration [wt.%]	σ_y [kg/mm^2]	σ_{max} at $\varepsilon = 0.1$ [kg/mm^2]	Vickers hardness
0*	0.00	6.29 ± *0.3*	8.50 ± 0.5	30 ± 1
1	0.00	12.61 ± 0.5	19.85 ± 0.1	57 ± 2
	0.25	13.23 ± 0.4	20.63 ± 0.6	51 ± 2
	0.50	13.39 ± 0.4	21.70 ± 0.8	64 ± 2
	0.75	14.08 ± 1.0	23.27 ± 0.6	69 ± 2
2	0.00	13.00 ± 1.1	20.16 ± 1.2	43 ± 1
	0.25	15.21 ± 0.8	22.71 ± 1.2	52 ± 3
	0.50	19.06 ± 0.9	26.70 ± 0.7	76 ± 1
	0.75	23.05 ± 1.7	33.08 ± 1.5	77 ± 4

* Reference sample.

Fig. 2 shows the compressive yield strength values of sintered Al-based nanocomposites as a function of MWCNT concentration. It is clear the effect of milling in

two ways: (i) the σ_y value (13 kg/mm^2) of pure Al, milled and sintered, compared with the σ_y value (6 kg/mm^2) for the reference sample (pure Al not milled and sintered) is increased by more than 100%, and (ii) the overall yield strength is enhanced as the milling time increases. In addition, it is evident that the presence of MWCNTs lead to an increase of the nanocomposite's yield strength. In this regard, the effect of composition was more significant for longer milling times; giving a variation of σ_y of less than 20% (from ~12 to ~14 kg/mm^2) for 1 h of milling time and around 80% (from ~13 to ~23 kg/mm^2) for 2 h of milling time. It is worthwhile to point out that with the addition of only 0.75% of MWCNTs, the yield strength σ_y increased by 80% and 300% with respect to the sample without MWCNT and the reference sample, respectively (see Fig. 2 and Table II).

The value of σ_{max} was arbitrarily evaluated at a strain value of $\varepsilon = 0.1$ in all nanocomposites tested. Table II shows the σ_{max} obtained. From these results, it is evident that σmax increased as the milling time and MWCNT concentration increased. The hardness of the Al-based nanocomposites with different MWCNT concentrations was also measured (Table II). It is important to point out that a substantial increase in hardness (57 HV) was measured for the milled pure Al samples, when compared with values reported for annealed bulk aluminum (15 HV) [9]. These results make apparent the effect of the nanocrystalline state of the samples. As expected, MWCNT had an important effect on hardness. It increased as the MWCNT fraction increased, reaching the maximum value of around 77HV for the nanocomposite prepared with 2 h of milling time and 0.75 wt.% MWCNT.

For the shorter milling time (1 h) the most important strengthening effect acting on the nanocomposites is the influence of the nanocrystalline state. However, as the milling time is increased to 2 h, the effect of MWCNTs as reinforcement phase becomes more important.

To facilitate the observation of MWCNTs within the Al matrix, a Al–2 wt.% MWCNT nanocomposite was produced. Fig. 3 shows bright field TEM images of this material. Fig. 3a shows that the MWCNTs are dispersed quite homogeneously in the composite (black lines in Fig. 3a indicated by arrows). In Fig. 3b continuous and well-defined lattice fringes of the CNT walls can be seen. Furthermore, some regions of the MWCNTs observed, suggest some amorphization of the outer-shells. We believe this is due to the milling process as amorphization of MWCNTs due to irradiation was not observed during TEM characterization. Nevertheless, the number of walls in the as-synthesized and milled processed MWCNTs was practically the same (Figs. 1b and 3b). The inset shows the corresponding selected area diffraction pattern of the nanocomposite, composed of rings and spots associated with the Al matrix and the MWCNTs, respectively. No additional spots were recorded, confirming that no further phase was present. This is important because in conventional carbon fiber/aluminum composites, aluminum carbide (Al_4C_3) usually growths on the prismatic planes of the carbon fiber [5]. In our case, carbides were not detected at the MWCNT/aluminum interfaces, which might be a result of the excellent chemical stability of MWCNT.

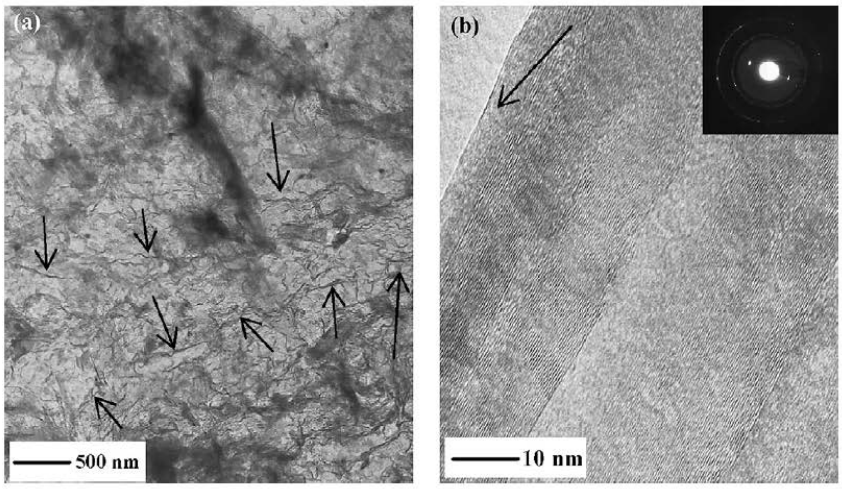

Fig. 3. (a) Bright field TEM micrograph of Al–MWCNT composite containing 2 wt.% of MWCNT, annealed for 3 h at 823 K in vacuum. The arrows show the location of MWCNTs. (b) HRTEM micrograph of the Al–MWCNT composite showing the interface between MWCNT and Al matrix; the inset shows the corresponding diffraction pattern. The arrow shows the transition layer between the MWCNT core and the Al-matrix.

These observations confirm experimentally the expected chemical and mechanical stability of the MWCNTs when processed by MM in an Al matrix; at least for the milling times used in this work (1 and 2 h). According to the theory of short fiber reinforced composites, the uniform distribution of MWCNTs in the matrix (Fig. 3a), effectively inhibits matrix deformation and produces a strengthening effect (Fig. 2 and Table II).

To fully understand the strengthening mechanisms operating in the Al-based nanocomposites, additional work is required. However, we should consider the following hypotheses: 1) inhibition of dislocation motion by MWCNTs, 2) wetting of MWCNTs by Al, 3) thermal mismatch between MWCNTs and Al and 4) formation of a transition layer between the MWCNTs core and the Al matrix.

With respect to the inhibition of dislocation motion byMWCNTs, our preliminary TEM observations seem to indicate the absence of dislocations within the nanocomposite. Although a more careful analysis is needed, these preliminary

observations seem to corroborate other investigations [10,11]. The second possible strengthening mechanism to consider is wetting of MWCNTs by Al, which is typically a necessary condition for interfacial shear stress transfer. However, this is not likely for MWCNTs reinforced Al-based composites as Al cannot wet MWCNT due to their large difference in surface energies [12]. In fact, only low surface tension liquids, with a threshold surface tension between 100 and 200 mN/m, will wet the MWCNT surface. However, the surface tension of aluminum is 865 mN/m. Thus, based on the values for surface tension, it is not possible to justify the transfer of load from the matrix to the reinforcement by interfacial shear stress. The third possibility is to take into account the thermal mismatch between MWCNTs and Al. Consequently, the volume contraction of the Al after the heat treatment may contribute to the mechanical adhesion of the MWCNTto the matrix. Finally, the existence of a transition layer between the MWCNT core and the Al-matrix should be considered. This transition layer (showed by the arrows in Fig. 3b) is composed of regions of CNT walls which have lost the periodicity and became apparently amorphous. This microstructure can be thought as a very rough MWCNT immersed in the Al-matrix, the roughness being the source of the stress transfer between the MWCNT reinforcement, and matrix.

Conclusions

Novel Al-based nanocomposites have been produced by mechanical milling followed by pressure-less sintering at 823K under vacuum. MWCNTs showed high mechanical and chemical stability; only some amorphization of the outer-shells due to the milling process was observed by TEM analysis. The yield stress (σ_y), maximum strength (σ_{max}) and hardness values obtained for the nanocomposites were

considerably higher than those for pure Al (not milled, and milled and sintered) reported in the literature. σ_y, σ_{max} and hardness values increased as the milling time and MWCNT concentration increased. The effect of milling time was to significant increase σ_y for the samples without MWCNT, when compared with the reference sample. In addition, it was found that the effect due to MWCNT concentration was more important as the milling time increased; leading to changes in σ_y (as the composition changed from 0 to 0.75 wt.%) of less than 20% to around 80% for 1 and 2 h of milling time, respectively. MWCNT are minimally intrusive and offer the promise of improving the mechanical properties without sacrificing structural integrity. Al–MWCNT nanocomposites could therefore advance the state-of-art in the field of composite materials.

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