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Microstructural features and mechanical properties of carbon nanotubes reinforced aluminum–based metal matrix composites

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The composites of aluminum-carbon nanotubes, produced using catalytic chemical vapour deposition method, are prepared with initial composition of aluminum homogeneously mixed with 1, 2, 4 and 10wt% nanotubes and subsequently hot-pressed. TEMs and a STEM have been used to study the as prepared carbon nanotubes and their distribution in aluminum matrix after reinforcement. A set of preliminary observations delineated that the yield of as produced nanotubes in carbonaceous is very high with an average diameter of about 45 nm and with straight and spiral shapes. In composites, these tubes have been seen uniformly distributed in aluminum matrix without any significant dimensional alteration. An enormous increase in microhardness of aluminum – 10wt% carbon nanotubes composites in contrast to pure aluminum has been a remarkable study. Some of the important microscopic details, electrical measurements and mechanical properties in the nanotubes and their composites have been elucidated and discussed.

Keywords*:* Carbon nanotubes, Chemical vapour deposition, Electron microscopy, Microstructure, Mechanical properties

The advent of carbon nanotubes has led to a new dimension of materials and is an important addition to the field of nano-structures. Due to the diameter of these tubes in nano-scale and length in micro-scale, the aspect ratio of the material is extraordinarily high and displays the properties of low dimensions[1-4]. The mechanical properties in particular high strength and modulus are expected as a result of their seamless cylindrical graphite structure[5-7]. The carbon known to its low density is an additional quality of nanotubes. The high modulus coupled with their light weight, results a very prospective usage of these materials as nano-scale fibers in strong light weight applications.

It is important to elucidate the significance of two-phase materials of metal matrix composites[8-12]. In the past several efforts have been devoted to examine the effect of second phase (in micro-scale) reinforcement in aluminum matrix to produce composites of desired microstructure and properties[8-10]. However, a very limited work has been reported experimentally using nano-scaled objects like carbon nanotubes as a composite reinforcement in a metallic matrix[13-17]. In case of carbon nanotubes–metal matrix composites the scale of the reinforcement phase has changed from micrometers (e.g. SiC particulates, glass, carbon fibers, metals) to nanometers[18-20]. The basic idea has been to utilize the properties of ductility and toughness of aluminum as matrix material to mix with carbon nanotubes as reinforcement, especially known for high stiffness and axial strength. Under the transmission electron microscope, by measuring the amplitude of isolated nanotubes' intrinsic thermal vibrations the modulus was measured in the scale of terapascal (TPa)[5]. It is worth noting that the modulus of aluminum alloy is in the range of gegapascal (GPa)[8,9]. The composites of these two materials would definitely change such properties in a drastic way. For an example a commercial aluminum alloy (2124 Al) and carbon nanotubes has the modulus values 71 and 1000 GPa, respectively. By rule of mixture, the composite modulus for 5 vol% reinforcement of nanotubes in aluminum alloy matrix would be 117 GPa, which is an extraordinary improvement in mechanical part of the composite. Moreover, due to the low density of carbon nanotubes the reduction in weight of the composite material for possible usage as structural components is also beneficial.

A significant change in matrix microstructure is expected when the reinforcement phase is in nano-scale. The lattice mismatch and difference in

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coefficient of thermal expansion between the matrix and reinforcement phase would lead to highly dense dislocation network, spread all around matrix–nanotube interface. Properties of the composite can be estimated correctly only if the interface is cohesive without any porosity or intermetallic phase formation due to reaction between matrix and reinforcement phase at nano-scale.

The present investigations deal a detail characterization of carbon nanotubes and aluminum–nanotubes reinforced metal matrix composites. The nanotubes prepared by catalytic chemical vapour deposition has been subsequently mixed with fine-grade aluminum powder in different volume fractions using the hot compaction technique to prepare the composites. Microstructural characterization of both the as prepared carbon nanotubes and metal matrix composites has been carried out to understand the fine details at nano-scale. Subsequently, the composites having different wt% of nanotubes in aluminum matrix have been evaluated for their mechanical strength.

Experimental Procedure

The carbon nanotubes have been produced by the catalytic chemical vapour decomposition (CVD) of the propylene. A schematic of the processing technique is displayed as in Fig. 1. The aluminum powder (Aldrich, USA) of purity higher than 99.5% with an average particle size of ~ 200 mesh (per square inch) has been mixed homogeneously with the different wt% (1, 2, 4 and 10) of carbon nanotubes by hand grinding for 30 min. The mixtures are hot-pressed at 793 K under a pressure of 25 MPa for 30 min. The hot-pressed samples with a size of 40 mm diameter and 6 mm in length are spark-cut into pieces for various measurements.

Transmission electron microscope (TEM) models Akashi EM-002B and JEOL JEM 200CX, both operated at 200 kV have been used for microstructural characterization. TEM, Akashi microscope has been equipped with Gatan CCD camera to perform high-resolution electron microscopy (HREM) experiments. A scanning transmission electron microscope (STEM, VG-HB 501) with a field emission gun operated at 100 kV has also been used to study the distribution of nanotubes in the aluminum matrix. The microhardness was measured with an ultramicro indentation system (Future-Tech Corporation, Japan; model FM 7e) fitted with a diamond indenter with a right pyramid and square base (Vickers indenter). Samples for electron microscopy were prepared from the slices of about 50 μm glued on a tripod for mechanical polishing[21,22]. The mechanical polishing was performed using successive grinding with diamond plastic films of different roughness (15, 6, 3, 1, 0.5 μm grains) and syton, a solution of colloid silica with 20 nm grains, on a rotating polisher kept under water. A specimen thickness of approximately 50 nm was obtained by mechanical polishing. A further finish was carried out using ion beam milling (PIPS, Gatan model 691) by focusing 3 keV Ar^+ ions at a glancing of 6° on the surface of the specimen for 10 min.

Results and Discussion

Morphology and microstructure of as processed carbon nanotubes

A systematic examination of the powder containing nanotubes has shown a variety of microstructures having fascinating fine details. Figure 2 (a-c) delineates a set of secondary electron images recorded under SEM. The micrographs reveal a significant yield of these tubes along with different diameters varying between few nm to about 130 nm (Fig. 2a). These tubes are forming a dense network in the carbon soot. The tubes are lengthy in case of their coarse diameter as compared to tubes with short length and fine diameter (Fig. 2 (b,c)). At some regions in carbonaceous product the tubes of large length (~ 6.5 μm) with coarse diameter about 90 nm have been seen (Fig. 2b). A very coarse diameter (~ 140 nm) tube with about 1.2 μm in length is also seen in the microstructure (Fig. 2c). It has been seen that the tubes are either spiral or straight in shape along the length depending upon their diameter.

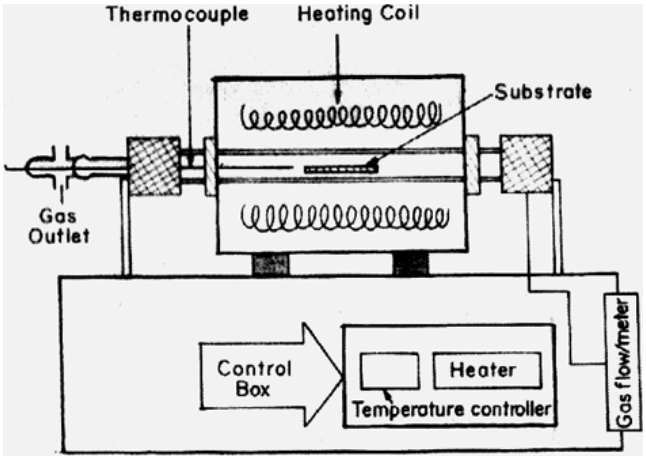

Fig. 1—A schematic showing the technique of chemical vapour deposition

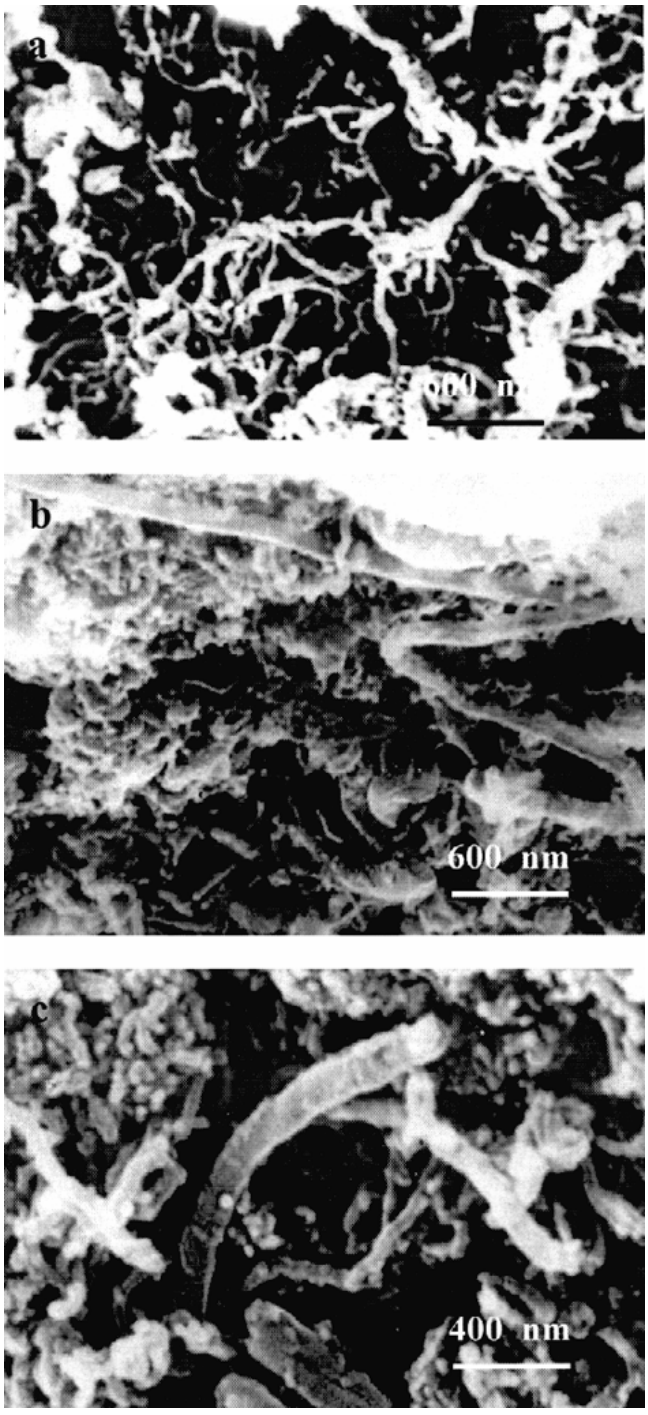

Fig. 2—SEM secondary electron images showing (a) a network of nanotubes with a high yield in carbon soot, (b) a lengthy coarse diameter tube of spiral shape and (c) different fine and coarse diameter tubes

A detailed microstructural characterization of carbon nanotubes at nano-scale has been carried out using transmission electron microscopes. Figure 3a shows a cluster of carbon nanotubes in the microstructure. Fine

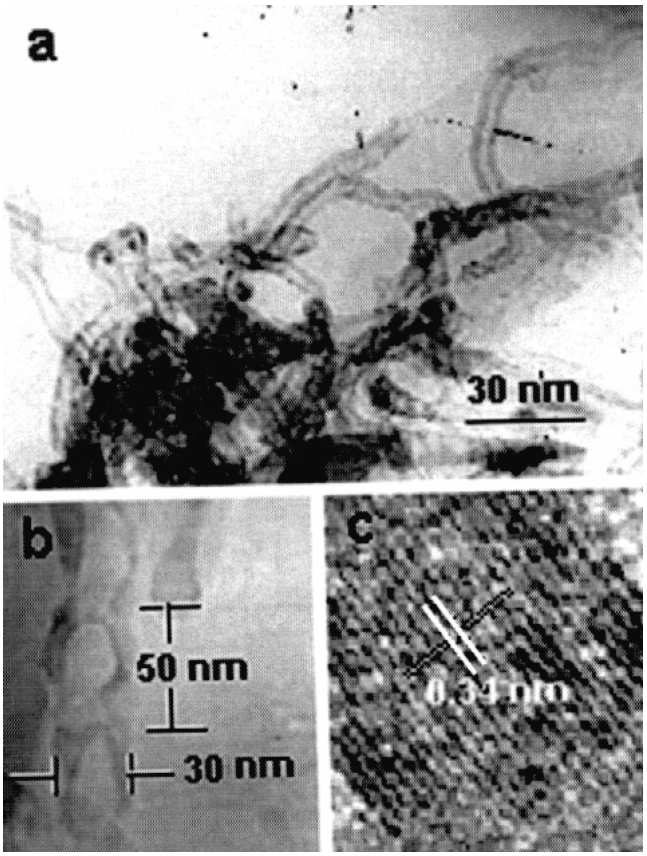

Fig. 3—Bright field electron micrographs showing (a) the carbon nanotubes of different diameter and length, (b) a compartmental structure of tube along the length and (c) a HREM image of a tube consisted of different graphene layers along the diameter.

tubes of diameters between 5-30 nm have been resolved. These tubes are visualized in bulk with a very high volume fraction and most of the instances the different size tubes, are inter mixed. It has been further seen that the coarse diameter tubes are normally helical or curly in shape in contrast to fine diameter tubes mostly straight along the length. The coarse diameter tubes are very lengthy even up to 80 μm. The diameter of these nanotubes itself signifies that the nanotubes produced by chemical vapour deposition are multi-walled. In general the aspect ratio of the tubes is high and every so often it is between 500-1000. It is understood that the nanotubes with high aspect ratios are excellent candidates as second phase reinforcements in aluminum matrix for the preparation of metal matrix composites.

It has been revealed that the nanotubes are basically consisted of different compartments along the length of the tube. These compartments are of about equal spacing (~ 45-50 nm) when the diameter of the tube is about 30 nm (Fig. 3b). High resolution electron

microscopy (HREM) studies on nanotubes have been carried out to reveal the details at lattice scale of graphene sheets constituting the different layers of the multi walled structure. Figure 3c shows a HREM image of multiwalls of a tube typically revealing the {002} lattice images of the graphite structure. The separation between two graphene sheets constituting the different walls of nanotubes is about 0.34 nm. This separation matches with that of bulk graphite structure[1]. The wall thickness of the tubules ranges typically from 2 to 50 sheets depending on the diameter of the nanotube. For an example a nanotube of 35 nm in diameter has the wall thickness of 30 sheets.

The diameters of individual tubes were carefully measured on the different micrographs (Figs 2 and 3) recorded from various regions of samples prepared from carbonaceous material. Figure 4 shows a histogram plotted for the diameters of about 95 tubules, ranging from 10 to 130 nm. Basically, short and terminated tubes around 45 nm are common as can be inferred from the peak on the histogram. As the diameter increases or decreases beyond 45 nm the number of observed tubes becomes less. The data revealed by the histogram may not be perfectly accurate, due to human and experimental errors involved and the limitations of the machines are beyond the scope to control. At the higher resolution it may be possible to visualize even smaller diameter tubes. A basic idea about the frequency of the occurrence of the nanotubes on a large range of their diameter has been possible to estimate from the histogram, which has been plotted after the careful measurements carried out on electron microscopy images. The microstructural study and dimensionality of the nanotubes investigated is beneficial in understanding the quality of tubes used for the preparation of aluminum-carbon nanotubes metal matrix composites.

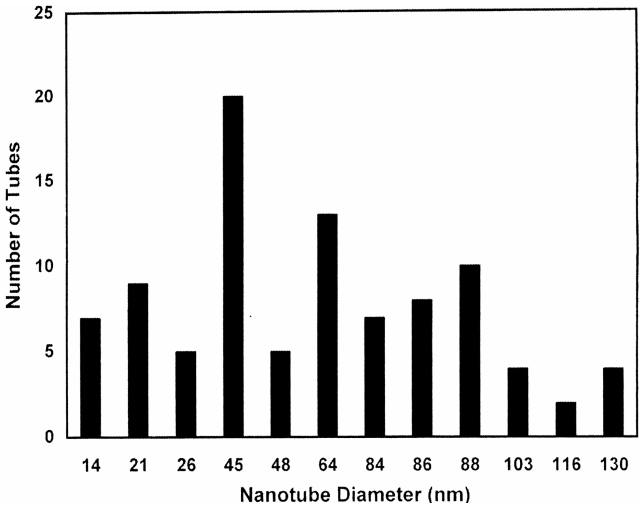

Fig. 4—A histogram showing frequency of multi-walled nanotubes of different tubule diameters

Microstructural features induced during preparation of aluminum-nanotubes composites

An investigation has been extended to study the different fine features evolved at nano-scale after the mixing and hot pressing of carbon nanotubes in aluminum matrix. The distribution of nanotubes in aluminum matrix is an important concern of the microstructural analysis. In this regard the composite of aluminum–10wt% carbon nanotubes has been characterized using bright field electron micrographs of TEM and STEM. Useful information has been gathered by studying the sample under the electron beam. Figure 5 is a STEM image recorded at high magnification. The micrograph shows that the tubes are distributed in matrix without noticeable distortion. The micrograph exhibits that these tubes are smooth along the length. There is no evidence of void formation or reaction phase due to aluminum and carbon at the interface between the matrix and the nanotubes. A remarkable feature is the distribution of nanotubes in the aluminum matrix. These tubes are seen uniformly all over the matrix with their clustering at the grain boundaries. The two grains marked as I and II are elucidated in the micrograph (Fig. 5).

A similar result has further been resolved under TEM. Microstructural investigations show that the

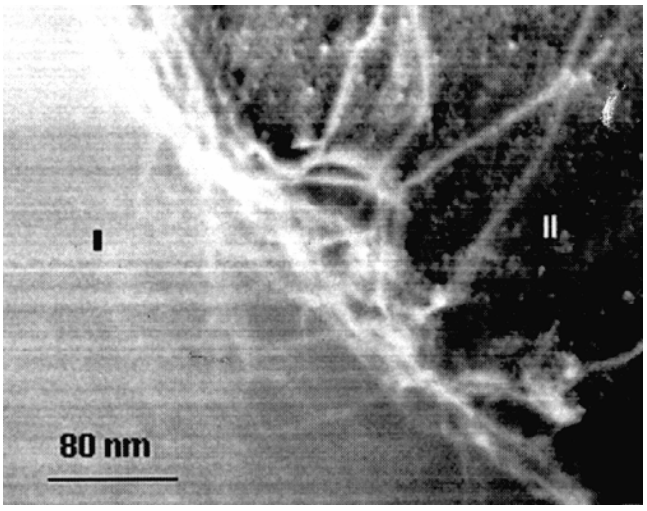

Fig. 5—STEM image of aluminum–10 wt% carbon nanotube samples showing the distribution of nanotubes within the aluminum grain and at the grain boundaries