CARBON NANOTUBES - REINFORCED ALUMINIUM WITH IMPROVED YIELD STRENGTH AND TOUGHNESS

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Abstract

Among carbon nanotubes (CNTs) based composites, aluminium/CNTs ones are rather promising for weight sensitive applications, such as in aerospace field, thanks to the combination of the low weight and high stiffness and strength of the reinforcement. In this work, a self-assembled apparatus, named Pressure Assisted Fast Electric Sintering (PAFES), has been employed for the sintering of commercial micrometre size aluminium powders with multi-wall carbon nanotubes (MWCNTs). To do this effectively, much effort was devoted to the fundamental step of the CNTs dispersion and mixing in the Al powders by high energy milling.

1 Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have been considered promising reinforcement materials for composites, due to their extraordinary properties. Their most significant application is in polymeric matrices, but in last decade a great interest in CNT-metal composites has grown, with potential applications to improve specific characteristics of metals, such as thermal [2-4] or mechanical properties [5-11]. In particular aluminium matrices have attracted great interest because of their excellent strength, low density and corrosion resistance [10-16].

One of the key problems with Al-CNTs composites is the dispersion and distribution of nanotubes into the metal matrix. To handle this problem, in this work we try to first disperse CNTs via ultrasounds, and then mix them with aluminium powders using high energy milling. The second fundamental step is the consolidation of Al-CNTs powders into dense samples. In this case it was obtained by cold uniaxial pressing followed by Pressure Assisted Fast Electric Sintering (PAFES), a particular technique of the Spark Plasma Sintering (SPS) family [15].This kind of technique is based on the use of a high intensity electric current passing directly through the graphite die containing the sample, coupled with uniaxial pressure continuously applied. The main advantages of PAFES are the decrease of the sintering temperature and time, which allow the consolidation of powders to almost full density with limited grain growth [16-17]. After sintering, the specimens were characterized in terms of density, microstructure, microhardness and mechanical behaviour (by three points flexural test).

2 Materials and testing methods

2.1 Materials

Micrometric aluminium powders (-365 mesh ≈ 44 μm, 99.5% purity) were supplied by Alfa Aesar. The multiwall carbon nanotubes were produced by Sigma Aldrich. They are characterized by O.D. 6-13 nm and 2.5-20 μm in length, with a purity higher than 99%. As shown in Figure 1, they appear tangled and form sort of nuggets of a few micrometre size. Each nugget is made of several elongated snake-like bundles with diameter of a few tens of nanometres and length around the micrometre. Because of this characteristic a pre-dispersion step is needed before the powders mixing. As dispersion mean, 2-propanol by Sigma Aldrich was used.

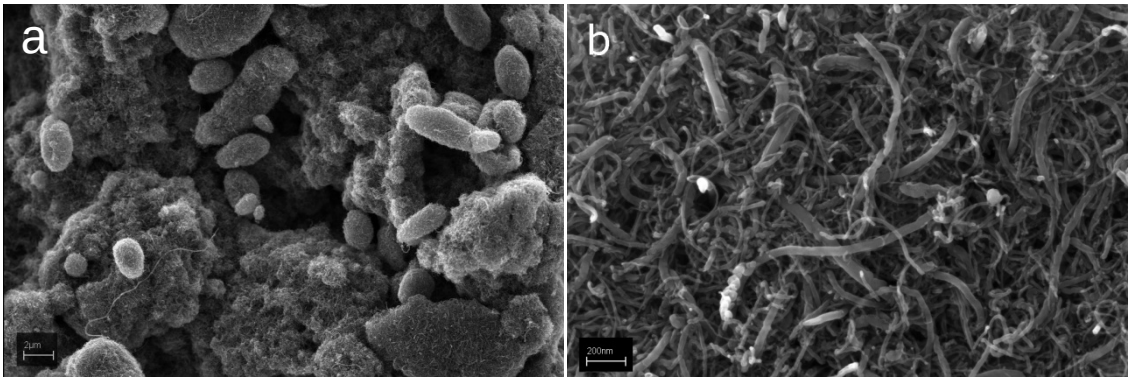

Figure 1. (a) MWCNTs as received in nuggets shapes; (b) a magnification

2.2 Al-CNTs powders preparation

A high energy milling system was used to prepare Al-CNTs powders. The content of MWCNTs vary from 0.3 to 3% in weight. We decide to test samples with different contents of carbon nanotubes trying to evaluate the reinforcement effect. The powders prepared were: 0.3, 1, 1.5 and 3% in weight. As stated before, the MWCNTs were first ultra-sonicated in 2-propanol for 15 minutes; the obtained suspension was then added to aluminium powders into a milling jar. High energy milling was performed in a Planetary mill Pulverisette 5, by Fritsch. Steel balls (5 mm diameter) with balls-to-powder ratio of 15:1 were used, and all the residual volume into the jar was filled by 2-propanol. Ball milling time was 1 h, with interim periods of 15 minutes every 15 minutes of milling, in order to avoid over-heating. The obtained powders were dried in an oven at 40°C for 12-24 hours, and after that were characterized by Scanning Electron Microscope Leo 1450 VP.

2.3 Sintering

The obtained Al-CNTs powders mix were first consolidated by cold uniaxial pressing (8 tons load and 30 seconds of loading time). Then the green disc-shaped specimens obtained (25 mm diameter, 2-4 mm height) were sintered by the PAFES device. This equipment is constituted by a hydraulic double effect press connected to an electric current generator, able to supply different kinds of waveforms (e.g. AC, DC, pulsed DC or combined cycles). The generator employs IGBT (Insulated Gate Bipolar Transistor)-type electronic devices. It can supply continuously varying current intensity and voltage values of 2000 A and 10 V, respectively, for a total maximum electrical power of 30 kVA. The frequency of the AC current is available in the 1–800 Hz range [15]. The green specimens were put inside a graphite cylindrical die of the same diameter; the temperature was monitored by a type K thermocouple in contact with one of the two graphite punches. The sintering was performed in a low vacuum atmosphere

and it consisted in a cycle (AC current used, 50 Hz frequency): 15 minutes at 630°C (reached in a couple of minutes) with a 60 MPa pressure applied continuously. After that, pressure and current supplies were interrupted. The sintered specimens were characterized by density measurements (on the basis of ASTM C373). After grinding and polishing, Vickers microhardness was determined using an Amsler Wolpert Dia Testor 2RC diamond indenter, with 50 g load. The microstructure of the polished section of the samples was observed by electron microscopy, combined with Oxford 7353 EDS analysis for assessing chemical composition. Small bars obtained cutting the samples were tested using a three point flexural test machine Sintech 10D.

3 Experimental

The main topic related to the preparation of aluminium-CNTs composite materials is surely the CNTs effective dispersion and distribution. As a consequence of several dispersion tests the above-described procedure was adopted: a first step involved ultra-sonication of CNTs in 2-propanol, the second step was the high energy milling.

The ultra-sonication is necessary and fundamental for unrolling the nuggets (Figure 1a) of CNTs and because during this treatment also the tight bundles (Figure 1b) could be partially untangled.

Thus, by high energy milling it has been possible to obtain good results for aluminium powders and CNTs mixing. The FESEM images show a general decrease of the Al particles grain size and shape that appear as platelets. Despite the presence of few CNTs bundles, which number increased with the percentage of the carbon nanotubes, the micro aluminium particles appear covered by well dispersed CNTs (Figure 3). So this kind of powders is expected to provide a good distribution and dispersion of CNTs inside the sintered specimens.

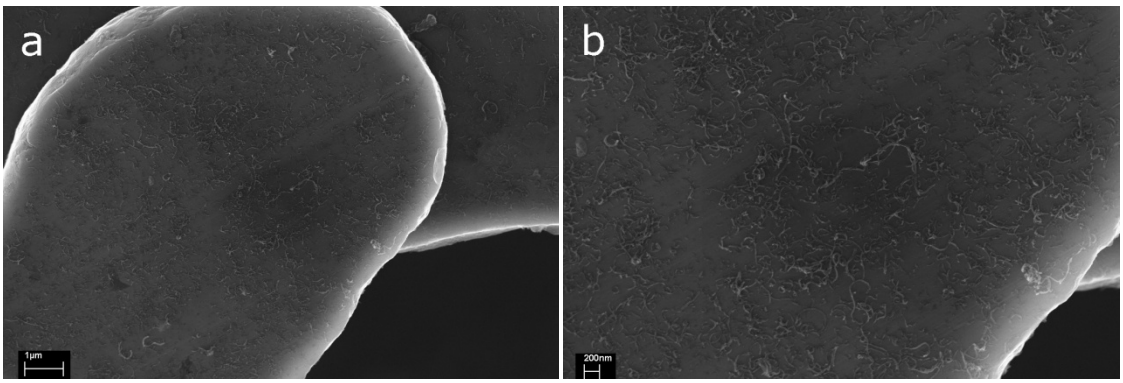

Figure 2. (a) A FESEM image of Al particles covered by 0.3% of CNTs after high energy milling; (b) a magnification.

Using PAFES process, more than 99% relative density was obtained considering a theoretical density varying between 2.67 g/cm^3 for the 3% in weight of CNTs and 2.7 g/cm^3 for pure Al. Micro-indentation tests showed a mean value of about 40 HV, while for pure Al powders, sintered using the same PAFES process described, the samples exhibited values of about 25 HV. It is interesting to remark that in this case the increased hardness values were obtained after PAFES process, without further treatments (e.g. hot extrusion process as reported by many authors [12,18,19]). The samples were then cut. From the centre of the disc two small bars were obtained and used for flexural tests. One section of the remaining portion of the sample was accurately polished (up to ultra fine alumina suspensions) and observed by scanning electron microscopy. The FESEM characterization of all specimens shows (Figure 3a) a uniform surface, without porosities. It is also possible to observe clusters of nanotubes

bundles that assumed an oval shape in the direction of pressing (dark elongated spots - Figure 3b). This is more evident for samples with high CNTs concentration, where the dispersion was not completely effective, due to the presence of a too high density of nanotubes. For the sample containing 0.3% CNTs, the clusters are very reduced in size and number.

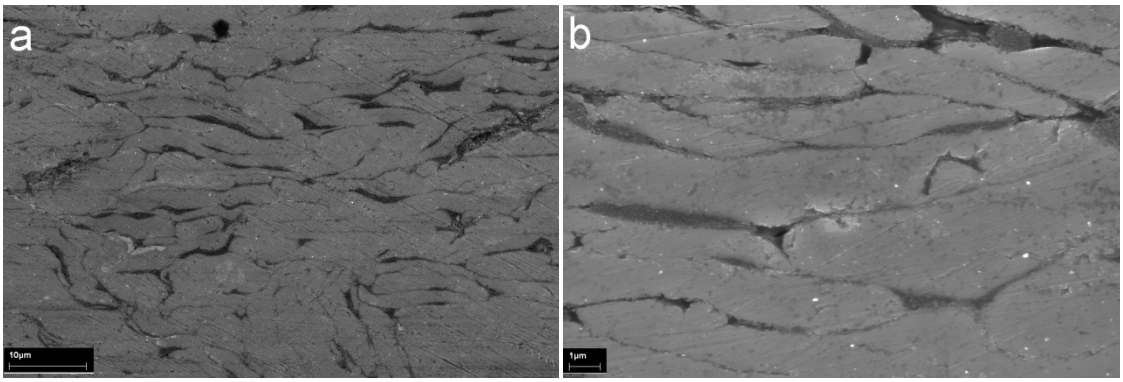

Figure 3. Different magnification FESEM images of CNTs/micro Al composites with a 3% in weight of CNTs

Three point flexural tests were finally conducted on the small bars previously cut. In figure 4 the stress-strain curves for the samples of pure aluminium and for 1 and 3% in weight of carbon nanotubes. On the figure, it must be noted that the pure aluminium bars did not break but the tests were interrupted due to the reaching of the maximum extension allowed by the instrument.

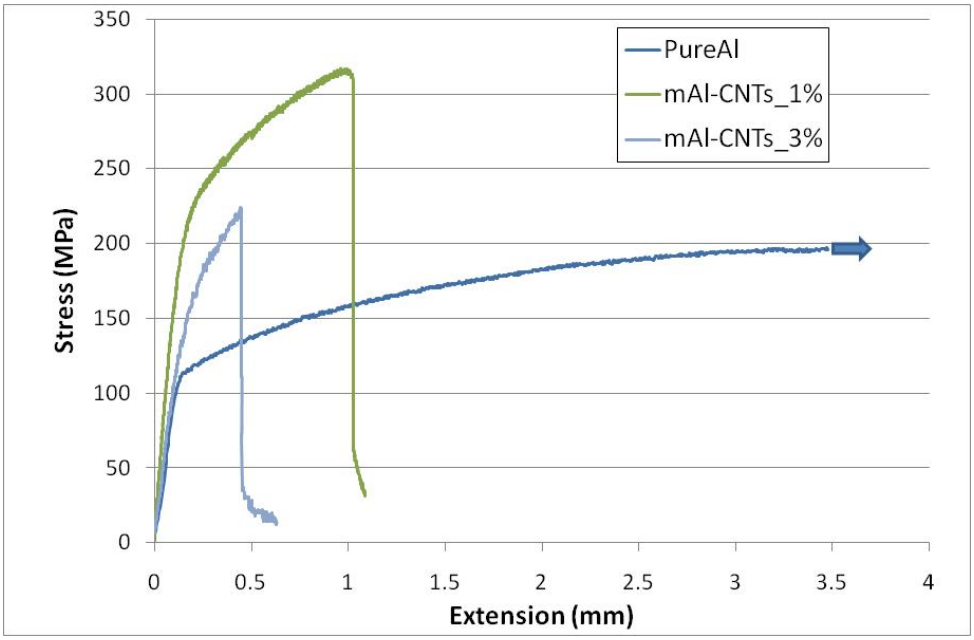

Figure 4. Stress-strain curves for pure Al, 1% and 3% of CNTs

The maximum load and strength values for the three samples are reported in table 1. It is possible to observe that the samples reinforced with1% of CNTs are characterized by a significantly higher resistance and a lower strain than pure aluminium. Further increasing the amount of carbon nanotubes brings instead to the decrease of the maximum strength and strain. This effect could be correlated with the presence of a higher number of bundles of not well dispersed CNTs that act as defects, worsening the properties of the composite.
After the three point flexural tests the broken bars were observed by FESEM to investigate their fracture surface. All the samples containing nanotubes presented the typical structure

reported in figure 5. The grains are elongated perpendicularly to the pressing direction, and the grain size is rather small, probably limited by the presence of carbon nanotubes, that can be easily observed in the image.

Sample	Maximum Load [N]	Maximum strength [MPa]
Pure Al	162.5	197
1% CNTs	204.1	324.5
3% CNTs	148.1	211.1

Table 1. Maximum load and maximum strength values for pure Al, 1% and 3% of CNTs

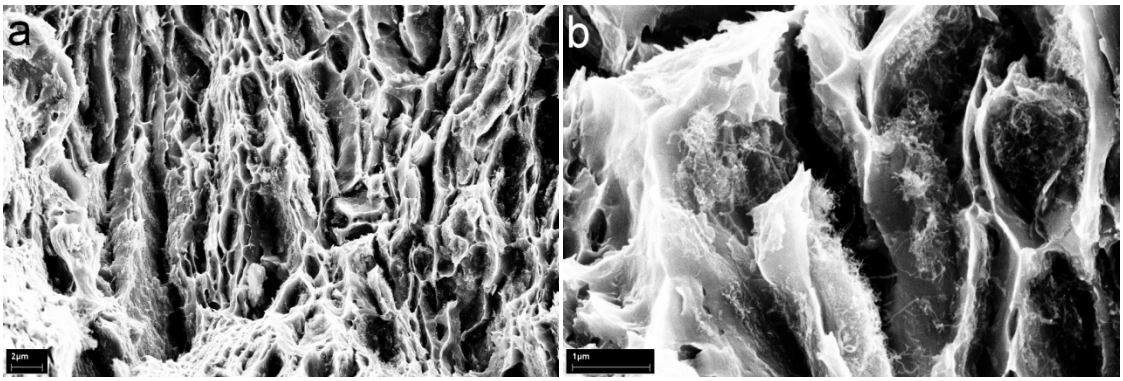

Figure 5. Fracture surfaces of a1% CNTs sample observed by FESEM at two different magnifications

4 Conclusion

High energy milling of pre-dispersed carbon nanotubes and commercial aluminium powders was found to be a good route to disperse CNTs inside aluminium powder. The obtained powders could then be used to create massive specimens by powder metallurgy, using an instrument of the SPS family, called PAFES. Fully dense samples were obtained using micro-powders. The composites specimens showed higher hardness values than pure aluminium, a uniform aspect and they maintained very small microstructures, without considerable grains growth. The flexural strength showed that the addition of 1% CNTs to the aluminium improves significantly the mechanical properties, even if maximum strain is reduced.

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