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Structural characterization of a mechanically milled carbon nanotube/aluminum mixture

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ABSTRACT

The structural evolution of carbon nanotubes (CNTs) during mechanical milling was investigated using SEM, TEM, XRD, XPS and Raman spectroscopy. The study showed that milling of the CNTs alone introduces defects but preserves the tubular structure. When milling the CNTs with aluminum (Al) powder in order to produce a composite, Raman spectroscopy has shown that most of the nanotubes are destroyed. During sintering of the CNT/Al milled mixture, the carbon atoms available from the destruction of the nanotubes react with the Al to form aluminum carbide (Al_4C_3). The effect of milling on the Al matrix was also studied.

1. Introduction

Since the landmark paper on carbon nanotubes (CNTs) by Iijima 15 years ago [1], researchers have demonstrated the exceptional potential and diversity of these materials. A single-wall carbon nanotube, i.e. a nanotube made of only one graphite sheet rolled-up in cylinder, has a Young's modulus as high as 1.8 TPa and a tensile strength as high as 63 GPa [2], which is one to two orders of magnitude superior to the best known steels. Multi-wall nanotubes display lower but still exceptional mechanical properties, and they are easier to synthesize. These superior mechanical properties combined with a low density generate several outlets for a composite reinforced by CNTs. The current prohibitive cost of CNTs (as high as \$500 g^{-1} and higher for single-wall purified carbon nanotubes) is predicted to significantly decrease in the next few years due to an increased efficiency of production combined with the development of new production routes (10–100× decrease in the next 5 years according to Cientifica[1]). At some point, it can be expected that an economical composite made of aluminum (Al) and CNTs could be suitable for the automotive or aerospace industries, where the decrease of fuel consumption by weight reduction is a priority.

CNTs have a strong tendency to form bundles due to their high aspect ratio and their van der Waals bondings [3]. This extensive agglomeration, detrimental for composite mechanical properties, is a main issue when trying to use them as reinforcement [4]. Mechanical milling, a solid state high-energy ball milling process where particles are repeatedly fractured and welded [5], has been used successfully to disperse uniformly a variety of reinforcements within Al matrix [6–8]. Furthermore, the mechanical properties of a CNT/Al composite made by mechanical milling would be further improved by Al grain refinement up to the nanoscale due to the intensive plastic deformation and by the incorporation and dispersion of the oxide layer initially present on the surface of Al powders [5]. However, different studies show that CNTs can be modified when milled alone, going from simple shortening [9–12] to amorphisation [13]. Also, studies of CNT milling with metals, such as iron [14] or magnesium for hydrogen storage [15,16] indicate accelerated CNT damages. Only few research groups have investigated the dispersion of CNTs in an Al matrix by mechanical milling [17–19], and their investigation of the effect of milling on the nanotube structure has been very limited.

In this present work, the possibility of producing CNT/Al nanocomposites by mechanical milling is studied, the emphasis being on the structural evolution of the CNTs and of the Al upon milling. Characterization of the milled mixtures was done using X-ray diffraction (XRD), Raman spectroscopy, scanning and transmission electron microscopy (SEM and TEM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Multi-wall carbon nanotubes used in this work were purchased from Nanostructured and Amorphous Materials Inc. They have a

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[1] www.cientifica.com, abstract of the "Nanotubes for the composite market" report (Augest 2005).

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purity higher than 95%, their inner diameter is between 10–30 nm and their length between 0.5 and 50 μm. As shown in Fig. 1a, most nanotubes were found to be stacked cones and to contain bends and other defects, which is typical of CNTs produced by chemical vapor deposition (CVD). While higher quality nanotubes are available, commercial composite applications will required a cheap and large scale production of CNTs, as it is the case with CVD [20]. Two types of Al powder were used: either spherical Al powder of A.P.S. 3.0–4.5 μm, 97.5% purity or equiaxed Al powder of A.P.S. 7–15 μm, 99.5% purity. In both cases, the main impurity is iron. It was stated elsewhere that the initial powder size does not affect the milling [5] and no differences were indeed found in this study while varying the Al powder size. Fig. 1 shows the initial constituents.

As a reference test, CNTs were first milled alone for times varying from 0 to 5 h in a high energy Spex 8000 mill. In this type of mill, a ball-containing vial is shaken in a figure of 8 motion at a fixed speed of 1200 rpm and it is the impact of the balls against the sample and the end of the vial that induces milling and mixing. Tungsten 7/16″ carbide balls and container with a 10:1 ball-to-powder ratio were used. A mixture of 10 vol% CNT/Al was then also milled using the same procedures. In that case, the milling was performed under argon atmosphere and 2 wt% stearic acid was added as a process control agent to avoid excessive sticking and agglomeration of the Al [21]. After 5 h of milling, some of the powder was heat treated at 630 °C in a tubular furnace under vacuum for 1 h to simulate the heat treatment induced during the sintering process. Also, the 10 vol% CNT/Al mixture was cold compacted in a 2 cm diameter cylinder and sintered at 630 °C in a tubular furnace under vacuum for 1 h to obtain a bulk material.

Morphology of the nanotubes and the powders was studied using a Field Emission SEM Hitachi S-4700. XPS technique performed on a VG Escalab MII with Mg source and 300 W powder allowed an evaluation of the bonding changes with milling. XRD characterization of the powders was performed with a Rigaku Rotaflex Ru-200B type using Cu $K\alpha_1$ radiation at 4.8 kW. Raman spectra were recorded with a Renishaw Invia Raman spectrometer with an argon laser light (514 nm). Nanotube structure was studied with a Field Emission TEM Jeol JEM-2100F. A thin film from the sintered 10 vol% CNT/Al compact, produced by focus ion beam (FIB) Hitachi FB2000A, was also observed by TEM. Phase transformation during heat treatment of the sintering process was studied with a Setaram Setsys 1750 differential scanning calorimeter (DSC). Hardness of the powders was evaluated using a Vicker microhardness indentor with a load of 50 g and a dwell time of 15 s.

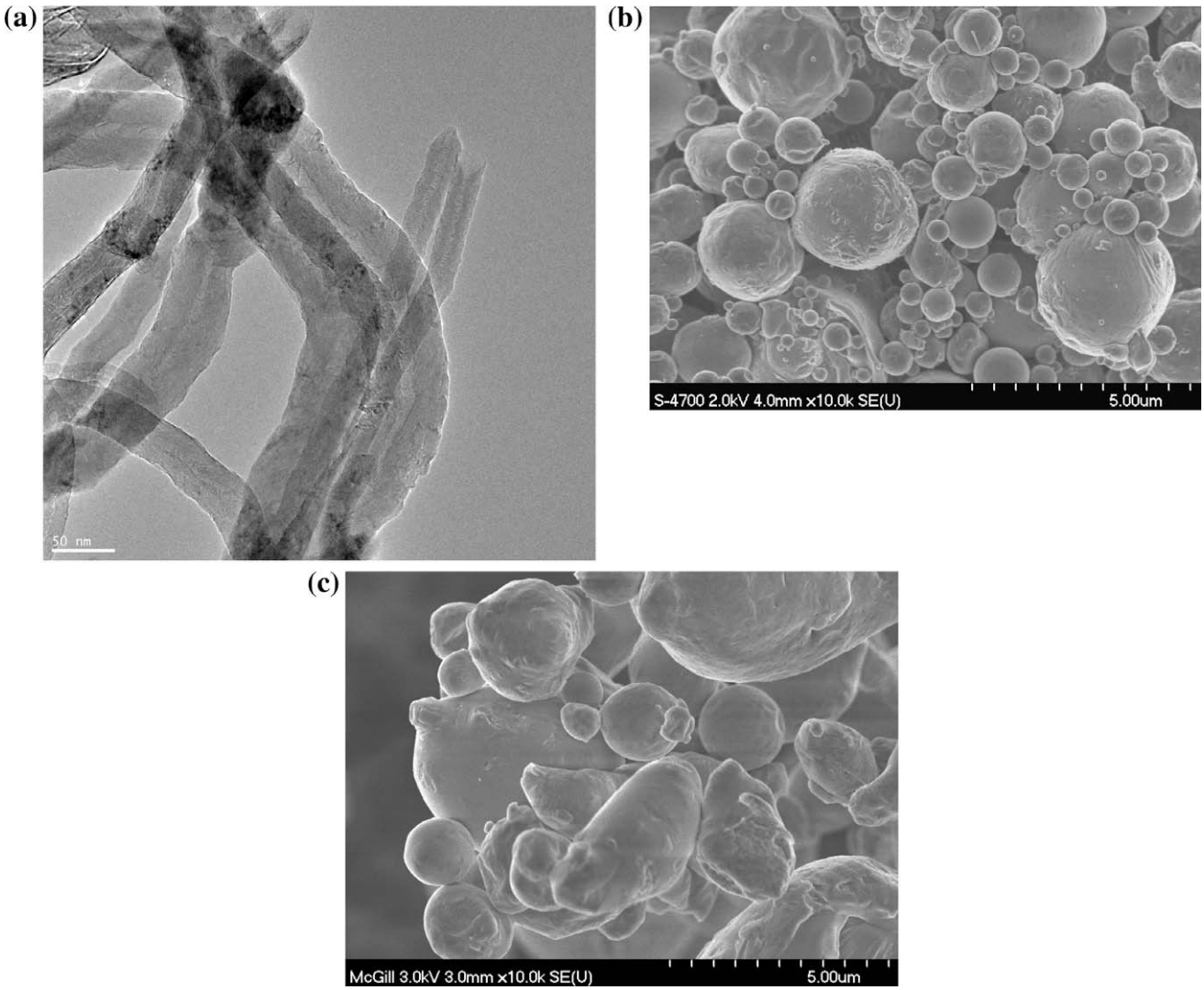

Fig. 1. The raw materials: (a) FEG-TEM picture of CNTs, (b) FEG-SEM micrographs of Al powder, 3.0–4.5 μm and (c) FEG-SEM micrographs of Al powder, 7.0–15.0 μm.