Microstructural and mechanical characterization of Al–MWCNT composites produced by mechanical milling

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Abstract

Novel Al-based nanocomposites reinforced with multi-walled carbon nanotubes were produced by mechanical milling. Next, pressure-less sintering at 823K under vacuum and hot extrusion at 773K were carried out. The interface between Al matrix and the multi-walled carbon nanotubeswas examined using transmission electron microscopy. The values of yield strength (σ_y), maximum strength (σ_{max}) and microhardness Vickers (HVN) of the compositeswere evaluated and reported as a function of carbon nanotubes content. The concentration of multi-walled carbon nanotubes has an important effect on the mechanical properties of the nanocomposite. Formation of aluminum carbide in the nanocomposites was observed. Possible strengthening mechanisms are presented and discussed.

Keywords: Composite materials, Carbon nanotubes, Mechanical properties, SEM, TEM.

Introduction

Major interest in composite materials started in the middle of the last century, mainly to meet the demanded materials by the aeronautic industry where lowerweight and higher strength materials are desired. Since then, important progress in the development of compositematerials has been achieved. In the field of composite materials, aluminum-based composites is an important area due to their low density and good workability, such properties are attractive for diverse industrial applications. However, the use of these alloys is limited due to their relatively low yield stress. Recently, the interest to increase aluminum strength for applications in the aerospace and aeronautic industries has motivated the study of aluminum matrix composites (AMCs), which can exhibit better mechanical properties at medium (473 K) and room temperatures. Additionally, one of the most important characteristics is their high specific stiffness while maintaining a lowdensity [1–4]. Aluminum and aluminum alloys can be strengthened by dispersing hard particles like carbides, oxides or nitrides into the aluminum matrix by the use of solid or liquid state techniques [5–7]. The reinforcement can be done by adding continuous or discontinuous fibers, particles, or whiskers. Recently, the unprecedented mechanical properties of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are attracting a great interest in the scientific community as a new kind of reinforcement material for the production of novel MMCs. In fact, it has been reported that carbon nanotubes (CNTs) possess not only an extremely high elastic modulus but also a high tensile strength [8]. These excellent mechanical properties, concomitant with their chemical stability, suggest that CNTsmight be suitable as a novel reinforcement material for aluminum-based metal matrix composites.

In the field of CNTs reinforcedmetal matrix composites (MMCs), a very scarce research has been made because of the complexity associated with the interfacial reaction between CNTs/metal matrices and the lack of a suitable synthesis technique.

Furthermore, the use of mechanical milling to produce CNTreinforcing Al-based MMC is still very limited [9,10]. In this regard, the work described herein deals with the production of novel Al-based nanocomposites by combining two immiscible phases, namelyaluminumandMWCNTs, bymechanical milling and powder metallurgy (PM). Mechanical and microstructural characterization is presented and discussed as a function of theMWCNTs concentration. Possible hardening (strengthening) processes are discussed.

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 [11]. Different nanocomposite compositionswere studied, namely through MWCNTs additions of 0.0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75 and 2.0 wt.%. Pure Al was also investigated for comparison purposes. Each mixture was mechanically milled during 5 h in a high energy mill (Simoloyer). Milling time was chosen from previous results [9,10]. Argon was used as the inert milling atmosphere. All milling runs were performed with 0.5 ml of methanol as a processing control agent (PCA). The obtained products were compacted under ∼60 tons during 2min. Compacted sampleswere pressure-less sintered during 3 h at 823K under vacuum with a heating rate of 50 ◦C/min. Sintered products were held for 0.5 h at 773K and hot extruded into a rod of 10mm diameter by using indirect extrusion and an extrusion ratio of 16. The pure Al reference sample was not milled; it was only consolidated, sintered and extruded at the same conditions. The characterization of CNTs was performed by scanning electron microscopy (SEM) in a JSM-7401F instrument at 3–5 kV. Also, microstructural observations of Al-based nanocomposites were realized in a SEM model JSM-5800LV operated at 20 kV, and by transmission electron microscopy (TEM) in a CM200 operated at 200 kV. For TEM observations, a foil was prepared from the specimen at 2.0 wt.% ofMWCNT in order to observe the dispersion of MWCNTs into the Al matrix. This sample was prepared according to the optimal conditions reported for pure aluminum by Necip Ünlü [12]. Mechanical properties (tensile test) of extruded nanocomposites were measured by using an Instron testing machine at room temperature and at constant crosshead displacement rate of 2 mm/s. Dogs bone tensile test samples with a gage length of 30mm were prepared in accordance to the ASTM E8 standard. The yield strength (σ_y) was measured at $\varepsilon = 0.2\%$ and the maximum strength (σ_{max}) at the maximum value of the σ–ε curve. Determination of melting point was carried out by means of differential scanning calorimetry (DSC) under argon atmosphere. For this test, specimens of approximately 50mg were cut from the extruded bars.

Results and discussion

Fig. 1a and b shows secondary electrons SEM micrographs of the as-prepared MWCNTs. From these figures, diameter and length observed in CNTs, range between ~40 to ~100 nm and ~10μm, respectively. High homogeneity in diameter along CNTs was observed.

Fig. 2 shows the mechanical evaluation (tensile and hardness) results as a function of nanotube concentration. Fig. 2a shows the tensile test results, a positive slope is observed in σ_y and σ_{max} values as MWCNTs concentration increases. In this graph the reference data is also included (pure aluminum not milled and 0 wt.%

MWCNTs). Concentration of MWCNTs has a significant effect on the enhancement of the mechanical properties of these composites. For sample Al–2 wt.%MWCNTs, σ_y and σ_{max} showamaximum increment of ~100 and ~95%, respectively, in comparison to the reference sample. The overall strength is enhanced as theMWCNTs concentration is increased.

The microhardness in the aluminium-based nanocomposites with different MWCNTs concentrations was also evaluated and presented in Fig. 2b. A similar behaviour was found in the hardness. Previously, higher hardness values were reported for similar composites after sintering process [9,10]. Apparently an additional thermo mechanical treatment (hot extrusion) decrease the hardness values, while maintaining the positive slope as a function of concentration of MWCNTs. Table 1 shows data from Fig. 2 compared with reported values for σ_y, σ_{max} and Vickers hardness in commercial known aluminum alloys [13]. The increase in σ_y, σ_{max} and Vickers hardness indicates that the Al–MWCNTs nanocomposites are successfully synthesized from carbon nanotubes and aluminum powder by high energy ball milling. Additionally, previous results [10] had shown an important effect of milling time on the mechanical properties using SPEX mill. This opens the possibility to investigate the effect on the mechanical properties and CNTs dispersion by using different milling times and different kind of ball mills. The reinforced effect in the sample without the addition of MWCNTs is attributed to a deformed structure produced by the high energy milling.

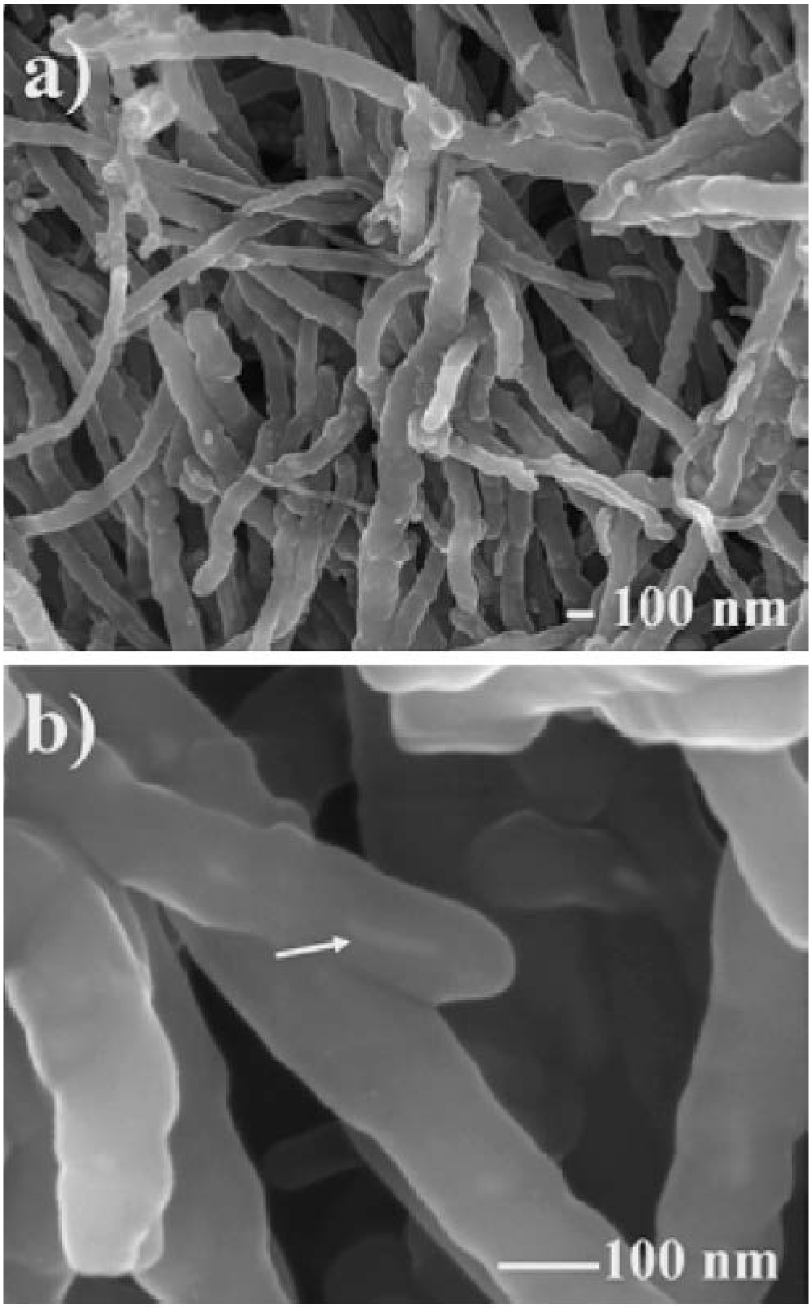

Fig. 1. SEM image by secondary electrons at: (a) 40 KX and (b) 150 KX.

Table 1
Comparative results from data found in the literature [13] for aluminum alloy and those found in this work for σ_y, σ_{max} and Vickers hardness.

Alloy or composite	σ_y (MPa)	σ_{max} (MPa)	Vickers hardness
7075-O[a]	103.0	228.0	68.0
Al–0.0 wt.% MWCNT	105.0	159.0	49.2
5005-H32[a]	117.0	138.0	36.0
5050-H32[a]	117.0	172.0	46.0
6009-T4[a]	125.0	230.0	70.0
3105-H12[a]	131.0	152.0	41.0
5005-H12[a]	131.0	138.0	38.0
Al–0.25 wt.% MWCNT	137.0	176.0	47.0
1100-H16[a]	138.0	145.0	38.0
5005-H34[a]	138.0	159.0	41.0
Al–0.50 wt.% MWCNT	138.3	180.7	54.9
3003-H14[a]	145.0	152.0	40.0
1235-H19[a]	145.0	165.0	45.0
6063-T5[a]	145.0	186.0	70.0
6463-T5[a]	145.0	186.0	68.0
Al–1.0 wt.% MWCNT	147.9	191.5	59.3
3105-H14[a]	152.0	172.0	46.0
Al–1.25 wt.% MWCNT	167.1	218.8	60.3
6010-T4[a]	170.0	290.0	88.0
Al–1.75 wt.% MWCNT	189.2	243.0	73.0

[a] [13]

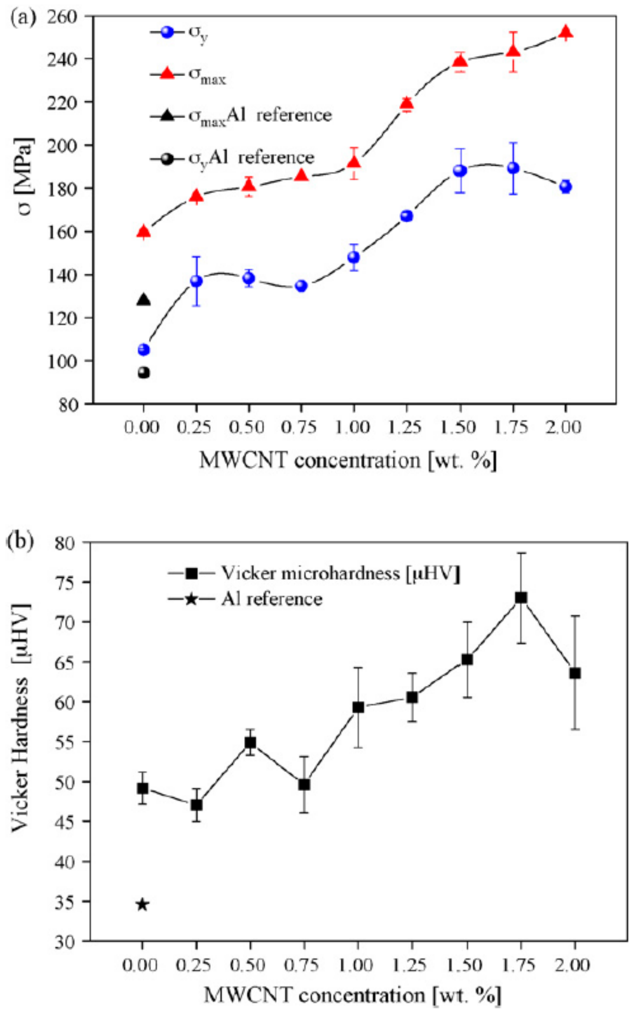

Fig. 2. (a) σ_y and σ_{max} and (b) Vickers hardness as a function of MWCNT concentration.

Fig. 3 shows SEM micrographs from fractured surface in an aluminum-based nanocomposite after tensile test. Fig. 3a shows randomly MWCNTs (indicated by arrows) dispersed into the aluminum matrix. Fig. 3b at higher magnifications of the same area shows theMWCNTs emerging frombroken surface after tensile test. This figure shows the adhesion of MWCNTs to aluminum matrix, additionally, nanotubes show damage in the ends, these characteristics indicate that there exists strong interface strength between aluminum matrix and the nanotubes.

Results obtained fromXRD analyses of extruded composites are shown in Fig. 4. There is no evidence of aluminum peaks shift, which indicates no solid solution formation. However, shortening of aluminum characteristic reflections is observed as theMWCNTs content increases, this phenomenon is observed from 0.25 wt.% of CNTs. The shortening could be attributed to absorption effects. It is important to notice the unexpected presence of aluminum carbide (Al_4C_3) in the composites. Fig. 4 shows details of base line of the XRD spectra from Al–MWCNTs composites, where the aluminum carbide can be observed. This carbide was found in all MWCNTs concentrations. Previously, it has been reported that Al_4C_3 usually grown on the prismatic planes of the carbon fiber [14] and because of the natural positioning of C atoms on the CNTs shells, aluminum atoms feel that are in contact with a graphite basal plane (0001), thus Al_4C_3 formation was not expected in Al–CNTs nanocomposites.

In this way there are four possible explications for the aluminum carbide crystallization: (i) Presence of amorphous carbon in nanotubes which reacts with aluminum during the process. (ii) Formation of amorphous phase at the Al–MWCNTs interface reacts with Al due to the presence of defects along this amorphous layer (structure), and the high temperature during sintering and hot extrusion processes will promote the precipitation of Al_4C_3. (iii) InMWCNTs with diameter higher than 80 nm, C atoms in the nanotube ends could present a similar ordering to prismatic planes $\{10\bar{1}0\}$ favouring the Al_4C_3 crystallization. (iv) MWCNTS ends present high amounts of structural defects, these imperfections favours the Al4C3 crystallization.

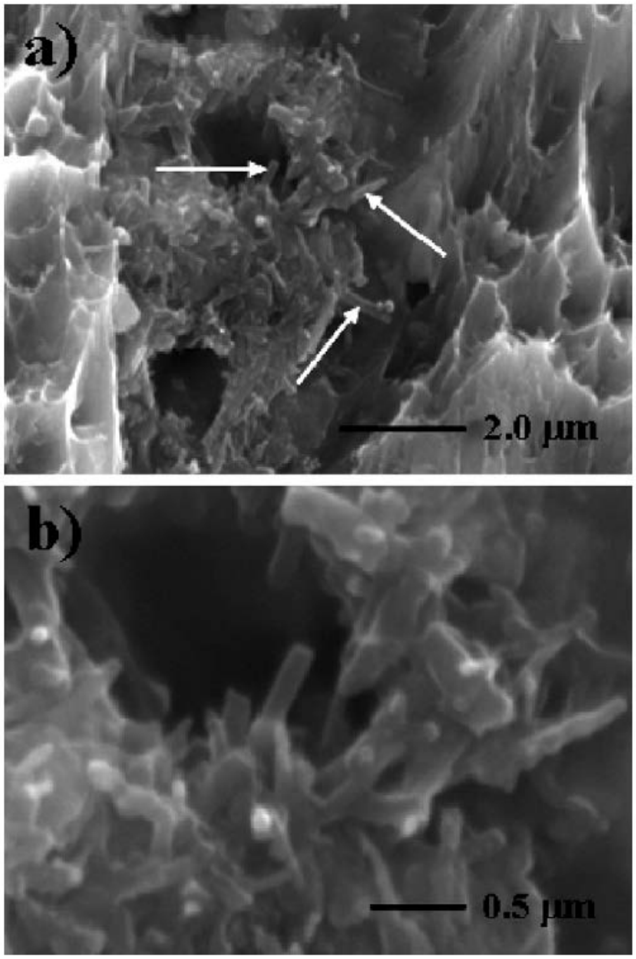

Fig. 3. (a) Secondary electrons SEM image showing the broken surface and (b) higher magnification of the same area showing CNTs outstanding from the broken Al matrix surface.

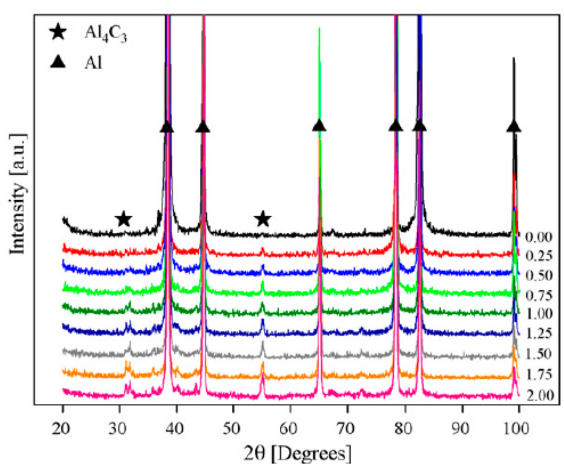

Fig. 4. XRD spectra obtained from the Al–CNT composites after hot extrusion process for different MWCNTs concentrations. Detail of base line, showing the aluminum carbide presence.

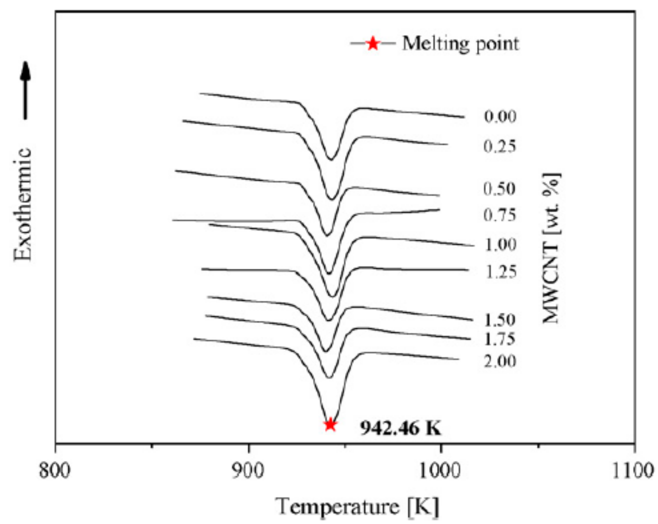

Fig. 5. DSC thermographs from hot extruded Al–CNT nanocomposites at different MWCNT concentrations. Very low thermal variation in melting point develops a high thermal stability.

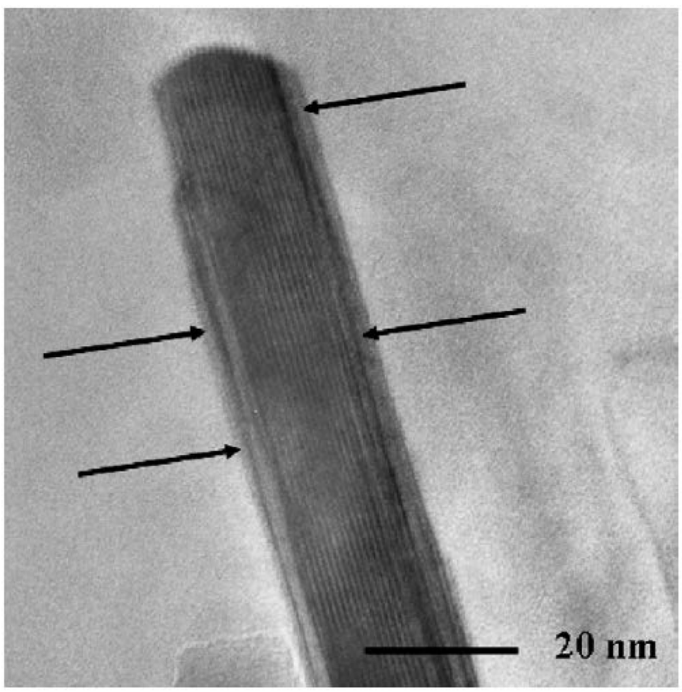

Fig. 6. Bright field TEM micrograph of a MWCNT dispersed into aluminum matrix. Notice the amorphization of the outer-shells (black arrows).

Differential scanning calorimetry thermographs are shown in Fig. 5. DSC analyses shown only one endothermic event, which correspond to pure aluminum melting point, these thermographs indicate thermal stability (melting temperature) in Al-based nanocomposites. However, due to the equipment limitations it was not possible to obtain thermographs over 1023 K.

Bright field TEM image of Al–2 wt.% MWCNTs composite is presented in Fig. 6. The figure shows aMWCNTs section where continuous and well-defined lattice fringes of the CNTs walls can be seen. Furthermore, some regions of the observed MWCNTs suggest some amorphization of the outer-shells, showed by black arrows in Fig. 5.

These observations confirm experimentally the expected chemical and mechanical stability of the MWCNTs when processed by MMin an Al matrix; at least for the milling times used in this work (5 h). According to the theory of short fiber reinforced composites, the even distribution ofMWCNTs in the matrix, effectively inhibits matrix deformation and produces a strengthening effect (Fig. 2a and Table 1).

A representative σ vs ε graph (Fig. 7) shows the important increment on mechanical properties as the CNTs content increases, and the ductility is almost constant (deformation over 10%). This opens the possibility to synthesize, by mechanical milling, stronger aluminum-based nanocomposites maintaining almost constant their intrinsic properties, like ductility.

During the development of this work, we have found that mechanical properties from synthesized composites have been greatly influenced by the mechanical milling and by the favorable reinforcing effect from the dispersed carbon nanotubes into the aluminum matrix.

There are several hypotheses about the possible reinforcing mechanisms that could explain the enhanced mechanical properties. To fully understand the strengthening mechanisms that take place in the Al-based nanocomposites reinforced with nanofibers (MWCNTs), additional work is required. Nevertheless, we should consider the following hypotheses: (i) inhibition of dislocation motion by MWCNTs, (ii) wetting of MWCNTs by Al, (iii) thermal mismatch between MWCNTs and Al, (iv) formation of a transition layer between the MWCNTs and the Al matrix, (v) grain refining produced by MM process, and (vi) formation (crystallization) of aluminum carbide at high MWCNTs contents.

The first assumption considers the interrupted movement of dislocations due to the presence of MWCNTs. 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 works [15,16]. 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 MWCNTs due to their large difference in surface energies [17]. Carbon nanotubes have been reported a surface tension of 100–200nN/m [15], and the surface tension of aluminum is 865 mN/m. There is an irreconcilable difference in these values. Thus, based on the surface tension values it is not possible to justify the load transfer from the matrix to the reinforcement by interfacial shear stress.

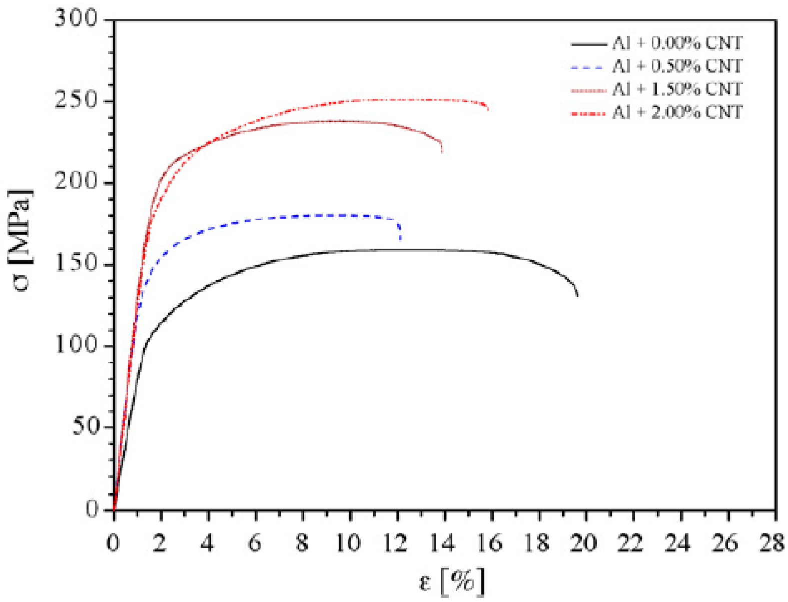

Fig. 7. σ_y vs ε graph showing the enhancement of the mechanical properties maintaining the ductility of representatives Al–CNT composites after hot extrusion.

The third possibility is to take into account the thermal mismatch between MWCNTs and Al. MWCNTs have a thermal expansion coefficient of ∼10^{-6} K^{-1}, which is considered to be the same as graphite; while pure aluminum have a higher one around 23.6×10^{-6} K−1. Consequently, the volume contraction of the Al after the thermo mechanical treatment may contribute to the mechanical adhesion of the MWCNTs to the matrix, as was shown in Fig. 3. The fourth mechanism involves formation of a transition layer between MWCNTs and Al matrix. External walls from CNTs seemed to loose its periodicity forming an amorphous coat. This transition layer (showed by the arrows in Fig. 6) is composed of regions where nanotubewalls have lost the periodicity and became apparently amorphous. This microstructure can be thought as a very rough MWCNTs immersed in the Al matrix, the roughness being the source of the stress transfer between the MWCNTs reinforcement and matrix. The fifth mechanism is related to the grain refinement by MM, and has a small effect in the increment of yield strength (as is shown in Fig. 2). This small effect could be due to the grain growth presented during sintering and hot extrusion processes. From Fig. 2, it is observed that the increment in yield strength by CNTs dispersion is more important than the increment observed by MM. Finally, the formation of aluminum carbide could have an important effect in the mechanical properties by the strengthening dispersion phenomenon (Table 1 and Fig. 2).

The six strengthening mechanisms showed above, give-rise to think that there is more than only one mechanism working in the enhancement of the mechanical properties.

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 were observed by TEM analysis. Formation of aluminum carbide at high MWCNTs concentration was found. The yield stress (σ_y), maximum strength (σ_{max}) and hardness values obtained for the nanocomposites were considerably higher than for pure Al (reference in this work) and those reported in the literature for some aluminum alloys. σ_y, σ_{max} and hardness values increased as the MWCNTs concentration increased. There exists more than one strengthening phenomenon in Al–CNTs nanocomposites. The most important strengthening mechanisms in Al–CNTs nanocomposites are strengthening by nanofiber dispersion and strengthening by aluminum carbide precipitation, and the interaction of both with dislocations.

MWCNTs are minimally intrusive and offer the promise to improve the mechanical properties without sacrificing structural integrity. Al–MWCNTs nanocomposites could therefore advance the state-of-art in the field of composite materials.

Acknowledgements

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