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Structure–property relationships in thermally-annealed multi-walled carbon nanotubes

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ABSTRACT

The mechanical properties of individual multi-walled carbon nanotubes (MWCNTs) synthesized by a catalytic chemical vapor deposition (CVD) method followed by a series of high temperature annealing steps at 1200, 1800, 2200 and 2600 °C are investigated by a manipulator tool operated inside a scanning electron microscope. To investigate the relationship between the MWCNT structure and mechanical properties, such MWCNTs with a significantly different nanostructure are separately tested in tension, and subsequently observed their nanostructure and fracture morphology by a transmission electron microscope. The results show that the thermal annealing is effective for improving both the strength and modulus of the catalytic CVD-grown MWCNTs. The MWCNTs annealed at 1800, 2200 and 2600 °C display enhancements to their strengths by factors of ~5.4, ~5.1 and ~15.6, and moduli by factors of ~5.9, ~13.2 and ~18.9, respectively, compared to the MWCNTs annealed at 1200 °C. This effect is associated with the degree of waviness of the graphitic planes along the nanotube axis as well as the degree of crystallinity of the MWCNTs: the strength and modulus of the MWCNTs increases with a higher degree of orientation of the 002 graphitic planes and with a lower degree of defect concentration in the MWCNT structure.

1. Introduction

The use of multi-walled carbon nanotubes (MWCNTs) to reinforce polymer, metal and ceramic matrices to achieve enhanced stiffness, strength and toughness in a wide array of applications has exploded in the last several years [1–6]. Certain properties of such composites may be sensitive to the mechanical integrity of MWCNTs, the nature of the MWCNT/matrix interface, and the dispersion of MWCNTs within the matrices. Concerning the first problem, the Young's modulus and axial strength of MWCNTs are well known to depend critically on nanostructure which, in turn, depends on manufacturing route and subsequent treatment [7,8].

In experimental studies of MWCNTs, a wide range of modulus and strength values has been measured. Treacy et al. [9] were first to show that arc-discharge-grown MWCNTs have Young's moduli ranging from 0.40 to 4.15 TPa (mean 1.81 TPa), using a thermal excitation method. A number of other studies have also produced Young's moduli in the TPa range, for arc-discharge-grown MWCNTs [7,8,10–12]. Within these studies, despite the focus on the ~1 TPa measurements as validation of the superior mechanical properties of MWCNTs, there are many instances of MWCNTs with lower

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moduli, on the order of tens to hundreds of GPa. In the work of Salvetat et al. [7], catalytic chemical vapor deposition (CVD)-grown MWCNTs were investigated and found to have Young's moduli ranging from 12 to 50 GPa (mean 27 GPa), which is dramatically lower than the modulus of ~1 TPa measured for arc-discharge-grown MWCNTs. Additional studies also observe lower moduli for catalytic CVD-grown MWCNTs, in certain cases as low as tens of GPa [13–15]. Peng et al. [8] performed a study on the effect of electron irradiation parameters on resulting MWCNT strength, using a MEMS-based tensile tensing device. They found that as the irradiation-induced defect density is increased the tensile strength decreases, with that of three non-irradiated samples and a sample irradiated at higher doses being ~100 GPa on average and 35 GPa, respectively. The wide range of moduli and strength observed indicates a need for further research in order to elucidate the structure–property relationships of MWCNTs.

Here, we present an experimental study in which we investigate the Young's modulus and fracture strength of MWCNTs synthesized by the catalytic CVD method followed by a series of high temperature annealing steps culminating with annealing at 2600 °C. These MWCNTs possess a significantly different nanostructure but with almost the same diameter and length. Structure–property relationships of such MWCNTs are investigated through tensile-loading experiments with individual MWCNTs, TEM observations and Raman spectroscopic analysis.

2. Experimental

The MWCNT materials (acquired from Hodogaya Chemical, Japan) synthesized by catalytic CVD process were prepared and then thermally-annealed in a graphite crucible using a resistance heated graphite element furnace at 1200, 1800, 2200 and 2600 °C under argon atmosphere. The temperature was raised at a heating rate of approximately 60 °C/min to the predetermined temperature and held there for 1 h, before cooling to ambient temperature. The geometry, Raman intensity ratio (R) and distribution of misorientation of the 002 graphitic planes along the nanotube axis (θ) for each MWCNT are summarized in Table 1. Scanning electron microscopy (SEM; Hitachi S-4300) and transmission electron microscopy (TEM; Hitachi HF-2000) observations showed that these MWCNTs possess almost the same geometric structures such as outer and inner diameter as well as length. (The observation was made for approximately 200 MWCNTs for each sample.) The details regarding R and θ will be discussed later.

Tensile-loading experiments of individual MWCNTs were performed with a manipulator [16] inside the vacuum chamber of SEM (JEOL JSM-6510). The details of sample preparation and mechanical evaluation can be found in the reference [17]. In brief, an atomic force microscope cantilever (PPP-ZEILR, nominal force constant 1.6 N/m; NANOSENSORS and NSC12/without Al/50, nominal force constant 0.3 N/m; Silicon-MDT) serves as force-sensing elements and the force constants of each were obtained *in situ* prior to tensile tests using the resonance method developed by Sader et al. [18]. A single MWCNT was clamped onto a cantilever and W wire tip by local electron-beam-induced deposition (EBID) of a carbonaceous material [19]. The applied force was calculated from the angle of deflection at the cantilever tip, and the nanotube elongation was determined by counting the number of pixels in the acquired SEM images [20]. After the MWCNTs broke, both the cantilever and W wire with attached MWCNT fragments were transferred to a TEM sample stage and examined in the TEM to observe their nanostructure and fracture morphology. We measured the fractured cross-sectional area of each broken MWCNTs by TEM and used the measured, not the average, values to calculate the Young's modulus and tensile strength. Nanotube slippage at MWCNT/AFM tip interface was observed for a subset of the sample sets during the tensile-loading experiment. The results from the successful tensile loading and breaking of 8–10 MWCNTs for each are reported here.

Raman scattering spectroscopy (Horiba Jobin–Yvon T64000) was used to analyze the vibrational modes of MWCNT powders. The measurements were carried out at room temperature under ambient conditions using an argon ion laser with an excitation wavelength of 488.0 nm. Selected area electron diffraction (SAED) technique was used to characterize the degree of misorientation of the 002 graphitic planes along the nanotube axis.

3. Results and discussion

Between the carbonization (~650–760 °C) and graphitization (~2600 °C) temperatures, carbon can transform from an amorphous carbon to a stable graphite planar structure at ambient pressure by cutting and reconnecting sp^2 covalent bonds [21]. We exploited this nature to synthesize MWCNTs having a different nanostructure in order to identify structure–property relationships in MWCNTs. First, we used Raman spectroscopic technique to investigate whether the structural evolution is indeed occurring during annealing

Table 1 – Measured properties for four types of MWCNT powders. Shown are the nanotube outer diameter (OD), inner diameter (ID), length, Raman intensity ratio (R), distribution of misorientation of the 002 graphitic planes along the nanotube axis (θ), respectively. The ranges of the measured parameters are indicated in the parentheses for the OD, ID and length, in addition to the averaged values.

Annealing temperature (°C)	OD (nm)	ID (nm)	Length (μm)	R (–)	θ (°)
1200	77 (23–195)	7 (4–9)	7.2 (1.3–29.8)	1.0	21.5
1800	63 (26–176)	6 (4–8)	7.5 (1.1–29.3)	1.4	14.1
2200	68 (26–136)	6 (3–9)	7.7 (1.6–41.4)	4.9	8.0
2600	70 (33–124)	7 (2–10)	8.7 (1.1–22.5)	10.1	5.3