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ABSTRACT

SYNTHESIS AND DEVELOPMENT OF BORON NANOTUBES AND METAL/CERAMIC-CARBON NANOTUBE COMPOSITES

by Jinwen Liu

The first part of this thesis will be focused on developing a facile and scalable solid – solid chemical vapor deposition (CVD) process using a solid boron precursor to synthesize crystalline boron nanotubes (BNTs) mixed with small amounts of boron nanofibers (BNFs). The synthesis involves the use of solid boron precursors - magnesium boride and magnesium borohydride, magnesium and nickel boride as co-catalysts, and porous MCM-41 zeolite as the growth template. Experimental parameters, such as temperature, grinding of constituents and starting precursor-catalyst-template compositions, were studied and optimized. Detailed characterization have been carried out using field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) coupled with energy dispersive x-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS) and Raman spectroscopy. The BNTs mixed with BNFs produced have a diameter of 10 nm and below and up to 1 micrometer in length. Lattice fringes were found by high resolution TEM (HRTEM) imaging, and the lattice spacing from the fringes is consistent with a recent theoretical calculation.

The second part of the thesis will focus on laboratory scale and scaled-up *in-situ* synthesis of high strength metal and ceramic-carbon nanotube (CNT) composites extending prior work in our group of iron-carbon nanotubes composites. Both laboratory scale and scaled up setups were developed and were successfully used in producing the uniformly nanotube filled composites. The synthesis of composites involved the use of

pure iron, stainless steel with two different particle sizes, aluminum and boron carbide ceramic. The starting powders were dry-coated with nano-sized Fe₂O₃ as catalyst of multiwalled carbon nanotubes growth. The samples produced were characterized by FE-SEM, together with EDS, Raman spectroscopy, and mechanical measurements, which include compressive stress-strain and hardness measurements. Compressive stress-strain measurements on nanotube composites of stainless steel mixed with some iron showed a yield strength increase of 153% (relative to a similarly produced pellet without nanotubes) with 5.2 wt% of infiltrated multiwalled carbon nanotubes (MWNTs). Rockwell hardness increase of 157% for stainless steel infiltrated with MWNTs relative to a similarly produced pellet without MWNTs, was observed.

SYNTHESIS AND DEVELOPMENT OF BORON NANOTUBES AND METAL/CERAMIC-CARBON NANOTUBE COMPOSITES

by Jinwen Liu

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Materials Science and Engineering

Interdisciplinary Program in Materials Science and Engineering

August 2011

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APPROVAL PAGE

SYNTHESIS AND DEVELOPMENT OF BORON NANOTUBES AND METAL/CERAMIC-CARBON NANOTUBE COMPOSITES

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Thanks to beloved Xi, father and mother for their endless love and support

ACKNOWLEDGMENT

My sincerest thanks go to Dr. Zafar Iqbal for his commitment, selfless and knowledgeable contribution toward my PhD study. It has been my honor to have him as my PhD thesis advisor. I greatly appreciate Dr. Nuggehalli Ravindra for his kind assist and considerations during my work in Physics department and proceeding PhD study. I would like to express my gratitude to Dr. Trevor Tyson for his guidance from my beginning of PhD study to my dissertation defense. I am thankful to Dr. Marek Sosnowski for his helpful advice on the experiments of chemical vapor deposition. I would also like to thank Dr. Frank Owens for his suggestion of my experiment and dissertation, and his time for serving as my dissertation committee.

I would like to thank Dr. Anna Zarow for showing me the proper use of EAZY Raman and the Mesophotonics Raman instruments. I would like to thank Dr. Anitha Patlolla for helping me with all laboratory work. I would like to thank Chi Yu for helping me with boron nanotubes experiments. I would like to thank Dr. Amit Goyal for his valuable data from his work on metal-nanotubes composites. I would like to thank Rajen Patel, Dr. Thelma Manning and their groups for all the sample preparation and testing at Picatinny Arsenal, New Jersey. I would like to thank Dr. James Scicolone and Dr. Dave's group for the dry coating of metal and ceramics, Prof. Manish Chhowalla of Rutgers University for TEM of boron nanotubes. I would like to thank Zhong He for the Raman data collection and process of metal-nanotubes composites. I would like to thank Dr. Chris Wang, Ying Ye, Shao-Chun Hsu and Dr. Iqbal's group for their help and collaboration in the laboratory.

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Finally, I grateful acknowledge the US Army RDECOM ARDEC Science Fellowship program and committee members for their financial support in achieving this goal.

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CHAPTER 1

INTRODUCTION

1.1 General Background

It was demonstrated theoretically (Lu 1997; Yakobson, Campbell et al. 1997; Hernandez, Goze et al. 1998; Sanchez-Portal, Artacho et al. 1999; Lier, Alsenoy et al. 2000) and experimentally (Treacy, Ebbesen et al. 1996; Wong, Sheehan et al. 1997; Krishnan, Dujardin et al. 1998; Salvetat, Bonard et al. 1999) that carbon nanotubes (CNTs) have high stiffness and strength, high electrical and thermal conductivity. The result of this research and emerging applications of carbon nanotubes led scientists to explore new nanomaterials, particularly nanotubes, composed of elements other than carbon. Boron nanotubes, nanofibers, nanowires and nanoribbons form one group of nanomaterials that are of growing interest. Boron-based nanostructures have unusual three-center bonding (Bethune, Klang et al. 1993; Iijima and Ichihashi 1993; Bachtold, Fuhrer et al. 2000), which have the potential for forming covalent intertubular bonds (Bethune, Klang et al. 1993) by contrast to CNTs which primarily couple via van der Waals interactions (Dekker 1999). In one study, theoretical calculations indicated that pure boron can form a very stable flat sheet similar to graphene which can roll up to form boron nanotubes (BNTs), and can be either a metal or a semiconductor depending on diameter and chirality (Javey 2003). In another study Boustani and Quandt (Boustani and Quandt 1998) using ab initio methods determined the structural and electronic properties of boron nanotubes and sheets. Because of their predicted exceptional mechanical strength and electronic properties comparable to or exceeding those of carbon nanotubes and their

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high oxidative stability, boron nanotubes have attracted a great deal of attention from researchers.

The first major objective of this thesis is the synthesis of boron nanotubes using a solid state dissociation process using boron precursors, such as MgB₂ and Mg(BH₄)₂. Nickel boride (Ni₂B) and Mg from MgB₂ or Mg(BH₄)₂ are used as catalysts and pure MCM (Mobil Crystalline Material)-41 zeolite (Figure 1.1) as the growth template, in a chemical vapor deposition reactor system under flowing argon. A solid boron precursor was chosen for BNT synthesis because typical gaseous boron precursors used in the only reported prior work (Ciuparu, Klie et al. 2004), such as BCl₃ or B₂H₆, are either corrosive or energetic, and would require special handling for safety reasons, particularly in scaled up operations.



Figure 1.1 MCM-41 zeolite structure schematic (left panel) and transmission electron micrograph (right panel).

[source: Zoelite and Nanostructured Materials Laboratory, cited July 31, 2011; Available from http://www.zeolite.utm.my/?Research:Projects:ZNMG_Project_4; University of Minnesota, cited July 31, 2011; Available from http://www.chem.umn.edu/groups/stein/researchtopic3A.html]

The second major objective of this dissertation involves the synthesis, optimization and initial scale-up of carbon nanotube-anchored metal (iron, steel and

aluminum) and ceramic (boron carbide) composites using a novel *in-situ* chemical vapor deposition (CVD) synthesis-infiltration approach previously demonstrated in the group (Goyal, Wiegand et al. 2005; Goyal, Wiegand et al. 2007). Metal nanocomposites of this type have the potential for use in a range of applications requiring high mechanical strength.

For the pure boron nanotubes mixed with some nanofibers (BNTs/BNFs) synthesis, a facile and scalable CVD process in flowing argon using a solid instead of a reactive gaseous boron precursor has been carried out. The synthesis of crystalline boron nanostructures comprising of relatively straight boron nanotubes involves the use of magnesium boride (MgB₂) powder as the precursor for both boron and magnesium catalyst, nickel boride (Ni₂B) powder as co-catalyst, and the mesostructured hexagonal framework MCM-41 zeolite powder as growth template. Characterization of the nanotubes produced was performed by scanning electron microscopy (SEM), Raman spectroscopy, transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). SEM and TEM images showed that the BNTs/BNFs produced have a narrow distribution of diameters between about 10 nm to 20 nm and length from about 500 nm to above 1 µm.

For nanocomposites of carbon nanotubes (CNTs) anchored to metal and ceramic particles, the primary objective was to fabricate lightweight composites with significant enhancement in mechanical properties and simultaneous improvement in electrical and thermal conductivity as well as corrosion resistance in harsh environments. Several metals, pure and mixed in different ratios, were used and optimized. CNT growth was catalyzed by nanoscale iron in steel and iron powder, whereas aluminum and boron

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carbide particles were coated with iron oxide using a magnetically assisted impaction coating (MAIC) (Ramlakhan, Wu et al. 2000) process was developed. During the synthesis process, CVD was conducted in flowing argon carrier gas mixed with carbon precursors, carbon monoxide (CO) and acetylene (C_2H_2).

A related key objective of this dissertation is related to the scale-up processes and equipment for both BNTs/BNFs synthesis and CNT-metal or ceramic composites. The scaled-up procedure will start with the synthesis of CNT anchored metal or ceramic composites, and will then be applied to BNTs. Several parameters will be involved in the scale-up, such as gas flow rate, gas ratio, etc., and a final scheme will be developed. Several questions arising during the experiments will be discussed in the thesis. The questions will not be entirely resolved but the phenomena involved would be interesting and challenging for future research and could lead to breakthroughs in nanomaterial synthesis.

This introductory Chapter 1 will provide a review of fundamental information about nanomaterials including carbon and boron nanotubes. It will also cover the application of carbon nanotubes involving CNT-anchored metal or ceramic composites, as well as methods used for nanotube synthesis, and techniques used to characterize the materials synthesized. Chapter 2 will focus on the CVD method using a solid boron precursor to synthesize boron nanotubes. The materials synthesized will be characterized by a number of techniques to determine the dimension and composition of the nanotubes. Chapter 3 will focus on the laboratory and larger scale CVD methods to grow carbon nanotubes in different metal and ceramic matrices. Detailed conclusions will be drawn and future work will be addressed in Chapter 4.

1.2 Nanomaterials

A nanomaterial is a material with a relevant and controllable dimension of the order of 100 nm or less (Rames 2009). Because most materials have structure in this range, the presence of nanoscale structure alone is not sufficient to define a nanomaterial. There are three different classes of nanomaterials: discrete nanomaterials, nanoscale device materials, and bulk nanomaterials. Discrete nanomaterials are material elements that are freestanding and 1 - 10 nm in scale in at least one dimension, such as carbon nanotubes. Nanoscale device materials are nanomaterials are nanomaterials are contained within devices, usually as thin 2-D films. Bulk nanomaterials are materials that are available in bulk quantities, define in 3-D volume, and yet have structure controlled at the nanoscale.

Nanomaterial Type	Dimension (D)	Morphology	Characteristics
Discrete nanomaterials	0 or 1	Particles, fibers	Large surface area
Nanoscale device materials	1 or 2	Thin films	Device components
Bulk nanomaterials	3D	Vol. ≤1 mm ³	Structural applications

 Table 1.1 Classification of nanomaterials on the basis of dimensionality and morphology

[Source: Rames 2009]

The methods by which nanomaterials are made vary widely, and the processes required to synthesize discrete nanomaterials (Brust, Walker et al. 1994) are typically quite distinct from the processes used to prepare bulk nanomaterials (Elsherik and Erb 1995). Discrete nanomaterials themselves are often made using bottom-up approaches, sometimes relying on self-assembly to generate the desired nanoparticles or nanofibers. Under some conditions, a properly tuned bottom-up process can be used to generate significant quantities of discrete nanomaterials such as nanopowders. Some of the typical approaches to creating discrete nanomaterials include: condensation from a vapor phase (Birringer, Gleiter et al. 1984), precipitation from solution (Meulenkamp 1998), chemical vapor deposition (Ren, Huang et al. 1998), chemical reaction (particularly reduction or oxidation) (Brust, Walker et al. 1994), processes used to generate a colloidal phase (Ahmadi, Wang et al. 1996), self-assembly using surfaces (Li, Schnablegger et al. 1999), and mechanical attrition or grinding (Nicoara, Fratiloiu et al. 1997). A large number processes are borrowed from various fields are utilized to produce discrete nanomaterials. It has been recognized recently that some nanoscale materials are byproducts of reactions that already exist in industry.

1.3 Types of Nanomaterials

1.3.1 Carbon Nanotubes

In the area of nanomaterials, scientists have continued to search for materials that have better properties, such as higher mechanical strength and improved electrical and thermal conductivity. In 1991, Iijima (Iijima 1991) reported the observation of multiwalled carbon nanotubes (MWNTs) during the direct current arcing of graphite electrodes, a process that is used for the synthesis of C_{60} . In 1993, two years after the discovery of MWNTs, single-walled carbon nanotubes (SWNTs) were found by Iijima and Ichihashi (Iijima and Ichihashi 1993) and by Bethune et al (Bethune, Klang et al. 1993; Iijima and Ichihashi 1993) by using transition metal catalysts incorporated in the graphite electrodes during the arc process. A new era of nanotechnology started with this discovery because both MWNTs and SWNTs were found to have unique properties due to their onedimensional structures. For example, CNTs, and in particular SWNTs, were found to be ballistic conductors which can conduct electricity at room temperature without significant scattering from atoms and defects (Bachtold, Fuhrer et al. 2000). Nanotubes, in particular SWNTs, have emerged as a promising class of electronic materials due to their nanoscale dimensions and outstanding properties, such as ballistic electronic conduction (Dekker 1999; Javey 2003), and insensitivity to electro-migration (McEuen, Fuhrer et al. 2002; Kreup, Graham et al. 2004). CNTs and related nanostructures may be used in many different kinds of applications, such as reinforcement of composite materials (Coleman, Khan et al. 2006), lubrication (Tenne 2006), fabrication of nano-electro mechanical devices (Fennimore, Yuzvinsky et al. 2003), heat-dissipation components in electronic devices (Iwai, Shioya et al. 2005), etc.

1.3.2 Boron Nitride Nanotubes

As pointed out above, during the last two decades there has been intense interest in the study of nanoscale materials. CNTs are the most representative example of a nanomaterial and have stimulated much interest both in academia and industry because of their extraordinary chemical, electronic and mechanical properties. In addition, nanotubular tungsten disulphide (WS₂) (Tenne, Margulis et al. 1992), titanium dioxide (TiO₂) (Wijnhoven and Vos 1998; Masuda, Kanezawa et al. 2003; Mor, Varghese et al. 2005; Qiu and Yu 2008), and boron nitride (BN) (Chopra, Luyken et al. 1995; Bae, Seo et al. 2003; Li, Chen et al. 2010) have been synthesized and investigated for applications. Among these nanotubes, boron nitride nanotubes (BNNTs) have generated the most interest because of their analogy to their carbon counterparts and novel properties. For example, boron BNNTs are chemically inert and electrically insulating, resistant to

oxidation at much higher temperatures than carbon nanotubes, and possess an electronic structure that is independent of structural chirality (Tans, Devoret et al. 1997). BNNTs were theoretically predicted in 1994 (Blase, Rubio et al. 1994; Rubio, Corkill et al. 1994) and experimentally realized in 1995 (Chopra, Luyken et al. 1995). They have similar structures and extraordinary mechanical properties as CNTs. The first measurement of the Young's modulus of BNNTs by Chopra and Zettl (Chopra and Zettl 1998) showed a value of 1.22 Tpa which was comparable to that of CNTs. BNNTs can therefore be considered as an alternative of CNTs. In addition, BNNTs were found to be highly polar and insulating, with a predicted band gap larger than 5.5 eV (Blase, Rubio et al. 1994), which is independent of the tube diameter and helicity in contrast to CNTs which are metallic or semiconducting depending on their diameter and chirality.

1.3.3 Boron Nanotubes

Boron is to the left of carbon in the periodic table of elements. Theoretically a nanotube is formed by "rolling up" the a boron nanosheet joining the two ends of the chiral vector (Gindulyté, Lipscomb et al. 1998). Variation of the tube diameter, and chiral angle control the properties of the various nanotubes formed (Dresselhaus, Dresselhaus et al. 1996). SWNTs are semiconducting or metallic depending on the variation of chiral angle and tube diameter as has been confirmed experimentally (Odom, Huang et al. 1998; Wildöer, Venema et al. 1998). It is expected that if boron nanotubes can be synthesized, their electrical properties, also controlled by variation of chiral angle and tube diameter parameters, would, like their carbon nanotube analog, be of very great interest.

Ciuparu et al. first reported the synthesis of single-walled boron nanotubes with diameter near 3 nm (Ciuparu, Klie et al. 2004). In what follows in this thesis double and

multiwall boron nanotubes mixed with boron nanofibers have been prepared with diameters below 10 to about 30 nm. Szwacki et al. predicted that the boron buckyball B_{80} would have a stable hollow cage, which is symmetrically similar to the isocosohedral structure of C_{60} (Szwacki, Sadrzadeh et al. 2007). A flat stable boron sheet has been predicted, which is composed of a hybrid of triangular and hexagonal configurations (Yang and Schaller 2004; Tang and Ismail-Beigi 2007). By first principles calculations, the vibrational frequencies, free energy, and heat capacity of the flat hybridized sheet and buckled triangular sheet are compared to verify the thermodynamic stability of the flat boron sheet (Lau and Pandey 2008).

1.4 Carbon-Metal and -Ceramic Composites

Carbon fibers, which has fifty times the specific strength of steel and are excellent loadbearing reinforcements in composites (Baughman, Zakhidov et al. 2002), have been used as reinforcements in high strength, lightweight, high-performance composites ranging from expensive tennis rackets to spacecraft and aircraft body parts (Table 1.2).

	Young's Modulus	Tensile	Density
Materials	(GPa)	Strength	(g cm ⁻³)
SWNT/MWNT	~1000	~100 -	~0.7 - 1.7
High tensile steel	210	1.3	7.8
Toray® carbon fibers	230	3.5	1.75
Kevlar®	60	3.6	1.44
Glass fibers	22	3.4	2.6

 Table 1.2 A comparison of the mechanical properties of carbon nanotubes compared

 with other structural materials making them attractive for composite applications

In the last decades, research of fullerenes and nanotubes promised an amazing range of application for these materials. Carbon nanotubes, both MWNTs and SWNTs, because of their intrinsic advantages, has been widely proposed for use in electronics (Gao, Zuo et al. 2003; Liu, Zhang et al. 2005), energy (Conway 1999; Shimoda and al 2002), sensor (Heinze, Tersoff et al. 2002; Bradley, Gabriel et al. 2003; Zhang, Boyd et al. 2006) and especially structural applications. However, except for the latter, these applications have yet to be commercialized.

The first experimental report of the measurement of the Young's modulus of multiwall carbon nanotubes was that of Treacy et al. (Treacy, Ebbesen et al. 1996) in 1996, in which the average value was found to be 1.8 TPa out of a sample of 11 different nanotubes with range from 0.4 to 4.15 TPa. The same experimental approach was later used by Krishnan et al. (Krishnan, Dujardin et al. 1998)to measure the Young's modulus of single wall carbon nanotubes, and a mean value (27 in total) of 1.25 TPa was obtained. The experiments of Treacy et al. (Treacy, Ebbesen et al. 1996)and Wong et al. (Wong, Sheehan et al. 1997) confirmed the expectation that carbon nanotubes indeed possess truly remarkable mechanical properties. Not only did nanotubes have the highest ever measured Young's modulus (twice as large as that of SiC rods); they were also shown to be extremely flexible in the experiments of Falvo et al. (Falvo, Clary et al. 1997).

Nanotubes are considered to be the ideal form of fibers with superior mechanical properties compared to the best carbon fibers, and it should perform far better than these fibers in mechanical applications. The observed tensile strength of individual nanotubes could come close to a few 100 GPa and their elastic modulus in the terapascal range (Treacy, Ebbesen et al. 1996; Wagner, Lourie et al. 1998; Yu, Lourie et al. 2000), far

better than traditional carbon fibers. Hence, recent approaches have all been based on chemically modifying the surface functionalities of nanotubes so that strong bonding interfaces can be created (Eitan, Jian et al. 2003), even though nanotubes in these products act more as matrix enhancers rather than as primary load-bearing structures.

1.5 Synthesis of Carbon Nanotubes

1.5.1 Arc Discharge

The carbon arc-discharge method was first introduced to produce the C_{60} fullerene in 1990 (Krätschmer, Lamb et al. 1990). Later in 1991, Iijima of the NEC Laboratory in Japan reported the first observation of multiwalled carbon nanotubes (MWNTs) made by arc-discharge (Iijima 1991). Bulk quantities of MWNTs and purification were achieved by Ebbesen and Ajayan (Ebbesen and Ajayan 1992) using this method in 1992. For the growth of single-walled carbon nanotubes (SWNTs), a metal catalyst is needed in one of the electrodes of the arc-discharge system. The first success in producing SWNTs by arcdischarge was achieved by Bethune and coworkers (Bethune, Klang et al. 1993), and Iijima (Iijima and Ichihashi 1993) in 1993. Among the non-carbon nanotubes systems, boron-based nanotubes were first synthesized by arc-discharge in 1995 (Chopra, Luyken et al. 1995).

In the arc-discharge method, a hot plasma is established between two graphite electrodes. Carbon atoms are evaporated in a plasma of helium gas ignited by high currents passed through opposing carbon anode and cathode, and carbon nanotubes are deposited on the cathode (Figure 1.2).



Figure 1.2 Schematic of an arc-discharge apparatus used for nanotube growth.

High temperatures are required for fullerene growth but are not necessary for nanotube synthesis, which can be achieved at much lower temperatures by highly scalable chemical vapor deposition techniques discussed below.

1.5.2 Laser Ablation

In the laser ablation method, a high power YAG laser vaporizes carbon atoms from a catalyst filled graphite target in a reactor held at 1200 °C to produce SWNTs in a flow of inert gas passed through the reactor to carry the grown nanotubes downstream to be collected on a water-cooled copper collector (Figure 1.3). The growth of high quality SWNTs at the 1 - 10 g scale coupled with an acid purification process was achieved by Smalley and coworkers by this technique (Thess, Lee et al. 1996).





[Source: Yakobson and Smalley 1997]

The laser ablation technique is also so far the best route to single wall boron nitride nanotubes (BNNTs) (Lee, Gavillet et al. 2001; Arenal, Stephan et al. 2007) in gram scale quantities. The synthesis of single wall BNNTs is achieved by heating an h-BN target using a continuous wave CO_2 laser under a partial pressure of N_2 gas. The temperature at the surface of the target is 3,200 - 3,500K. The products obtained consist of an inhomogeneous mixture of nanotubes and nanoparticles. The ratio of single wall to multiwall BNNTs obtained is 4:1 and are either isolated or organized in small bundles of 2 - 10 tubes with diameter of 2 nm and lengths exceeding 1 μ m (Arenal, Stephan et al. 2007).

1.5.3 Thermal Chemical Vapor Deposition (CVD)

The success in producing high quality SWNTs by arc-discharge and laser-ablation has led to wide availability of samples useful for studying fundamental physics in these low

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dimensional materials and exploring their applications. The synthesis techniques however have some drawbacks. First, both methods rely on evaporating carbon atoms from solid carbon sources in excess of 3000 °C, making them energy inefficient and thus limiting scale-up. Secondly, purification of the nanotube samples produced by oxidizing away amorphous carbons and metal catalyst coated with carbons is difficult (Ebbesen and Ajayan 1992; Liu, Rinzler et al. 1998).

Thermal chemical vapor deposition (CVD) first reported to produce MWNTs by Endo and his research group in 1993 (Endo, Takeuchi et al. 1993) was found to be a more energy-efficient lower temperature and scalable method for the production of SWNTs.



Figure 1.4 Schematic diagram of a chemical vapor deposition (CVD) apparatus.

The experimental set-up for synthesizing carbon nanotubes using CVD is shown in Figure 1.4. The CVD process for carbon nanotubes uses gaseous hydrocarbons as carbon sources. Gases typically used are methane (CH₄), carbon monoxide (CO) or acetylene (C_2H_2). The hydrocarbons flow through a quartz tube placed in a furnace at temperatures ranging from 700 °C to 1200 °C to decompose the source molecules to pure carbon over metallic nanoparticle catalysts, such as Co, Ni or Fe alone or in combination with Mo. The reaction times are typically from minutes to hours, compared with extremely short reaction times at more than 3000 °C in the arc and laser ablation methods. The more controllable parameters (such as, hydrocarbon molecules, transitionmetal catalyst, temperature and pressure) in the CVD process makes it possible to control the type (Kong, Cassell et al. 1998; Kong, Soh et al. 1998; Cassell, Raymakers et al. 1999; Dai, Kong et al. 1999), the length and orientation (Zhang, Chang et al. 2001; Huang, Maynor et al. 2003) of the growing nanotubes together with in some cases their diameter (Li, Kim et al. 2001; Bachilo, Balzano et al. 2003). In addition, the controllability and scalability of CVD make it the most promising approach for scale-up to commercial production (Dai, Kong et al. 1999; Dai 2002; Dai 2002). Over the past decades, CVD was extended to a family of different approaches to make CNTs, such as methane CVD (Kong, Cassell et al. 1998; Kong, Soh et al. 1998; Cassell, Raymakers et al. 1999), HiPCO (high-pressure catalytic decomposition of carbon monoxide) (Nikolaev, Bronikowski et al. 1999), CO CVD (Dai, Rinzler et al. 1996), alcohol CVD (Maruyama, Kojima et al. 2002) and PECVD (plasma-enhanced CVD) (Li, Mann et al. 2004; Zhang, Mann et al. 2005; Zhong, Iwasaki et al. 2005; Kato, Hatakeyama et al. 2006; Wang, Bai et al. 2006). In addition, CVD was also used to synthesize boron nanotubes (BNTs) as shown by Ciuparu et al (Ciuparu, Klie et al. 2004) who reported the first synthesis of pure single-walled boron nanotubes (BNTs) in 2004 by this method. Here BNTs were grown using gaseous BCl₃ mixed with hydrogen as the boron source and Mg as catalyst supported on nano-porous MCM-41 zeolite templates at 870 °C.

1.6 Characterization Techniques

1.6.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is one of the most widely used of all electron beam instruments used to map the nanoscale structure of nanomaterials because of its various modes of imaging, excellent spatial resolution, easy micrograph interpretation, modest sample preparation and friendly user interface. A prototype of an SEM was first built in 1938 (Ardenne 1938; Ardenne 1938), and the first instrument with most of the features of current SEM instruments, such as cathode-ray-tube display and secondary electron detector, was built in 1942 (Zworykin, Hillier et al. 1942). At this time the spatial resolution of an SEM reached 5 nm on solid specimens. Currently, the resolution of an SEM can approach 0.5 nm, rivaling that of a transmission electron microscope (TEM), and it can handle specimens as large as commercial size silicon wafers.

Similar to the facsimile machine, the scanning probe microscope and the confocal optical microscope, scanning electron microscope (SEM) is a mapping, rather than an imaging device. The sample is probed by a beam of electrons scanned across the surface. Radiation from the specimen, stimulated by the incident beam, are detected, amplified, and used to modulate the brightness of a second beam of electrons scanned, synchronously with the first beam, across a cathode ray tube display.




[Source: Purdue University, cited December 10, 2010; Available from : http://www.purdue.edu/rem/rs/sem.htm]

Figure 1.5 shows the basic components of an SEM. These can be divided into two main categories, the electron-optical and detector systems, and the scanning, processing, and display systems. The source of electrons is the gun which produces them either thermionically, from tungsten or lanthanum hexaboride cathodes, or from a field emission source. These electrons are then accelerated to an energy which is typically in the range from 500 eV to 30 keV. The beam of electrons leaving the gun is then focused on to the specimen by one or more magnetic condenser lenses. Typically, the final objective lens is of the pin-hole design with the sample sitting outside the magnetic field of the lens since this arrangement gives good physical access to the specimen. A variety of detectors are provided in the SEM, including a scintillator detector for secondary electrons, a detector for back-scattered electrons and a detector for fluorescent X-rays to

permit chemical microanalysis with the beam. Signals from any of the detectors are amplified and provided to the display screens in the console.

1.6.2 Transmission Electron Microscopy (TEM)

Image formation in transmission electron microscopy is essentially via a diffraction phenomenon. A modern transmission electron microscope can be schematized as a threelens system: an objective lens, an intermediate lens and a projector lens as shown in Figure 1.6.



Figure 1.6 Schematic illustration showing the basic components and principle of the transmission electron microscope.

[Source: University of Hamburg, cited December 10, 2011: Available from: <u>http://www.biologie.uni-hamburg.de/b-online/e03/03e.htm</u>]

The electron beam produced by an electron source is collimated by the condenser lens system and scattered by the specimen. An image is formed in the image plane of the objective lens. The selector aperture allows the selection of one area of the image which is then magnified by the intermediate lens. The intermediate lens I focused on the image plane of the objective lens and an intermediate image is formed in the image plane of the intermediate lens. This image is the object for the projector lens which forms a final image on a fluorescent screen or on the entrance plane of a recording device.

1.6.3 Raman Spectroscopy

In 1928, the Indian physicist Chandrasekhara Venkata Raman discovered the effect named after him for which he won the Nobel Prize in Physics in 1930. His discovery was that when light traverses a transparent material, some of the light that is deflected changes in wavelength. This phenomenon now called Raman scattering is the result of the Raman effect which can be explained as follows:

In Raman effect, when light is scattered from a molecule or a solid, liquid or gas, most photons are elastically scattered (Rayleigh scattering), such that the scattered photons have the same energy (frequency) and wavelength as the incident photons. However, a small fraction of the scattered light (approximately 1 in 10 million photons) is scattered by an excitation in the molecule or solid, liquid or gas due to change in electron polarizability of the right symmetry, with the scattered photons having a frequency different from, and both lower (with higher intensity) and higher than, the frequency of the incident photons (Harris and Bertlucci 1989). In a gas, Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule (see energy level in Figure 1.7). The vibrational Raman effect in solids is primarily used for materials analysis.



Figure 1.7 Schematic illustration of the energy transitions involved in Raman spectroscopy.

[Source: Professor Z. Iqbal lecture, MTSE 748: Nanomaterial, NJIT, Fall 2009]

There are two components in Raman scattering, Stokes scattering (downshifted in frequency) and anti-Stokes scattering (upshifted in frequency) as shown in Figure 1.7. Because of its higher frequency only Stokes spectra are typically recorded. The interaction of light with matter in a linear regime allows the absorption and emission of a photon precisely matching the difference in energy levels of the interacting electron or electrons. The Raman effect corresponds, in perturbation theory, to the absorption and subsequent emission of a photon via an intermediate electronic state, having a virtual energy level. There are several possibilities, such as, no energy exchange between the incident photons and the molecules (and hence no Raman effect), energy exchanges occurring between the incident photons and the molecules (the energy differences are

equal to the differences of the vibrational and rotational energy-levels of the molecule), molecule absorbs energy: Stokes scattering (the resulting photon of lower energy generates Stokes lines on the red side of the incident spectrum), and molecule loses energy: anti-Stokes scattering (incident photons are shifted to the blue side of the spectrum, thus generating anti-Stokes lines).

Raman spectra are typically expressed in wavenumbers, which have units of inverse length. In order to convert between spectral wavelength and wavenumbers of shift in the Raman spectrum, the following formula can be used:

$$\Delta \omega = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right) \tag{1.1}$$

where $\Delta \omega$ is the Raman shift expressed in wavenumbers, λ_0 is the excitation wavelength, and λ_1 is the wavelength of a Raman line.

Raman spectroscopy is widely used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. Therefore, it provides a fingerprint by which the molecule can be identified. A typical Raman spectrum of SWNTs has three important features: low frequency lines assigned to radial breathing modes (RBM) of the nanotubes, intermediate frequency disorder-induced mode due to defects and/or amorphous carbon on the nanotube sidewalls (D-peak), and a higher energy tangential mode (G-peak). One should note that in the G-peak region there is shoulder also labeled as the G⁻ peak due to the breakdown of the degeneracy of the G mode in graphite due to rolling up of the graphene sheet.

A more sensitive approach Surface Enhanced Raman Spectroscopy (SERS) is used as a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on a nanostructured metal (typically gold or silver) surfaces. Under special conditions, the enhancement factor can be as much as 10^{10} to 10^{11} (Ru, Blackie et al. 2007; Blackie, Ru et al. 2009), which means that the technique may be able to detect single molecules (Nie and Emory 1997; Ru, Meyer et al. 2006).

1.6.4 Energy Dispersive X-ray Spectroscopy (EDS/EDX) and Electron Energy Loss Spectroscopy (EELS)

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another.

Electron energy-loss spectroscopy (EELS) measures the spectral distribution of energy inelastically scattered from a monochromatic incident electron beam into a specimen. Elemental composition and atomic bonding state in the specimen can be determined by analyzing the energy using a spectrometer attached under the electron microscope. An electron passing through a material can interact with electron clouds of the atoms present and transfer some of its kinetic energy to them. EELS uses electrons from 0.1 to 10 keV and passes them through a thin foil of the material of interest. At high

energies, the transmitted beam contains inelastically scattered electrons whose energy has been decreased by amounts corresponding to characteristic absorption frequencies in the solid. At lower energies, the reflected beam is monitored for the same transitions. Bulk and surface plasmons are the principal features of these spectra. The incoming electrons take note of the oscillating dipoles that are present on the surface. Most often these arise from the vibrational modes of molecular adsorbates that are present. It also probes the chemisorption bonds to the surface. Furthermore, phonons on the surface of semiconducting but not metallic substrates also interact with the electron beam.

EELS is often regarded as being complementary to energy-dispersive x-ray spectroscopy (variously called EDX, EDS, XEDS, etc.), which is another common spectroscopy technique available on many electron microscopes. EDX excels at identifying the atomic composition of a material, is quite easy to use, and is particularly sensitive to heavier elements. EELS has historically been a more difficult technique but is in principle capable of measuring atomic composition, chemical bonding, valence and conduction band electronic properties, surface properties, and element-specific pair distance distribution functions (Egerton 1996). EELS tends to work best at relatively low atomic numbers, where the excitation edges are sharp, well-defined, and at experimentally accessible energy losses (the signal being very weak beyond about 3 keV energy loss). EELS is perhaps best developed for the elements ranging from carbon through the 3d transition metals (from scandium to zinc) (Ahn 2004). For carbon, an experienced spectroscopist can tell at a glance the differences among diamond, graphite, amorphous carbon, and "mineral" carbon (such as carbon in carbonates). The spectra of 3d transition metals can be analyzed to identify the oxidation states of the atoms. Cu(I),

for instance, has a different so-called "white-line" intensity ratio than does Cu(II). This ability to "fingerprint" different forms of the same element is a strong advantage of EELS over EDX. The difference is mainly due to the difference in energy resolution between the two techniques (~1 eV or better for EELS, perhaps a few tens of eV for EDX). Comparing these two, the advantages and disadvantages are as follows: For EDS- low collection efficiency (small solid angle), good peak/background ratios, good for high-Z elements, SEM(~500 nm spatial resolution) or TEM (less than ~10 nm spatial resolution), stray x-rays in the column can be mistaken for trace elements. For EELS- Can be used in TEM only and with thin samples, high collection efficiency (~90%), poor peak/background ratios (especially in thick samples), best for low-Z elements(large signals), bonding information for Z<33, and high spatial resolution (0.1 – 1 nm).

1.6.5 Mechanical Measurements

Mechanical measurements typical involve hardness tests and stress-strain measurements. The hardness test consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a load of 1 to 100 kgf (see Figure 1.8). The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is the quotient obtained by dividing the kgf load by the square mm area of indentation (Figure 1.8).

The Vickers hardness can be calculated from the formula when the mean diagonal of the indentation has been determined. It is more convenient to use a conversion table. A

Vickers hardness of 800, which was obtained using a 10 kgf (kilogram force) force should be reported like 800 HV/10. Practically identical hardness numbers on a uniform material are given by several different loading settings, which is much better than the arbitrary changing of scale with the other hardness testing methods. The reason why Vickers hardness test is more widely used is because it provides an extremely accurate reading method, and just one type of indenter is used for all types of metal and surface treatments. It is adaptable and very precise for testing materials from the softest to the hardest under varying loads, however the equipment used is more expensive than for other methods, such as Brinell and Rockwell testing.



Figure 1.8 Schematic of a Vickers hardness test measurement and the formula used to calculate the hardness value.

[Source: Gordon England, cited March 10, 2011; Available from: http://www.gordonengland.co.uk/hardness/vickers.htm]

$$HV = \frac{2Fsin\frac{136^{o}}{2}}{d^{2}} = 1.854 \cdot \frac{F}{d^{2}}$$
(1.2)

Where

F = Load in kgf

d = Arithmetic mean of the two diagonals, d1 and d2 in mm

HV = Vickers Hardness

The Rockwell test is the most common method used to measure hardness because it is simple to perform and requires no special skills. Several different scales may be utilized from possible combinations of various indenters and different loads, which permit the testing of virtually all metal alloys. With this system, a hardness number is determined by the difference in depth of penetration resulting from the application of an initial minor load followed by a larger major load; utilization of a minor load enhances test accuracy. On the basis of the magnitude of both major and minor loads, there are two types of tests: Rockwell and superficial Rockwell. For Rockwell, the minor load is 10 kg, whereas major loads are 60, 100, 150 kg. Each scale is represented by a letter of the alphabet. When specifying Rockwell and superficial hardnesses, both hardness number and scale symbol must be indicated. For example, 80 HRB represents a Rockwell hardness of 80 on the B scale. For each scale, hardnesses may range up to 130.

The stress – strain curve is a graphical relationship representation of the relation between stress, the measured load applied to a sample, and strain, the deformation of the sample. Measurements of stress and strain can be carried out in a compressive stressstrain set up or in an Instron apparatus. The slope of the stress – strain curve at any point is the tangent modulus, whereas the slope of the linear elastic portion of the curve is the Young's modulus.

CHAPTER 2

BORON NANOTUBES

2.1 Introduction

Carbon nanotubes led the field of nanomaterials in the years before 2007. Starting in 2008, however, carbon nanotubes (CNTs) started to lose their monopoly over the nanoworld, and it could be the year when materials like boron and boron nitride nanotubes and other carbon materials, such as graphene, started to come to the forefront. CNTs have been appearing up in all sorts of technologies that require strong building blocks and fast electronics at the microscopic scale. Boron nanotubes (BNTs), which were synthesized in 2004 (Ciuparu, Klie et al. 2004) and 2010 (Liu, Shen et al. 2010), could replace CNTs in electronics, while matching their carbon analog in the mechanical strength department. Moreover, compared to CNTs, BNTs have some better properties such as resistance to oxidation at high temperatures and when doped with nitrogen are a stable wide band-gap semiconductor. They also can be used for applications at high temperatures or in corrosive environments, such as electrodes in batteries, fuel cells, and supercapacitors as well as solid lubricants in high temperature applications.

Bulk boron nitride has traditionally been used in high-temperature equipment as ceramics because of its thermal and chemical stability. By analogy with CNTs, boron nitride can be converted to a nanomaterial, such as boron nitride nanotubes (BNNTs). As mentioned in Chapter 1, BNNTs which were first prepared in 1995 (Chopra, Luyken et al. 1995), have diameters of several nanometers to around 100 nm, and lengths of a number of micrometers. They are electrically insulating with electronic properties that by contrast with CNTs independent of chirality and diameter. Nine years after the first synthesis of BNNTs, pure BNTs were first synthesized (see Chapter 1). Prior to the work described in this thesis, it remained the only synthesis of this nanomaterial to date.

All well-established techniques of carbon nanotube growth, such as arc-discharge, laser ablation and chemical vapor deposition (CVD), have been used to synthesize BNNTs. A new approach for BNNTs involves ball milling amorphous boron with catalyst of iron powder followed by thermal annealing. In this research a modified CVD approach using solid boron precursors was adopted to synthesize BNTs since this method is expected to be cost-effective and easy to scale up.

2.2 Boron Nanotubes mixed with Nanofibers Synthesized From MgB₂

2.2.1 Precursor Preparation

BNT synthesis involves a catalytic and templated solid – solid reaction under flowing neutral gas (for example, argon) which does not react with any of the chemicals used. A well ground mixture is expected to guarantee growth of high quality BNTs in sufficient quantities. 50 wt% MgB₂ (Alfa Aesar) boron and magnesium catalyst precursor, 30 wt% of Ni₂B (99%, GFS Chemicals) co-catalyst powder and 20 wt% of mesostructured hexagonal framework MCM-41 (Sigma Aldrich) template powder were mixed in a mortar. Typically 0.02 - 0.1 gms. of mixture were ground under acetone or alcohol in an agate mortar for about an hour to make sure that the powders are uniformly mixed. The mixture was then loaded into a quartz boat for BNT synthesis.

2.2.2 Synthesis

Apparatus Setup

The schematic of the experimental setup used to synthesize BNTs mixed with small amounts of boron nanofibers (BNFs} is shown in Figure 2.1 together with a photograph of the equipment used. Here the thermal decomposition of solid boron precursor, magnesium boride (MgB₂), is used under the flow of argon to produce BNTs/BNFs. This process is simpler than that using a gaseous boron precursor, easy to scale up and costeffective. Parameters that influence the yield, diameter and length of the boron nanomaterials produced, comprise of the following: The type of boron precursor used, uniformity and nanoscale mixing of the boron precursor with catalyst and template, and the growth temperature. These parameters will be investigated as was initially discussed by Liu and Iqbal (Liu and Iqbal 2011).





Figure 2.1 (a) Photograph of experimental setup, and (b) schematic illustration of the set up used for BNT synthesis.

Heat Treatment

The finely mixed powders were placed in a transparent quartz boat and the boat was put inside an 80-cm long, 2.5-cm diameter horizontal quartz tube reactor inside a three-zone, microprocessor-controlled high temperature furnace, which was connected to a bubbler at the exit end (Figure 2.1).

The quartz tube was pumped down to 10^{-3} torr and heated to 950 °C at a rate of 10 °C/min under flowing argon at 150 sccm (standard cubic centimeters per minute). The temperature was held at 950 °C for 60 minutes. After completion of the reaction, the furnace was switched off and the reaction tube was allowed to cool down to room temperature under flowing argon (Figure 2.2). A dark powder was obtained and removed from the boat for purification.



Figure 2.2 A generalized schematic of the temperature-time protocol used to synthesize BNTs/BNFs. The precursors and catalyst were heated to the heat treatment temperature under flowing argon. The heat treatment temperature was held for about 60 minutes. The furnace is shut down when the reaction is complete and the prepared sample is allowed to cool down to room temperature.

Purification

Samples prepared as above were placed in a 2M NaOH solution and sonicated for 30 min using a tabletop ultrasonic cleaner B-521 (Bransonic Inc.) in order to remove the MCM-41 template. Typically, 15 - 20 ml of solution is used to remove MCM – 41 in 0.1 gms of sample. The solution with sonicated sample was then vacuum-filtered. The solids deposited on the filter paper (Millipore, PTFE 47 mm dia, 0.1 µm pore size) and were washed with de-ionized water and allowed to dry overnight in an isothermal vacuum oven (Fisher, Model-281) at 50 °C. Scanning electron microscopy (SEM) was used to examine the sample before and after purification.



Figure 2.3 (a) SEM image of BNTs/BNFs before purification where template is present in large amounts in the background, and (b) SEM image of BNTs after purification indicates that most of the MCM-41 template has been removed.

Fibrous growth in the light-colored background of MCM-41 is observed in the SEM image shown in Figure 2.3 (a). After purification the SEM image in Figure 2.3 (b) taken with the same resolution indicates that the MCM-41 templates were dissolved and removed by the purification process. The average diameter of the fibrous nanostructures was found to be less than 30 nm with lengths up to above 1 micrometer. Both purified and partially purified samples were then characterized in detail as discussed below.

2.2.3 Characterization

Scanning Electron Microscopy (SEM)

Field emission (FE)-SEM was used to get high spatial resolution images of the boron nanostructures. In this work, a VP-1530 Carl Zeiss LEO (Peabody, MA) field emission scanning electron microscope was used with samples mounted on aluminum stubs with double-sided carbon tape.

Figures 2.4 (a) and (b) show FE-SEM images at low and high-resolution respectively from a partially purified sample. The BNTs/BNFs appear to grow from the left over MCM-41 template and are quite abundant in quantity. The tubular and fibrous

structures grown are very straight and have a diameter range of 10-30 nm and up to a few micrometers in length. However, the diameters observed are much larger than those of the approximately 4 nm pores in MCM-41 suggesting that growth is only seeded in the pores and occurs largely outside the pores. This is in contrast to the conventional CVD growth of short, about 3 nm diameter single wall BNTs by Ciuparu et al (Ciuparu, Klie et al. 2004). The bulbous tips indicated by arrows in Figure 2.4 (b) are typical features of many nanotubular structures. Similar features were observed in boron nitride nanotubes synthesized by Lourie et al (Lourie, Jones et al. 2000).



Figure 2.4: (a) SEM images of purified BNTs/BNFs from MgB₂ which indicate that the structures appear to grow out from the MCM-41 template in large quantities. The tubes are mostly straight and stable in the electron beam; and (b) Higher magnification image showing bulbous tips (arrowed) which are typical features of the BNTs/BNFs made from MgB₂.

The structures produced are stable under the electron beam both in SEM and transmission electron microscopy (TEM, see below) in contrast to instability under the electron beam irradiation observed in the single wall BNTs prepared by Ciuparu et al (Ciuparu, Klie et al. 2004).

Transmission Electron Microscopy

A transmission electron microscope (TEM;TOPCON 002B ultrahigh resolution) at Rutgers University operating at 200 kV was used to obtain high resolution TEM images. TEM imaging, electron energy loss spectroscopy (EELS) and energy dispersive spectroscopic (EDS) microanalysis data were obtained at the Evans Analytical Group Inc.

High-resolution TEM (HRTEM) images of highly purified samples of BNTs and BNF are shown in Figure 2.5. Figure 2.5(a) shows nanotubes with diameter down to about 10 nm and an apparently double-walled structure. Lattice fringes are evident at the tips and also on the sidewalls of the 30 nm diameter BNT structure with 8 nm thick walls lying flat on the lower left side of the image. This observation suggests that the BNTs produced are crystalline consistent also with the observation of selected area electron diffraction patterns from the samples (not shown here). Figure 2.5 (b) shows a tilted 20 nm diameter BNT on the right, and two 8 nm nanofibers lying flat on the TEM substrate on the bottom left of the image, which can also be interpreted as arising from a 30 nm multiwalled BNT with 8 nm walls, Figure 2.5 (c) shows a lower resolution dark field image of very straight BNTs lying on the holey carbon grid with their tips curved up. Sharp image contrast evident at the tips is due to the presence of metallic catalyst particles, consistent with the EDS data discussed below.



Figure 2.5 (a) TEM image of relatively thin BNTs with diameter down to about 10 nm and apparently double walls; (b) TEM image of a tilted 20 nm diameter BNT with wall thickness of about 5 nm and that of a flat 30 nm diameter BNT with about 8 nm wide walls. The tube tip with some lattice fringes can be seen on the tilted vertical BNT and also on the walls of the flat BNT; and (c) Dark field lower resolution TEM image showing very straight BNTs that are bent upwards at the tips. Contrast of the images at the tips is due to the presence of metallic catalyst particles (see EDS data below).



Figure 2.6 (a) and (b), DFT calculated 5 Å BNT structures; and (c) and (d), HRTEM images with lattice fringes of purified BNTs from MgB₂.

Theoretical first-principles calculations based on density functional theory (DFT) performed to study crystalline bundles of zigzag and armchair-type single-walled boron nanotubes with a diameter around 5 Å (Lau, Orlando et al. 2008) are shown in Figure 2.6 (a) and (b). The calculated structures are consistent with the HRTEM images with lattice fringes shown in Figure 2.6 (c) and (d), respectively. Although the diameter of the

observed tube is 10 nm, much larger than that of the theoretically calculated structure of 5 Å diameter, the observed tubes may correspond to the same boron sheet, since the observed lattice spacing is about 3.8 Å which is similar to that used in the DFT calculation. This suggests that the boron nanotubes produced correspond to rolling of a pure boron sheet.

Raman Spectroscopy

Raman spectroscopy is one of the most powerful and widely used characterization techniques for single- and double-walled carbon nanotubes, and by analogy is expected to be capable of characterization of narrow diameter BNTs. Two different Raman instruments have been used in this work to obtain the Raman spectra: (i) A confocal Horiba- Jobin Yvon LabRam micro-Raman spectrometer with a 20 mW He-Ne laser source emitting at a wavelength of 632.81 nm and focused to a spot size of 10 μ m with a 10x lens; and (ii) A Mesophotonics SE 1000 Raman spectrometer with a 250 mW near-infrared laser operating in the near-infrared at 785 nm with a 130 μ m diameter spot size and calibrated to 2 cm⁻¹.



Figure 2.7 Raman spectrum of a purified boron nanotube sample after purification taken with 785 nm excitation.

A Raman spectrum taken from a purified boron nanotube sample with a 785 nm laser is shown in Figure 2.7, indicating lines at 298, 404, 480 and a broad feature at 760 cm⁻¹. Figure 2.8 (a) shows micro-Raman spectra excited with 632.8 nm laser radiation from different parts of a purified BNT sample with peaks at 285, 410, 495, 846 and 908 cm⁻¹. Figures 2.8 (c) and (d) show the Raman spectra of boron nanoribbons from Xu et al (Xu, Zheng et al. 2004) with main peaks below 1000 cm⁻¹ at 490, 705, 746, 795 and 910 cm⁻¹ and of single-walled BNTs with peaks at 210, 460, 495, 580, 800 and 908 cm⁻¹ from Ciuparu et al (Ciuparu, Klie et al. 2004), respectively. The radial breathing mode (RBM) lines in single and double-wall carbon nanotubes usually appear in the low frequency region below 300 cm⁻¹, and therefore the peaks at 298 and 285 cm⁻¹ in the present samples can be assigned to the RBMs in small diameter BNTs prepared via MgB₂ which appear to be double-walled based on the TEM images shown above. The single-walled

nanotubes grown by Ciuparu et al show a low frequency line at 210 cm⁻¹, which can be assigned to a radial breathing mode. The lines appearing around 490 cm⁻¹ in both boron nanotubes and nanoribbons in Figure 2.8 can be assigned to a B-B stretching mode corresponding to the tangential mode in carbon nanotubes. This mode is much lower in frequency than in carbon nanotubes probably because of the electron deficiency of the boron structures. It is not clear however why this mode is so much lower in frequency than in carbon nanotubes.



Figure 2.8. (a) Raman spectra of different regions of a purified boron nanotube sample, (b) Raman spectrum obtained for a sample boron nanoribbons by Xu et al (Xu, Zheng et al. 2004); and (c) Raman spectrum of as-synthesized ca. 4 nm single-walled boron nanotubes from Ciuparu et al(Ciuparu, Klie et al. 2004). TEM image of a single-walled tubular structure is shown in the inset.

Electron Energy Loss Spectroscopy (EELS)

EELS microanalysis carried out in the TEM was used to map the elements within the tubes imaged by TEM and initially by SEM. EELS data (Figure 2.9) taken from a nanotube sidewall clearly show the boron K-edge spectrum with three primary features – a pre-peak shoulder at 190 eV, a peak at 193 eV and a broad signal near 200 eV associated with boron dangling bonds satisfied by adsorbed oxygen. Neither the Ni $L_{2,3}$ -edge (around 850 eV) nor the Mg K-edge (around 1300 eV) is observed consistent with the EDS data discussed below. Note however that EELS cross-sections are higher at relatively low atomic numbers.





Figure 2.9 (a) TEM image and EEL spectrum from the region indicated showing the boron edge discussed in the text. (b) The EEL spectrum at the location of the Ni and Mg edges showing the absence of Ni and Mg on the walls of the BNT.

Energy Dispersive X-Ray Spectra (EDS)

EDS data taken from the tip and sidewall of the nanotube in the TEM are shown in Figure 2.10 (a), (b) clearly indicate the presence of Ni from the Ni₂B catalyst. No magnesium is found at the tip, but surprising Si, probably due to partial decomposition of the MCM-41 template is detected. EDS taken on the sidewall away from the tip [Figure 2.10 (c), (d)] shows only traces of Mg catalyst and Si, and Ni is not observed. The data therefore suggest that Ni and Mg act as catalysts in the reaction, leaving Ni at the tip where the reaction ends.





Figure 2.10 TEM image of boron nanotube and EDS taken from the tip (a, b). TEM image of boron nanotube and EDS taken from the sidewalls (c, d).

2.3 Boron Nanotubes/Nanofibers Synthesized From Mg(BH₄)₂

An alternative solid state precursor route to boron nanotubes using magnesium borohydride was also investigated. Magnesium borohydride would decompose at much lower temperatures than magnesium boride and the decomposition process would also be quite different which may affect the diameter, length and morphology of the nanotubes produced.

2.3.1 Sample Preparation

Typically, magnesium borohydride, $Mg(BH_4)_2$ {95% Sigma Aldrich) powder, Ni₂B (99%, GFS Chemicals) powder were mixed with mesostructred hexagonal framework MCM-41(Sigma Aldrich) powder in a mass ratio of 6:3:2. A total of 0.04 – 0.1 g solids were ground in an agate mortar soaked in 15-20 ml acetone (99.7%, Fisher Chemical) for about 20 minutes until the acetone evaporated and a gray powder was obtained.

2.3.2 Growth of Nanotubes/Nanofibers

The mixed powders were placed in a quartz boat in the 80-cm long, 2.5-cm diameter horizontal quartz tube reactor inside a three-zone, microprocessor-controlled high temperature furnace, connected to an oil bubbler at the exit end as shown in Figure 2.1 above. The quartz tube was pumped down to 10^{-3} torr, back-filled with flowing argon at 100 sccm (standard cubic centimeters per minute) and atmospheric pressure, and heated to 750 °C at 10 °C/min. The temperature was held at 750 °C for 60 minutes. After completion of the reaction, the furnace was switched off and the reaction tube was allowed to cool down to room temperature under flowing argon. A dark powder was obtained and removed from the boat for characterization.

2.3.3 Characterization of Nanotubes/Nanofibers

FE-SEM was carried out to investigate the morphology of BNTs/BNFs made from Mg(BH₄)₂. Figures 2.11 (a) and (b) show FE-SEM images at low and high magnifications, respectively. The SEMs indicate that abundant web-like, curved and very thin fibrous nanostructures are obtained. The boron nanostructures obtained are however unstable in the electron beam at high resolutions in the scanning electron microscope similar to observations by Ciuparu et al (Ciuparu, Klie et al. 2004) for their single wall BNT samples. It was also found that the nanostructures obtained are unstable in sodium hydroxide solution used for removing MCM-41 and hydrochloric acid used for removing excess catalyst. Low hydroxide and acid concentrations would therefore be needed for purification which may not be strong enough to provide complete removal of template and catalyst. High temperature post-synthesis annealing may therefore be necessary to stabilize the boron nanostructures so that both efficient purification and high resolution SEM and TEM, as well as Raman spectroscopic characterization can be carried out. This work is planned to be carried out in the future.



Figure 2.11 (a) Low magnification SEM image of as-prepared boron nanotubes/nanofibers made using $Mg(BH_4)_2$, and (b) High magnification SEM image of as-prepared boron nanotubes and nanofibers from magnesium borohydride showing extensive web-like growth of nanotubes/nanofibers.

2.4 General Results and Discussion

Influence of Grinding on Nanotube/Nanofiber Growth

In order to find out how grinding influences the growth of BNTs/BNFs, several experiments were conducted as a function of grinding parameters. Two grinding methods were used in this study: manual grinding and a ball mill. A ceramic pestle and mortar were utilized when grinding manually. For mechanical grinding, a 3-lb capacity ball mill was used, filled with grinding media of 13/16" non-sparking alumina cylinders to reduce the materials to a fine powder.

All raw materials were prepared with the same amount of MCM-41 and Ni₂B but the MgB₂/Mg(BH₄)₂ amounts were varied. Mixtures prepared were annealed under the same conditions and SEM was used to examine the samples. The results indicate that smaller particles are obtained with longer grinding. Grinding in a ball mill provides powders down to the sub-micron level but care must be taken not to overfill the barrel with powder. For MgB₂ the best results were obtained using manual grinding for approximately 60 minutes.

Influence of Catalyst Support System on Boron Nanotube/Nanofiber Growth

Mg-MCM-41 (Ciuparu, Klie et al. 2004) has been reported as catalyst/support for the growth of single walled boron nanotubes, since pure MCM-41 under the same conditions did not produce boron nanotubes. The first observation of growth of BNTs/BNFs was with pure MCM-41 as template and MgB₂ or Mg(BH₄)₂ as boron and Mg catalyst source mixed with Ni₂B as co-catalyst or catalyst precursor. If only MgB₂ or Mg(BH₄)₂ is used together with MCM-41, no BNTs/BNFs are produced which suggests that Ni₂B is needed as the co-catalyst.

Influence of Growth Temperature

To optimize the growth temperature of BNTs/BNFs several experiments were conducted at different temperatures. For BNTs/BNFs made from MgB₂, ten parallel experiments were carried out with ten different temperatures from 860 °C to 950 °C with steps of 10°C. For BNTs/BNFs made from Mg(BH₄)₂, three different temperatures of 650 °C, 750 °C and 850 °C were used. All sample powders were prepared with the same Ni₂B catalyst and MCM-41. Note that the MgB₂ or Mg(BH₄)₂ and Ni₂B in the presence of MCM-41 had provided the best results in terms of growth of boron nanotubes/nanofibers. The BNTs/BNFs grown were investigated by SEM and results shown in Figure 2.12 indicate that as the growth temperature increases the qualitative yields also increase.



Figure 2.12 Growth temperature and qualitative yield based on SEMs of BNTs/BNFs from MgB_2 precursor. Corresponding representative SEM images are shown below each temperature range in the plot.

Qualitative Formation Mechanisms

Boron nanotubes or nanofibers are catalytically grown from MgB₂ by a decomposition process as follows:

$$MgB_2 \rightarrow Mg + 2B$$
 (2.1)

This reaction occurs at $\geq 950^{\circ}$ C in the presence of Ni₂B as co-catalyst. Mg functions also as catalyst for growing primarily nanotubes. The optimal carrier gas during growth is argon. Nitrogen was found to prevent the growth of nanotubes because it "poisons" the emerging magnesium catalyst. Nanotube/nanofiber growth does not occur effectively when MCM-41 template is absent because Ni₂B is encapsulated in the zeolite pores and initiates the growth of the boron nanotubes consistent with the TEM images discussed above.

 $Mg(BH_4)_2$ yields copious amounts of BNTs/BNFs at much lower temperatures than MgB_2 via a decomposition process as follows:

$$Mg(BH_4)_2 \rightarrow MgH_2 + 2B + 3H_2 \rightarrow Mg + 2B + 4H_2$$
(2.2)

This reaction starts to produce nanotubes and nanofibers at temperatures as low as 650°C with Ni₂B support in MCM-41 as co-catalyst together with growing Mg. Nascent hydrogen produced during the reaction can stabilize smaller diameter nanotubes than in the reaction using MgB₂. The boron nanotube/nanofiber structures have however to be stabilized by thermal or plasma annealing so that chemical purification followed by high

resolution electron microscopy and Raman characterization can be conducted. This work will be conducted in the future.

2.5 Conclusions

In this chapter, the solid - solid chemical vapor deposition method using MgB₂ was developed and boron nanotubes were produced and purified. Two key parameters were determined for BNTs/BNFs growth: reaction temperature and grinding of the constituents of the reaction. A laboratory scale furnace with a small boat type reactor was set up for BNT growth using a Mg-Ni catalyst system. It was observed that, when using MgB₂, boron nanotubes growth initiates at a temperature of 900 °C and the optimum temperature is around 950 °C. Pure BNTs/BNFs synthesized from MgB₂, Ni₂B and MCM-41 support/template system by the modified CVD process discussed here are mostly straight and stable. Detailed characterization of the boron nanotubes have been carried out using SEM, HRTEM coupled with EDS and EELS, and Raman spectroscopy. The smallest nanotubes observed appear to be double-wall boron nanotubes from HRTEM images, are around 10 nm and below in diameter and up to 1 micrometer in length in contrast to much shorter single walled nanotubes of 4 nm observed by Ciuparu et al (Ciuparu, Klie et al. 2004). The boron nanotubes obtained are crystalline as indicated by lattice fringes in HRTEM images. The lattice spacing from the fringes are found to be consistent with recent theoretical simulation of boron nanotube formation.

BNTs/BNFs, when synthesized using magnesium tetrahydroborate, start to grow at 650 °C and can be grown in large amounts at 750°C as web-like structures with small diameters, which are unstable in the electron beam under high resolution conditions. The nanotubes and nanofibers are also chemically unstable under purification conditions. For this reason further work on this approach was not conducted in this thesis and left for future work.

CHAPTER 3

IRON AND STAINLESS STEEL-CARBON NANOTUBE COMPOSITES

3.1 Abstract

The synthesis and characterization of metal-carbon nanotube composites that have novel mechanical properties are discussed in this chapter. Continuous, aligned carbon-fibers are the dominant constituent for several important composite application areas. State-of-theart high-performance polymer composites are based on reinforcements with carbon fibers derived from polyacrylonitrile (PAN) or pitch precursors and are utilized in product forms consisting of 3,000 to 12,000 fiber bundles of diameters in the 7 to 10 micron range. Key properties such as modulus and tensile strength and electrical and thermal conductivity are related to the microstructure and are dependent upon the precursor used and the fiber manufacturing process. Carbon nanotubes have been incorporated in polymer and ceramic matrices to provide improved mechanical properties. However, only sparse results are available for carbon nanotube-metal composites, with no substantial improvement in mechanical properties reported so far. For example, Kuzumaki et al. (Kuzumaki, Miyazawa et al. 1998) fabricated aluminum composites using 5 and 10% by volume of pre-synthesized, arc-grown multi-wall carbon nanotubes (MWNTs) dispersed in an aluminum matrix, but these composites showed no improvement in mechanical properties. Yang and Schaller (Yang and Schaller 2004) prepared MWNT/magnesium composites by gas pressure infiltration of liquid magnesium into a porous array of nanotubes and investigated their damping characteristics; but no improvement relative to damping characteristics of conventional metal matrix materials was observed. Flahaut et
al. (Flahaut, Peigney et al. 2000) fabricated carbon nanotube-iron-Al₂O₃ composites by hot-pressing *in-situ* formed carbon nanotubes using a H₂-CH₄ mixture as the carbon source. The carbon nanotubes made using this process are however damaged during the high temperature (1500° - 1600° C) processing step used and disordered graphene layers precipitate at the grain boundaries of the matrix. The nanotubes therefore do not provide an increase in mechanical strength. A method to incorporate carbon nanotubes homogeneously over the entire metal matrix at relatively low temperatures and with negligible amounts of disordered carbon, is therefore required for significant enhancement of the mechanical properties. Processes for *in-situ* growth of single wall and multiwall carbon nanotubes into metal matrices were developed by Goyal et al (Goyal, Wiegand et al. 2005; Goyal, Wiegand et al. 2007), a chemical route to a ceramic-single wall carbon nanotube composite was developed by Wang et al (Wang, Iqbal et al. 2006), and a Cu-carbon nanotube composite was developed by Li et al (Li, Misra et al. 2009).

The primary objective of this part of the thesis is to fabricate lightweight metal (iron and steel)-carbon nanotube composites with significant enhancement in mechanical properties. Many of the applications of these metal composites will have a direct bearing on everyday life. For example, the chassis and body of an automobile are made largely of commercial grade steel and related alloys. Automobile manufacturers routinely perform crash tests at high speeds to determine the integrity and mechanical properties of the structural materials used. The use of nanotube-filled metal composites will not only increase the mechanical strength substantially but it will also reduce the weight of the vehicles, thereby driving down fuel costs. The density of carbon nanotubes is between 1.20-1.30 gm/cm³, whereas most metals have densities between 2.5 and 8 gm/cm³.

Therefore, the weight of the nanotube-filled metal composites fabricated can be reduced by increasing the loading of carbon nanotubes. The work performed will specifically increase the loading of carbon nanotubes by utilizing *in-situ* growth into a porous metal matrix using chemical vapor deposition (CVD).

Steel and aluminum (to be discussed in Chapter 4) structures are also widely used in construction and aerospace industries. It is very well known that the inclusion of carbon in iron, referred to as carburization of steel, is performed to obtain hardened steel. Hardened steel using carbon is divided into three subcategories: (1) Carbon steels with less than 0.25% carbon, (2) Carbon steels with between 0.25 and 0.55% of carbon, and (3) Carbon steels containing 0.55 to 1.00 % carbon. As the degree of carbon loading is increased the metal alloy is hardened, but concomitantly it becomes brittle and therefore can fracture easily. It is important to point out that the carbon phase used to harden steel is essentially amorphous or microcrystalline. Carbon nanotubes on the other hand have a high degree of atomic scale order and bonding strength which leads to its extremely high intrinsic tensile strength. Therefore, the increase in loading of carbon nanotubes in the composites will not only increase the hardness but also enhance the tensile strength of the composite. This significant difference between carbon-hardened steel and carbon nanotube-filled steel is due to the unique nanoscale structure of carbon nanotubes.

3.2 Overview of Composites

Composites are materials that are composed of dissimilar sub-units. Among the most important composites are those in which the dispersed phase is in the form of a fiber (Huang, Zhang et al. 2003). In such composites, the fiber matrix interactions become a

dominants term in determining the mechanical properties. Design goals of fiberreinforced composites often include high strength and/or stiffness on a weight basis. These characteristics are expressed in terms of specific strength and specific modulus parameters, which correspond, respectively, to the ratio of tensile strength to specific gravity and modulus of elasticity to specific gravity. Fiber-reinforced composites with exceptionally high specific strengths and moduli have been produced that utilize lowdensity fiber and matrix materials. Metal-matrix composites (MMCs) comprise of a ductile metal which may be utilized at higher service temperatures than their base metal counterparts: furthermore, the reinforcement may improve specific stiffness, specific strength, abrasion resistance, creep resistance, thermal conductivity, and dimensional stability. Some of the advantages of these materials over polymer-matrix composites include higher operating temperatures, decreased flammability, and greater resistance to degradation by organic fluids. Therefore, composites are widely used at the leading edge of materials technology.

Advanced industrial materials require superior stiffness, chemical corrosion resistance, and electrical conductivity at low weights and within small volumes. Therefore, a composite with a novel balance of high strength, high modulus, and high thermal and electrical conductivity is required to enable novel new structures, and industrial components. Recent advances in Nanotechnology and in the synthesis of nanomaterials present novel options to create new materials with combinations of key properties. Carbon nanotubes represent a class of nanoparticles that can be deposited or infiltrated into porous metal matrices to form monolithic metal-nanotube composites with a uniformly distributed and firmly pinned nanostructured network for use in the manufacture of lightweight advanced metal structures with superior stiffness, and thermal and electrical properties.

Conventional composites show enhancement of mechanical properties but sometimes other critical properties may have to be sacrificed. Metal composites using carbon nanotubes can be a potential breakthrough technology for applications requiring high mechanical properties. They can therefore have extensive potential applications, such as in armored vehicles, barricades, airplanes and automobiles.

The carbon nanotubes may be oriented randomly within the material, but it is also possible to be oriented preferentially in the direction expected to have the highest stresses. In addition to the properties of the fibers/nanotubes and matrix materials, the properties of these composites are determined by the orientation and distribution of the nanotubes. If a volume fraction V_f of fibers/nanotubes in a region of material are all oriented in a single direction, the matrix volume fraction is then $V_m = 1 - V_f$. and the stiffness of the composite E in terms of stiffness E_f of the fiber and E_m of the matrix is:

$$\mathbf{E}_{\text{composite}} = \mathbf{V}_{\mathbf{f}} \mathbf{E}_{\mathbf{f}} + \mathbf{V}_{\mathbf{m}} \mathbf{E}_{\mathbf{m}}$$
(3.1)

This relation is referred to as the rule of mixtures which is used to predict the overall modulus in terms of the moduli of the constituent phases and their volume fractions. According to this equation, for a fixed material (fixed $E_{\rm f}$), the stiffness of the composite depends on the volume percentage of fibers or nanotubes.

3.3 Experimental Details

A detailed study of specific factors influencing the growth of carbon nanotubes in iron and stainless steel to form nanocomposites has been performed. Chemical vapor deposition was used to infiltrate metal pellets with multi walled carbon nanotubes (MWNTs). Compared with single walled carbon nanotubes (SWNTs), MWNTs are more robust, have similar mechanical properties as SWNTs and are easier to grow in large quantities. Therefore, to control the cost for industrial production as well as simplify the experimental procedure, the work performed was focused on the laboratory and small pilot scale synthesis of MWNT-metal composites.

The nanotubes were grown using chemical vapor deposition for both laboratoryscale and pilot scale processes. The small scale experiment used a 2.5 cm quartz tube reactor placed in a high temperature (up to 1100° C) three-zone microprocessor controlled furnace (Applied Systems. Inc.). A mechanical pump (General Electric) was used to pump the system down to 10^{-3} Torr, and backfill with the carrier gas, argon (Matheson, 99.999 % ultra-high purity), to atmospheric pressure before each experiment. Carbon monoxide (CO) (Matheson, 99.9 % research grade) and acetylene (Matheson, 99.6 %,) were used as carbon sources with CO used primarily to prevent formation of metal carbides. Pressed pellet matrices were produced from: Stainless Steel 430 (Alfa Aesar, APS 15 micron) powders, stainless steel 316 powder (Atlantic Equipment Engineers, 99.9%, plasma spray grade), and iron powder (Sigma Aldrich). No additional catalyst or catalyst precursor was used for steel, iron powders were dry-coated with nano-sized Fe₂O₃ catalyst precursor and infiltrated with cobalt and molybdenum catalyst precursor solutions. Uncoated, dry-coated and wet-infiltrated metal powders (after drying) were formed into pellets using a die and a Carver press.

The chemical vapor deposition apparatus used was similar to that employed to synthesize boron nanotubes described in Chapter 2 (Fig. 2.1).

3.3.1 Dry Coating Process

Dry coating of the metal powders with iron oxide precursor was carried out at the New Jersey Institute of Technology. Micron-sized iron and in particular, aluminum, and boron carbide (see Chapter 4), exclusively, alone cannot be used to grow carbon nanotube without any catalyst. However, after dry-coated with 1 wt% of nano-sized Fe₂O₃, CNTs were able to be grown and infiltrated in these particles matrices to form nanocomposites.

Dry coating using Magnetically Assisted Impacting Coating (MAIC), is a surface modification method that can improve the flowability of the host particles, as well as reduce their hydrophilicity, making them more suitable for use in other procedures. The surface modification is to alter the properties of powder (such as flowability, wettability, flavor, color, etc.) is very important to many industries (Naito, Kondo et al. 1993). Dry particle coating attaches fine materials (guest particles) onto the surface of larger core particles (host particles) by mechanical means without using any solvents, binder or even water. A schematic of the MAIC device is shown in Figure 3.1.

A weighed amount of host and guest particles with a specific ratio is placed into a processing vessel (200-ml glass bottle) (Ramlakhan, Wu et al. 2000). A measured mass of magnetic particles is also placed in the processing vessel. The magnetic particles are made of barium ferrite and coated with polyurethane to prevent contamination of the coated particles. An external magnetic field is created using a series of electromagnets surrounding the processing vessel. A fluidized bed system is assembled by the agitated magnetic particles when a magnetic field is present. Energy is then imparted from agitated magnetic particles to the host and guest particles, which causes collisions and allows coating to be achieved by impaction of the guest particles onto the host particles.



Experimental set-up of MAIC

Figure 3.1 Schematic of the MAIC process for dry coating. [Source: Ramlakhan, Wu et al. 2000]

 Fe_2O_3 was used as the guest particle to coat host particles of iron in experiments discussed in this chapter. The coated iron particles were examined with a scanning electron microscope (SEM) to study the surface morphology and particle shape after coating.

Figure 3.2 shows FE – SEM images with the same magnification of metal particles before and after it was dry coated by Fe_2O_3 . The average size of the guest particle (Fe_2O_3) was found to be less than 50 nm and the size of host particle (iron) is about 10 µm, which is about 200 times larger than the guest particle. Before coating, the host particle sample surfaces were smooth and clean. After processing in the MAIC device, small Fe_2O_3 particles are observed attached to the surface of the host particles and uniformly distributed.



Figure 3.2 SEM images of iron powder before (a) and after (b) dry-coating with nanosized Fe₂O₃.

3.3.2 Metal Powder Processing

Stainless steel powders of two different sizes, and an iron powder of 10 μ m in average size were used for laboratory scale CVD synthesis. The iron powders were wet-coated with catalyst precursors as follows: The catalyst precursors, 0.01 wt % of cobalt acetate and 0.01 wt % of molybdenum acetate, which were typically 0.0015 - 0.003 gms, with ratio of 1:1 were dissolved in 15 ml of pure ethanol. The catalyst precursor solution obtained was then sonicated for about 20 min to make sure that the precursors were completely dissolved. Steel powder (Alfa Aesar) with particle size of <10 μ m was then

soaked in the solution overnight and then dried. The dried powders with and without catalyst were pressed into cylindrical pellets under a load of 10,000 kg for about 30 seconds. Pellets made as described below were 13 mm in diameter and between 4 and 5 mm in thickness. The density of the pellets was determined from their weight and volume.

- Pure Stainless steel: Typically 2 3 grams of powder was used to make a cylindrical pellet in a Macro/Micro KBr Die (International Crystal Laboratories, 13 mm in diameter) using a Carver Press under applied load of 10 tons or 110,000 psi (Figure 3.3).
- 2) Mixed powders: Two powders were chosen out of iron and stainless steel with two different particle sizes every time to make mixed powders. Different ratios (Table 3.3) were used and the powders were soaked in acetone and mixed for 24 hours using a ball mill (3-lb capacity, Chromium grinding media) (Figure 3.4). The powders were dried and pressed to pellets using the same load (10,000 kgf) as described in step (1) above.



Figure 3.3 Carver Press and die used to fabricate pellets.

Iron (wt %)	Stainless steel 316 (wt %)	Stainless steel 430 (wt %) 0	
100%	0		
0	100%	0	
0	0	100%	
25%	75%	0	
0	25%	75%	
0	50%	50%	

 Table 3.1 Weight percentages of iron and two types of steel powders used for making metal-carbon nanotube composites.



Figure 3.4 3 lb capacity media ball mill used to mix and grind metal powders. Barrel measures 4.75" high x 4.5" diameter.

3.3.3 Carbon Nanotube Synthesis and Infiltration

In this section the laboratory and pilot scale processes for synthesis and infiltration of carbon nanotubes after pellet formation are described.

Lab-scale Process

In the lab-scale apparatus, metal composite (powder or pellets) were placed in a quartz boat in an 80-cm long, 2.5-cm diameter horizontal quartz tube reactor inside a three-zone, microprocessor-controlled high temperature furnace, which was connected to an oil bubbler at the exit end.



Figure 3.5 Schematic diagram of the laboratory-scale CVD set-up.

The quartz tube was pumped down to 10⁻³ torr, back-filled with pure argon and brought to 800 °C at a rate of 10 °C per minute, under flowing argon at 100 sccm (standard cubic centimeters per minute) at atmosphere pressure. As soon as the temperature approached 800 °C, the gas flow was switched to acetylene and CO in argon with flow rates of 6, 100 and 300 sccm at atmospheric pressure for CO, argon and acetylene, respectively. The power was shut down when deposition was complete, the system was pumped down again, back-filled with argon, and allowed to cool down to room temperature under 100 sccm of flowing argon. Pellets darkened by carbon nanotube deposition were obtained and removed for characterization.

Pilot-scale Process

In the pilot scale apparatus (Figure 3.6), the metal pellets were placed in a quartz tube 5 cm in diameter and 152 cm in length. The quartz reaction tube was positioned inside a vertical single zone microprocessor-controlled high temperature furnace located in a walk-in hood, with the bottom connected to a gas controller system and top open to the venting system of the walk-in hood. The pellets were placed next to the thermocouple in

the furnace to assure that the sample temperature is measured accurately. The quartz tube was purged by argon at 1000 sccm (standard cubic centimeter per minute) for 30 min and brought to reaction temperature within 30 min at atmosphere pressure. Carbon monoxide and acetylene were introduced into the system at a flow rate of 1000 sccm and 60 sccm,



Figure 3.6 The schematic of CVD process in a scaled up pilot scale vertical furnace.

while the carrier gas argon was kept at the same flow rate. The power was shut down after 45 - 60 min of dwelling time at the reaction temperature (typically 800°C), carbon monoxide and acetylene were turned off, while argon was kept at a flow rate of 1000

sccm as the system was cooled down to room temperature. After measuring the increase in weight, the pellets were characterized as discussed below.

Reference Samples

Reference pellets without carbon nanotubes prepared and heat-treated under exactly the same conditions and using the same weights and compositions of the starting powders, were prepared to compare mechanical measurements on the nanotube-filled composite samples. For accurate comparisons the reference pellets were pressed to approximately same bulk density as the pellets that were infiltrated with nanotubes.

3.4 Characterization of Steel and Iron Carbon Nanotube Composites

Several methods were used for characterization: field-emission scanning electron microscopy (FE-SEM) together with energy dispersive x-ray spectroscopy (EDS), Raman spectroscopy and mechanical property hardness and stress-strain measurements. Raman measurements were carried out using an Optronics LE Raman Analyzer system with 785 nm laser excitation coupled to a Leica microscope with 5 μ m and 10 μ m spot sizes. Raman spectroscopy will be used to determine the structure and disorder/defects in the nanotubes formed.

For FE-SEM, a VP-1530 Carl Zeiss LEO (Peabody, MA) field emission scanning electron microscope coupled with EDS was used with the metal composite pellets mounted on aluminum stubs using double-sided carbon tape. The experimental details on the mechanical hardness and stress-strain measurements are discussed below.

3.4.1 Scanning Electron Spectroscopy (SEM)

Composites using coated Iron

SEM imaging showed that MWNTs did not grow in a pure iron matrix because nanoscale catalytic iron particles are not present. However, with dry-coated Fe₂O₃, nanotubes were grown as evident from Figure 3.8. The total amount grown is however small since the weight increase of 0.3% is very low and hardness measurements show no change in hardness relative to a reference sample. At higher magnification [Figure 3.7 (right)] nodules can be seen on the nanotube sidewalls which may be associated with leftover catalyst particles from the tip growth process of nanotube formation. The dry-coated Fe₂O₃ nanoparticles are expected to be reduced by hydrogen from the decomposition of acetylene to either nanoscale, catalytic Fe or an iron sub-oxide.



Figure 3.7 SEM images showing CNTs in a pure iron matrix made using dry-coated iron powder. Clusters of nanotubes are indicated by the arrows. At higher magnification nodular growths are observed as discussed in the text.

Composites using pure Stainless Steel

For stainless steel 316 nanoscale elements such as Mn, Ni and Mo can function as growth catalysts for nanotube growth. SEM images in Figure 3.8 A and B show extensive and uniform growth of nanotubes. It is also evident that the nanotubes bridge and anchor the metal particles, which would improve the mechanical properties of the metal-nanotube composites. This assumption is shown to be validated by mechanical measurements discussed below. The % weight increase after the growth of carbon nanotubes is 5.87 %, which is higher than those achieved previously. The average diameter of the nanotubes is near 20 nm as shown by the higher resolution images in Figure 3.8 C and D.



Figure 3.8 (**A**) and (**B**) are low magnification SEM images of CNTs in a pure stainless steel 316 matrix. Background particles are from the matrix metal pellet. Nanotubes are uniformly distributed and all over the metal matrices. (**C**) and (**D**) are high resolution SEM images, from which the diameter of the nanotubes are mostly less than 20 nm.

Composites using mixture of coated Iron and Stainless Steel

Carbon nanotubes were also successfully grown and infiltrated into pellets made by a mixture of dry-coated iron (25 weight %) and stainless steel 430L (75 weight %) powders as shown by SEM images in Figure 3.9.





For the mixture of stainless steel 430L and iron, some metal elements other than Fe (e.g. Mn, Ni, and Mo) in the steel as well as nano-Fe₂O₃ on the iron acted as catalyst for nanotube growth. The SEM images show extensive nanotube growth and infiltration with weight increase near 6% similar to that for the pure steel sample. The average nanotube diameter of 30 nm is somewhat higher than that for the sample prepared using pure steel.

3.4.2 Energy-dispersive X-ray Spectroscopic (EDS) Analyses

EDS data for representative pure steel and mixed Fe-steel-nanotube composite samples are shown in Figure 3.10 together with the corresponding SEM images. The EDS data taken from the surfaces and crevices of the metal particles clearly show the presence of carbon with no other element showing because of the uniform coverage of the matrix with nanotubes.





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Figure 3.10 EDS data and corresponding SEM images of: (a) Composite with pure stainless steel 316 and carbon nanotubes, and (b) Composite with 25 weight % dry coated iron and 75 weight % 430L stainless steel and carbon nanotubes.

3.4.3 Raman Spectroscopy

Raman spectroscopy was used to study the nature of the nanotubes formed in the infiltrated iron and steel matrices. The Raman spectra taken from the surfaces of the following five samples are displayed in Figure 3.11:

- 3- and 4- 316: Nanotube-pure stainless steel 316 composites
- 4, 5, 6 si: Nanotube 75% steel 430L 25% dry-coated iron composites

Lines in the low frequency region below 300 cm⁻¹ due to radial breathing modes, typically observed for single wall carbon nanotubes, are not evident in the spectra shown in Figure 3.11. This indicates that only multi walled carbon nanotubes are produced in the composites. The line at 1580 cm⁻¹(G band) corresponds to the high frequency E_{2g} first-order mode, and the peak with a shoulder centered at 1354 cm⁻¹ (D band) corresponds to the disorder or defect induced mode. The presence of two components in the D band suggests a mix of disorder and defects in the nanotubes produced. The presence of defects is also reflected in the relatively strong intensity of the broad lines centered about 700 and 1000 cm⁻¹, that can be attributed to second order scattering. The broad peak

centered at 2300 cm⁻¹ particularly evident for sample 4-316 can be attributed to free carrier scattering from this novel nanocomposite comprised of a metal (iron) and a semimetallic conductor (MWNTs).





3.4.4 Mechanical Property Measurements

Rockwell hardness measurements were carried out using a load of 10 kilogram force at ambient temperature with a dwell time of 5s. An optical image of the indentation sites using a fine pixel camera attached to the micro-hardness tester was obtained before and after indentation. Three measurements were made with clear indentations, and an average value of the hardness is reported. The data for different samples are listed in Table 3.3. For the pure stainless steel 316 sample an increase in hardness by a factor of 2.6 or 157% is observed, whereas for the stainless steel 430L sample mixed with dry-coated iron, a high Rockwell B hardness number of 81.8 was obtained. The control corresponding to this sample was too soft however to be measured indicating that the increase in hardness with nanotube infiltration in this composite may be much higher than that for the stainless steel 316-nanotube composite. This is supported by the stress-strain data shown in Figure 3.12.

Weight percentage (wt%) in composition			Wt% increase after MWNTs	Rockwell B Hardness (HRB)	
Iron	Stainless steel 430L ($d = 15\mu m$)	Stainless steel 316 (d > 40µm)			
0	0	100	Control	27.2	
0	0	100	5.87	70	
0	25	75	Control	Too soft to measure	
0	25	75	5.19	Cracked	
25	75	0	Control	Too soft to measure	
25	75	0	3.98	81.8	
100	0	0	0	32	

Table 3.2 Composition and Rockwell B hardness numbers of nanotube-metal composites and control (reference) pellets.

A MTS servo-hydraulic system operated at a constant displacement rate, which gave a strain rate of about 0.00004 /s, was used to obtain stress-strain data on selected samples in collaboration with the University of Denver, Denver, Colorado. A simple compression along the cylindrical sample axis was performed to obtain the data. A flow stress and a work hardening coefficient were obtained from the stress-strain curves for

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nanotube-iron and nanotube-stainless steel composites compared with the control reference samples without nanotubes.

Compressive stress-strain curves were measured on samples containing MWNTs and compared with stress-strain curves measured for the control, reference samples. In Figure 3.12 stress-strain curves for a stainless steel 316 sample with and without nanotubes are shown indicating a large difference between the nanotube composite and control samples. The yield strength corresponding to the deviation from linearity (Figure 3.12) of the nanotube-filled composite is about 48% higher compared to that of the reference sample.



Figure 3.12 Stress versus strain curves for pure stainless steel 316-nanotube composite (red) and for a stainless steel 316 reference control sample (blue).



Figure 3.13 Stress versus strain curves for stainless steel 430L-coated iron-MWNT composite samples and control reference samples. (a) Lower three curves are for stainless steel- coated iron samples and the upper three curves are for stainless steel-coated iron MWNT composite samples. (b) Lower curve (red) for stainless steel-coated iron control sample and the upper curve (blue) is for stainless steel-coated iron – MWNT composite sample. The yield points are taken as the points (arrowed) where the curves deviate from linearity indicated by the straight lines drawn as a guides to the eye.

For pellets made from 75 wt% of stainless steel 430L and 25 wt% of dry-coated iron, three pairs of samples were chosen for compressive stress-strain measurements. The collected are shown in Figure 3.13. The upper curves in Figure 3.13 (a) displaying the plots for the composite samples are significantly higher than the lower curves for the control samples indicating a significantly and highly reproducible enhancement of the elastic moduli and yield strengths with nanotube infiltration. The intersections of the initial linear (elastic) part of the stress-strain curves and the linear work hardening part of the eye. Picking up the best sample from the nanotube-filled composite group and the control group as shown in Figure 3.13 (b) , the yield strength of nanotube-metal composite is 153% higher than the control sample. In addition, the elastic modulus is also increased by about 46%. Since all sample pellets were prepared under the same load, the bulk densities should be approximately the same and small differences in porosity between the nanotube-filled and control pellets can be ignored when considering the observed enhancement in mechanical strength with nanotube loading.

The mechanical properties of the metal-CNT composite made from 75 wt% of stainless steel 430 and 25 wt% of iron with and without nanotubes are compared with those of full density stainless steel 430 and iron taken from the literature as shown in Table 3.3.

Metal	Density (g/cm ⁻³)	Rockwell B Hardness (HRB)	Yield Strength (MPa)	Reference
Iron	7.874	<50	80-100	[Source 1]
Stainless steel 430	7.75	89	379	[Source 2]
75 wt% stainless steel 430 + 25 wt% iron	6.00	32	236	This work
75 wt% stainless steel 430 + 25 wt% iron - CNT composite	6.00	81.8	597	This work

 Table 3.3 Mechanical properties of iron, stainless steel and the mixed metal-CNT composite

[Source: 1, A.M. Howatson, P.G. Lund, and J.D. Todd, Engineering Table and Data 2, Fiber Stone Product, cited July 28, 2011; Available from:

http://www.azom.com/article.aspx?ArticleID=996#_Mechanical_Properties]

According to Equation (3.1), the mixed pellet, with the same density as stainless steel, will have lower HRB and yield strength because the properties will be dragged down by iron in the composite. In addition, the density of the pellet made from 75 wt% of stainless steel and 25 wt% of iron without nanotubes is only 77% of the full density of stainless steel, so the HRB and yield strength would be even lower than the full density mixture, which was shown to be in agreement with the data: HRB = 32 and yield strength = 236 MPa.

After carbon nanotube infiltration, the Rockwell B Hardness of the pellet was increased to 81.8 which approaches the HRB value of full density stainless steel 430, even though the density of the pellet was only 77% of the full density stainless steel. Moreover, the CVD process increased the yield strength significantly to 597 MPa, which is approximately 57% higher than the yield strength of 379 MPa of full density 430 stainless steel.

3.5 Conclusions

An *in-situ* chemical vapor deposition method coupled with a dry-coating process to deposit nano-sized catalytic particles was developed to create metal-carbon nanotube composites. Both laboratory- and pilot-scale set-ups were optimized. The results indicate that dry coating with nano-sized Fe_2O_3 provides an ideal catalyst precursor for nanotube growth in steel and iron-steel matrices.

Characterization of the samples was performed by SEM coupled with EDS, Raman spectroscopy and mechanical measurements. SEM indicated extensive nanotube growth bridging across and anchoring the metal particles, while EDS data showed only carbon on the sidewalls with no contamination from oxygen or other light elements. Raman spectroscopy indicated that the carbon nanotubes grown and infiltrated into the metal matrices are multiwalled and fairly disordered and defected. Mechanical measurements indicated enhanced hardness and compressive yield strengths relative to control specimens of similarly treated metal matrices without nanotubes. The yield strength increased 48% with 5.8 wt% of infiltrated nanotubes in a composite prepared with pure stainless steel relative to that of a control sample. However, when the composite comprised of 75 wt% of stainless steel with 25 wt% of iron dry-coated with nano-sized Fe₂O₃, the yield strength was enhanced by 153% relative to a control sample, with 5.2 weight % loading of nanotubes. In addition, Rockwell Hardness B values for a similar sample showed an increase of 157% relative to a control sample.

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

In the first half of this thesis a new solid state chemical vapor deposition (CVD) method was developed and initially optimized for the production of boron nanotubes (BNTs) in a scalable manner. In contrast to the only other method known to the best of our knowledge to produce boron nanotubes, the method developed in the present work involves only a carrier gas, argon, and solid state dissociation of a boron precursor in the presence of catalyst and a zeolite template to produce largely boron nanotubes mixed with small amounts of the corresponding fibers. A Mg-Ni catalyst system was studied and it was found that Mg and Ni act as co-catalysts in BNT synthesis. The optimum conditions for BNT growth using a small scale CVD set up were determined in this study. It was observed that nanotube growth initiates at a temperature of 900 °C and the most optimum temperature is 950 °C when synthesis is carried out using commercially available magnesium boride, MgB₂, as the boron precursor. Extensive characterization of the samples were carried out using field emission SEM to aid the process optimization. Another commercial boron precursor, $Mg(BH_4)_2$, was identified which was shown to produce thinner boron nanotubes in larger quantities with nanotube growth initiated at a temperature of 650 °C and grown optimally at 750 °C. Purification of BNTs to remove MCM-41, the zeolite template, was achieved by sonication in weak sodium hydroxide solution and remnant catalyst can be removed by an additional step of sonication in a weak acid such as HCl. Low and high resolution TEM images of samples produced from MgB₂ showed a significant hollow structure with a rolled up lattice and lattice spacings in accordance with a theoretical calculation. EELS data revealed that the composition of the nanotube is that of pure boron, without any Ni and Mg. EDS data taken in the TEM showed that the tips of the nanotubes comprised of Ni catalyst and small amounts of Mg co-catalyst. Raman spectroscopy showed two primary lines below 500 cm⁻¹ consistent with a tubular boron structure. Boron nanotubes produced from $Mg(BH_4)_2$ were found to be rather unstable in the electron beam, thus precluding characterization by high resolution SEM and TEM.

The second half of the thesis is focused on the development of a scalable one step process using conventional CVD to synthesize and initially optimize metal (iron, stainless steel and aluminum) and ceramic (boron carbide) -carbon nanotube composites. Two CVD systems, one a laboratory scale system similar to that used for boron nanotubes with a horizontal three-zone furnace, and the other, a pilot scale system with a large vertical furnace, were set up and optimized for nanotube growth within metal and ceramic matrices. Extensive characterization of the composites prepared by SEM showed uniform growth of multiwalled carbon nanotubes (MWNTs), with an average diameter of 20 nm. In pure stainless steel and iron mixed with stainless steel, and in aluminum matrices, the nanotubes grow across crevices to bridge and anchor the composite particles. Although nanotubes were grown on boron carbide powder, uniform and extensive growth on hot-pressed boron carbide matrices has not been achieved. It was also discovered that magnetic dry-coating of nano-sized Fe_2O_3 on iron, steel, aluminum and boron carbide powders in collaboration with other group provided catalytic particles for uniform nanotube growth. Analysis by Energy Dispersive x-ray Spectroscopy (EDS) in the SEM showed the presence of carbon, metal (iron or aluminum) or ceramic (boron). The presence of uniformly distributed, somewhat disordered and defected MWNTs was determined by micro-Raman spectroscopy with a fiber optic near infrared laser emitting at 785 nm.

Compressive stress-strain measurements on nanotube composites of stainless steel mixed with some iron showed a yield strength increase of 153% (relative to a similarly produced pellet without nanotubes) with 5.2 wt% of infiltrated MWNTs. Rockwell hardness increase of 157% for stainless steel infiltrated with MWNTs relative to a similarly produced pellet without nanotubes, was observed. Mechanical property measurements on aluminum- and boron carbide-nanotube composite pellets have been left for future work because of issues of making control pellets for these respectively ductile and extremely hard matrices.

The following future work is suggested for boron nanotubes:

- Optimization of a stabilized boron nanotube using Mg(BH₄)₂ followed by high resolution TEM studies
- Modeling of boron nanotube growth from MgB₂ and Mg(BH₄)₂ using density functional theory
- Scaled up boron nanotube synthesis

The following future work is suggested for metal/ceramic-nanotube composites:

- Optimized synthesis of boron carbide-nanotube composite
- Characterize mechanical properties of aluminum- and boron carbidenanotube composites
- Perform theoretical modeling of strengthening mechanism in ironnanotube composites

Future work related to boron nanotubes would be the scale up of the solid-solid reaction for developed boron nanotubes, further more precise Raman spectra, and mechanical measurements of BNTs. For carbon nanotube composites, suggested future work, related to the work presented, would be approaches to further improve the scaled up MWNTs synthesis process, the parameters for MWNTs growth within boron carbide, and use of more metal matrices and other non-metallic materials.

APPENDIX A

PRELIMINARY RESULTS ON ALUMINUM AND BORON CARBIDE NANOTUBE METAL COMPOSITES

A.1 Abstract

Besides iron and stainless steel, carbon nanotubes have also been successfully infiltrated into aluminum and boron carbide matrices in preliminary experiments to form metal and ceramic nanocomposites. A novel feature of this approach, also discussed in Chapter 3 regarding nanotube deposition in iron matrices, has been the use of dry-coating to deposit nanoscale Fe₂O₃ on the starting powders to function as the catalyst precursor for nanotube growth. Aluminum, as a light metal, is widely used in the aerospace industry, and boron carbide is an extremely hard lightweight ceramic material used in armored vehicles and related industrial applications. It was expected that the formation of aluminum- and boron carbide- nanotube composites would further improve the mechanical strength of aluminum and the deformability of boron carbide. Chemical vapor deposition (CVD) was utilized in the formation of aluminum- and boron carbidenanotube composites in a similar fashion as described in Chapter 3 for the growth of pure steel and mixed iron and steel-nanotube composites. Detailed characterization by SEM imaging combined with EDS and Raman spectroscopy for chemical analysis was carried out to help optimize and scale-up the growth process. It was found that nano-sized Fe_2O_3 , when coated onto the surface of large particles was an effective catalyst for nanotube growth since nanotubes were found in large quantities in coated aluminum and boron carbide compared to the observation of no nanotubes in pure non-coated samples.

Mechanical testing of the aluminum- and boron carbide-nanotube composites will be conducted in future studies.

A.2 Synthesis of Aluminum- and Boron Carbide- Carbon Nanotube Composites Pure aluminum powders (20 μ m in diameter) were coated with 1% by weight of nanosized Fe₂O₃ (average of 50 nm in diameter) by the dry-coating process described in Chapter 3. Pellets were made using a Carver press (see Chapter 3) under a force load of 7, 000 – 8, 000 kg, with a small amount (less than 1%) graphite added to provide lubrication so that the pellets could more easily removed from the die. This was followed by CVD infiltration with acetylene (10 sccm), CO (100 sccm) and Ar (300 sccm) at 580 °C in both laboratory scale and pilot scale CVD systems described in Chapter 3 for nanotube deposition and infiltration. Control pellets were also made with the same weight of metal powders under the same conditions but without carbon nanotubes.

Boron carbide powders were also dry-coated with 1% by weight of nano-sized Fe_2O_3 (10 nm in diameter) by the same process described in Chapter 3. Since consolidation of the coated powders by cold pressing was not possible, they were hot pressed into a pellet at ARDEC, Picatinny Arsenal. Carbon nanotube deposition was carried out by CVD with acetylene (10 sccm), CO (100 sccm) and Ar (300 sccm) at 800 °C using the pilot scale reactor only because the pellets prepared were larger than 2.5 cm in diameter. To evaluate the nanotube deposition process on boron carbide, deposition was also carried out on the powders in the pilot scale reactor.

A.3 Powder and Composite Characterization

A.3.1 Scanning Electron Spectroscopy (SEM)

Aluminum-carbon nanotube composites

Figure A.1 shows FE-SEM images of aluminum particles before and after dry coating with Fe_2O_3 . SEM images at the same resolution clearly show the difference in morphology of the particles before and after coating. The host particle surfaces are clean and smooth before coating, after the coating process, nanoscale Fe_2O_3 attach uniformly to the host particle surfaces.



Figure A.1 SEM images of aluminum powder before (left) and after coating (right) with nano-sized Fe₂O₃ (arrowed).

The sizes of the guest particles averaged 50 nm whereas the host aluminum particles are $\geq 20 \ \mu\text{m}$. In a reference experiment 99 wt% of aluminum and 1 wt% of iron powder was mixed by ball milling (see Chapter 3, Figure 3.4) followed by CVD reaction in the laboratory-scale furnace to grow nanotubes. SEM images in Figure A.2 after CVD reaction clearly show that nanotube deposition does not occur on these mixed particles. By contrast nanotube growth is clearly seen in SEM images in Figure A.3 after CVD reaction using the laboratory scale furnace on dry-coated aluminum particles. Carbon nanotubes are formed in large quantities around the dry-coated Fe_2O_3 particles with diameters around 20 nm and lengths of 1 µm. This suggests that the dry-coating process is critical to providing catalytic particles for nanotube growth.



Figure A.2 Low (left) and high (right) resolution SEM images of 99% by weight of aluminum powder ball milled with 1% of iron after CVD reaction.



Figure A.3 SEM images of dry-coated aluminum powder after CVD reaction showing nanotube growth.

The same procedure was used for growing and infiltrating carbon nanotubes in aluminum pellets prepared with dry-coated aluminum powders in the pilot-scale furnace with flow rates of: Ar (1000 sccm), CO (100 sccm) and C_2H_2 (40 sccm), and the



Figure A.4 SEM images of composite pellets of carbon nanotubes in dry-coated aluminum matrix prepared in pilot-scale CVD system. Images A to D show aligned growth of nanotubes in a crevice at different magnifications. Images E and F show another cluster of nanotubes with higher magnification. Nanotube diameters are around 20 nm. Overall, dense and uniform growth of nanotubes can be observed over the whole surface and inside crevices.

temperature of 580 °C. Representative SEM images from a sample is shown in Figure A.3 indicating extensive and uniform growth of nanotubes in the aluminum matrix. Of particular interest is the growth of aligned bundles of nanotubes in crevices bridging the aluminum particles. The diameter of the nanotubes is approximately 20 nm and the lengths are near and greater than 1µm similar to what was observed in samples made in the laboratory scale CVD system.

Boron Carbide-Carbon Nanotube Composites

For boron carbide the same dry-coating method was utilized and SEM images shown in Figure A.5 were taken from the samples before and after coating. Dry coating attaches a large number of nano-sized Fe₂O₃ particles to the particle surfaces. Figure A.6 shows SEM images after the CVD process at a flow rate of Ar (1000 sccm), CO (100 sccm) and C_2H_2 (60 sccm), and a temperature of 800 °C on the dry-coated boron carbide powders. Extensive growth of the nanotubes is observed. Unlike nanotubes grown on steel, mixed iron and steel and aluminum, some of the nanotubes grown on boron carbide show what are probably catalytic particles at the tube tips. This indicates that the nanotubes grow via a base-growth mechanism similar to that in boron nanotubes discussed in Chapter 2. From the magnified SEM image in Figure A.6(c), the nanotube diameter is larger than that seen on the metals and can be estimated as about 40 nm.



Figure A.5 SEM images of boron carbide powder before and after coating with nanosized Fe_2O_3 .




Figure A.6 SEM images of carbon nanotubes grown on boron carbide powder using pilot-scale CVD set-up. Panels (a), (b) and (c) show SEM images with different magnifications taken from the same spot. Panels (d), (e) and (f) show nanotubes from other spots in the boron carbide sample.



Figure A.7 Low (left) and high (right) resolution of SEM images taken from boron carbide pellet. From the image on the left we can see that the average distance between particles is larger than 20 μ m in the pellet.

The SEM image in Figure A.7 (left) is from a boron carbide pellet showing that the average crevices are larger than 20 μ m. The image depicted in Figure A.7 (right) shows that nanotubes are formed on the pellet but the growth is not extensive and well distributed as on the powders. One reason for this may be that the dry-coated iron oxide catalytic particles on the boron carbide particle surfaces are poisoned during the hot

pressing process. Another reason is that the boron carbide pellets produced have greater than 20 μ m pores and crevices which are not conducive for uniform and extensive infiltration as in the metal matrices.

A.3.2 Energy-dispersive X-ray spectroscopy (EDS)

EDS taken from an aluminum-nanotube composite is shown in Figure A.8. Figure A.8 (a) shows data from a crevice where aligned carbon nanotubes are formed. Signals from both carbon from the nanotubes and the aluminum background are evident in the data.



Figure A.8 EDS data taken from aluminum-nanotube composite. (a) Shows data from a crevice in the composite showing oriented or textured growth of carbon nanotubes, and (b) Shows data from another region of the composite.

Figure A.8 (b) shows data from a region where random but extensive nanotube growth had occurred. Here EDS from carbon is much stronger than from the background

aluminum matrix. Aluminum was found in Figure A.8 is from the background aluminum metal. EDS data shown in Figure A.9 are from boron carbide after dry-coating showing only boron and carbon signals. The EDS data after nanotube deposition only shows carbon because of the extensive nanotube growth covering the surface.



Figure A.9 EDS data taken from coated boron carbide powder before (a) and after (b) nanotube deposition.

A.3.3 Raman Spectroscopy

Micro-Raman spectra were obtained using a 785 nm laser focused through an optical microscope to investigate the chemical nature of the nanotubes formed. A representative Raman spectrum taken from an aluminum-nanotube composite is shown in Figure A.10.

The spectrum obtained is similar to that for the stainless steel-nanotube composites. Lines below 300 cm⁻¹ are absent indicating that the nanotubes formed are multiwalled. The disorder/defect line near 1300 cm⁻¹ has two components indicating a combination of disorder and defects in the nanotubes formed. This is reflected in the relatively high intensity of the broad peaks due to second order scattering near 500 and 1000 cm⁻¹. The increased background in the Raman spectrum is likely to be associated with the surface roughness of the composite sample.



Figure A.10 Raman spectrum of aluminum-nanotube composite using 785 nm laser excitation.

The Raman spectrum of nanotube coated boron carbide together with that for the dry-coated boron carbide powder is shown in Figure A.11. Broad amorphous scattering is observed for the coated boron carbide powder in Figure A.11 (top panel). The spectrum of multiwalled carbon nanotubes similar to that in the metal matrices superimposed on

the broad spectrum of boron carbide is evident in the spectrum shown in Figure A.11 (bottom panel).



Figure A.11: Raman spectrum of dry-coated boron carbide (top) and that nanotube coated boron carbide (bottom).

A.4 Conclusions

The catalyst particle dry coating method was successfully applied, as with iron and stainless steel powders, to produce aluminum- and boron carbide-nanotube composites. Both laboratory scale (Goyal, Wiegand et al. 2005; Goyal, Wiegand et al. 2007) and pilot scale CVD (Chapter 3) set ups were used to synthesize the aluminum-nanotube composites, whereas the pilot-scale set up was used to synthesize the boron carbide

composites. Extensive growth and infiltration was observed in the aluminum-nanotube composites. In the case of boron carbide, extensive nanotube growth was observed on the powders but limited growth was observed in hot-pressed pellets. Nanotube diameters on boron carbide particles were larger than in the metal composites and some of the nanotubes synthesized showed bulbous tips probably comprising of catalytic particles. The Raman spectra clearly showed the formation of multiwall carbon nanotubes with sizable disorder and defects. Reliable mechanical property characterization of the aluminum- and boron carbide- nanotube composites could not be obtained because optimal pellets could not be prepared.

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