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RESEARCH PAPER

Preparation of carbon nanotube monoliths by high-pressure compaction

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Abstract: High-pressure compaction was used to produce monolithic multiwall carbon nanotubes (MWCNTs) from different sources: (1) high-purity commercial Baytubes®, (2) chemical-vapor deposited MWCNTs without purification at the Laboratory of Production of CNT/UNIFRA, and (3) the same MWCNTs as (2) purified with HCl. Pressures of 4.0 GPa and 7.7 GPa were applied at room temperature using two different pressure-transmitting media, lead and graphite. Cylindrical monolithic MWCNTs with diameters of about 6 mm were obtained. The samples were characterized by Raman spectroscopy, X-ray diffraction, elemental analysis, N2 adsorption and transmission electron microscopy. Results showed that the best sample was obtained with MWCNTs without purification, containing residues of MgO catalyst, and using lead as the pressure-transmitting medium at 7.7 GPa. High-pressure may cause compressive stress and shear stress for the MWCNTs. The lead container, as a quasi-hydrostatic pressure-transmitting medium, provided more compressive stress than shear stress while the impurities acted as binding materials. Both helped to obtain better densification of the MWCNTs.

Key Words: Multiwall carbon nanotubes; High-pressure; Bulk MWCNTs samples; Raman spectroscopy; TEM

1 Introduction

The discovery of carbon nanotubes (CNTs) has opened a new frontier in the chemistry and physics of carbon, attracting the attention of world-wide research since the early 1990s[1-3]. These cylindrical structures are formed by hexagonal arrays of carbon atoms, having a diameter between few angstroms to tens of nanometers and the length can be of the order of centimeters[1]. CNTs are unique structures with remarkable electronic and mechanical properties and have been extensively studied, aiming at the applications in several fields such as medical sciences[4-6], electronics[7], and composite materials[8-13]. During the last decade, ceramic matrice composites reinforced by CNTs have been studied, seeking to improve the intrinsic brittleness of these materials. One of the techniques used to produce ceramic compacts with CNTs as reinforcement is the high-pressure. Andrade et al. obtained dense compacts of silica/CNT with great tenacity (greater than 60% compared to silica without reinforcement) by this technique[12]. High-pressure (up to 8.0 GPa) has been used as an important tool for compaction and densification of nanometric powders, producing new materials. This process promotes the improvement of mechanical properties, allowing the production of hard and dense materials, optically transparent, and crack free[12,14-17]. In these works it was only possible to obtain such impressive properties using lead (Pb) containers as quasi-hydrostatic pressure-transmitting medium assembled in toroidal-type high-pressure chambers and making the processing at room temperature.

Recently, the preparation of macroscopic CNTs has been investigated, here including sheets, fibers, pellets and films, targeting at exploring the important properties, such as mechanical and electrical, of the individual nanotubes. If these properties were preserved in macroscopic samples, they could present numerous applications in various systems such as solar cells, capacitors, electrodes, chemical sensors and others[18]. However, the actual performance of CNTs macroscopic samples is still far from the expectations, requiring a great deal of research yet. There are few studies in literature dealing with the preparation of self-supported CNTs bulk samples, i.e. a matrix formed only by CNTs, or with a very high content of CNTs. Some studies showed the preparation of pellets obtained from solutions of CNTs functionalized with HCl[19,20]. Cha et al.[18] produced other kind of samples prepared with CNTs interconnected via functional groups acquired during chemical treatment and plasma sintering. Xu et al.[21] prepared pellets by CVD method obtained from nanosized MgO powders, containing CNTs and

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other carbonaceous species, showing interesting and controllable electrical properties depending on the synthesis conditions. Li et al.[22] reported the production of MWCNTs pellets produced by spark plasma sintering and hot pressing (1600 °C and 60 MPa). Cao A et al [23] and Cao C et al [24]reported the compression up to 25 MPa, of vertically aligned CNT arrays films. They showed that the CNTs form zigzag buckles that can be fully unfolded to their original length upon load release, behaving as foams. Liu et al. [25,26] studied agglomerates of CNTs under compression, and the compaction responses were employed to characterize the structural and mechanical performances of CNTs agglomerates. They applied hydrostatic pressure up to 275 MPa and reported that the different compaction responses are related to the different microstructures and interactions between CNTs, where the catalyst core played a role in the compression behavior. These are very interesting works, exploring the mechanical properties of the CNTs, however we would like to draw attention, that in these studies the compression was performed at pressures at least two orders of magnitude lower than those used in our work (4.0 GPa and 7.7 GPa). Thus, the expected effects would be quite different.

There are also several studies concerning the effect of high-pressure (up to 30 GPa) on CNTs using Diamond Anvil Cell (DAC)[27], however the samples obtained in this system are tiny (diameters less than 300 μm) making it difficult to evaluate mechanical or electrical properties. In this work we apply pressures of 4.0 GPa and 7.7 GPa at room temperature, to obtain bulk MWCNTs, and to evaluate the effects of the high-pressure on the physical properties of the MWCNTs. Two different pressure-transmitting media were used: Pb, where the pressure is more evenly distributed (quasi-hydrostatic) and graphite (Gr), where the pressure is not so uniform. Macroscopic samples (diameters between 5 mm and 8 mm) of MWCNTs were obtained using high-pressure and they were characterized by transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction and nitrogen adsorption/desorption isotherms.

2 Experimental

The MWCNTs were supplied by two sources, described as follows: (1) MWCNTs from Bayer (Baytubes®), produced using chemical vapor deposition (CVD) and Co as catalyst, with purity greater than 95%, called sample B; (2) MWCNTs synthesized at the Laboratory of Production of Carbon Nanotubes from Centro Universitário Franciscano (LPCNTs/UNIFRA), using CVD with iron and MgO as catalysts, without purification, called sample F; (3) the same MWCNTs produced in LPCNTs/UNIFRA, with the impurities removed as follows: a heat treatment was performed in an oven at ambient pressure at 450 °C for approximately 90 min. In the sequence, it was made a treatment with 4 $mol \cdot L^{-1}$ hydrochloric acid (HCl) solution at 90 °C for 3 h upon stirring. The sample was filtered, washed with deionized water, and dried at 50 °C for 4 h. This sample was called FP.

The raw density for the pristine sample B is 120 to 170 $kg \cdot m^{-3}$. The morphology of all pristine samples can be seen in the TEM images shown in Fig. 3 (sample B), Fig. 5 (sample F) and Fig. 7 (sample FP). A detailed discussion regarding the impurities, morphology of the pristine samples and pressed samples will be discussed later in the text in the appropriate section.

For the high-pressure processing, the MWCNTs samples were placed in a Pb or Grcontainers, with 8 mm of internal diameter that acted as pressure-transmitting media. The containers were put in a ceramic gasket assembled in a toroidal-type high-pressure chamber[28]. The compaction was then accomplished in a 1 000 T on hydraulic press at room temperature at 4.0 GPa and 7.7 GPa, for 10 min[29]. The samples obtained in this system have volumes of about $300mm^3$. The pressure calibration was performed by the fixed point's technique using Bi and Yb as pressure sensors[30]. Table 1 shows the samples nomenclature and processing conditions.

Table 1 Samples nomenclature with their respective processing conditions.

Sample	Pressure *p*/GPa	Transmitting medium
B4Pb		
F4Pb	4.0	Pb
FP4Pb		
B4Gr		
F4Gr	4.0	Gr
FP4Gr		
B7Pb		
F7Pb	7.7	Pb
FP7Pb		
B7Gr		
F7Gr	7.7	Gr
FP7Gr		

Images of the pristine samples and pressed samples were obtained by transmission electron microscopy (TEM) with a JEOL-JEM1200 ExII. This technique allowed a comparative analysis of the morphological aspects of MWCNTs before and after pressure application. Raman spectra were obtained using a confocal microscope Alpha300-Witec with excitation source of 532 nm from a Nd-YAG laser. X-ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, operated with Copper(Cu) target($\lambda_{CuK\alpha}$=0.154 18 nm) in the geometry $\theta/2\theta$ with 2θ ranging between 4° and 100° in order to identify the CNTs and verify their purity. The specific surface area was determined by N_2 adsorption/desorption isotherms of degassed samples at 200 °C for 2 h and calculated by the multipoint method of Brunauer, Emmett and Teller (BET)[31]. The pore size distribution was calculated using the BJH method. All the fitting procedures and area calculations for the Raman spectra were done using the software ORIGIN[32].