EXPLOSIVE SHOCK-WAVE CONSOLIDATION OF ALUMINUM POWDER/CARBON NANOTUBE AGGREGATE MIXTURES: OPTICAL AND ELECTRON METALLOGRAPHY.

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by

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Abstract

The formation of conventional metal-matrix composites from carbon nanotubes has proven to be difficult because of their agglomeration and inability to disperse. We have explored the explosive consolidation of 150 μm aluminum powder/multiwalled carbon nanotube (MWCNT) aggregates (including multiconcentric fullerenes) at volume percentages of 2 and 5%. These consolidated mixtures formed 2-phase, monolithic systems with the MWCNT aggregate material spreading along the Al grains and forming carbon phases at the Al particle triple points. The Al powder particle (or grain) hardness increased from HRE 22 to HRE 40 for the consolidated Al while the 2-phase system hardness dropped from HRE 40 to HRE 39 and 33 respectively for 2 and 5% (volume) MWCNT aggregate additions. TEM and SEM observations illustrate a laminate-like structure of the consolidated MWCNT aggregate material, which is easily delaminated, causing intergranular (Al) failure. The Al grains exhibited a shock-induced dislocation substructure (0.5-3 μm) and recrystallized sub-grains, which increased the individual particle/grain Vickers hardness from HV 24 to HV 43.

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Chapter 1: Introduction

The scientific investigation and applied research on composite materials can date back to the 1940’s [1] with the advantages behind the development of metal matrix composites being the capability to combine phases providing a potential for tailoring material properties to meet specific and challenging requirements. Composites offer an approach for producing “designer” materials used to provide specific types of material behavior, such as their improved strength and stiffness[2], outstanding corrosion resistance[3], friction resistance[4] and wear resistance[5], high electrical and thermal conductivity[6], and high temperature mechanical behavior[7]. Metal matrix composites (MMCs) are structured engineering materials in which a reinforcement, usually a hard ceramic component, is homogenously dispersed in a ductile metal matrix in order to obtain properties that are altered compared to those of the conventional monolithic metallic matrix or alloy. Composites are recognized as high-tech materials, which are not only finding recreational applications in such sports as tennis, golf and sailing, but also constitute an increasing proportion of engineering materials in the aerospace industry for airframe and spacecraft structures[8]. More recently, the automotive and electronic industries have been working extensively with these composites to increase cost savings, enhance performance and evolve emerging applications. In order to obtain the desired properties of a metal matrix composite, certain variables should be evaluated for optimum results including the choice of the matrix, the type and degree of the reinforcement, and the composite processing method.

Currently, metal matrix composites can be classified by reinforcement component into either fibers (continuous or discontinuous), whiskers, particulates, or wires. Theses reinforcements have been placed in matrices of aluminum, magnesium, copper, titanium, nickel, nickel-based superalloys, and various alloys of iron. However the aluminum matrix alloy composites are those that have become an industry standard because they offer the advantage of lower cost when compared to most other MMCs. Aluminum based composites also offer the added benefits of excellent thermal conductivity, high shear strength, excellent abrasion resistance, high-temperature operation, and the ability to be formed and treated on conventional equipment [1].

The fabrication of metal matrix composites is focused on the combining of the reinforcements into the metallic phase, with the goal of manufacturing a new material free of defects such as pores. Conventional metal matrix composites have been manufactured through several various processing methods. These processes can generally be categorized into four general groups: solid-state processes, liquid-state processes, deposition processes and in-situ processes. Solid-state and liquid-state processes are the two most widely used and developed methods. The fabrication and mechanical properties of metal matrix composites has been published in a general review book [9, 10].

Particulate composites reinforced with micron-sized particles of various materials are perhaps the most widely utilized composites in everyday materials. Particles are typically added to enhance the matrix elastic modulus and yield strength. By scaling the particle size down to the nanometer scale, it has been shown that novel material properties can be obtained [11]. The nanocomposite materials, especially those using carbon nanotubes as reinforcement, have recently garnered great interest and tremendous growth from scientists and engineers in the research field [12]. This spurt of interest in nanocomposites stems from the unprecedented flexibility and improvements in physical properties that may be attained by using building blocks with the dimensions in the nanoscale range. It may be possible to design and create new tailored composites by using nanosize building blocks of heterogeneous dispersed phases. Thus, the materials designed from them can be multifunctional because the constituents of a nanocomposite have different structures and compositions and therefore properties. In many cases, the interesting range may be located near the transition where properties are changing from the molecular to bulk-like, a size range in which properties can be manipulated in many cases in an positive way in order to design a material for a particular application [13].

Currently much attention has been given to the possibilities of incorporating carbon nanotubes (CNTs) as the nano reinforcement in a matrix. This is not only due to the well known remarkable mechanical properties of CNTs but also in the belief that they may very well be the ultimate fiber reinforcement based on their high aspect ratio and defect-free structure. Application and innovations will take advantage of the special properties based on carbon nanotubes including electrical, mechanical, and other unique properties. The construction of composites with extraordinary properties will be related to the multifunctional materials that can be developed. Most investigators who are developing new

composite materials with nanotubes work with nanotube concentrations below 10 wt.% due to limited availability of nanotubes. With continued developments in the synthesis and production of carbon nanotubes, new possibilities in the field of composite materials based on carbon nanotubes are emerging [14].

Although much of the present research is in the area of polymer composites, efforts in metal and ceramic matrix composites are also of interest. Studies, especially in polymers, focus on dispersion, untangling, alignment, bonding, molecular distribution, and retention of nanotube properties. Nanotube composites will be used as a replacement for existing materials where properties superior to conventional composites are achieved and to create materials for applications where composites traditionally have not been used before. Therefore, one of the most important outcomes from current nanocomposite research will be knowledge that is gained about preparing materials for the development of the nanocomposites in the future. The applications for NMCs are nanowires, lightweight structures, electronic materials for avionics, wear coatings, novel magnetic and super conducting systems and new multifunctional metals [14, 15].

Bulk nano-based metal matrix composites (NMCs) have been processed using conventional powder metallurgy where matrices of aluminum, copper, magnesium and silver have been used. This approach has been used because the processing is accomplished below the melting temperature of the metals (melting temperature for Al is 660C) [15]. Powder metallurgy routes using powders and in some cases extrusion have produced an Al metal matrix composite, copper electrodes, and macroscopic composite wires (where extrusion was used). Some of these materials have taken advantage of precoating the nanotubes using electroless plating While there have been several recent examples of carbon nanotube/metal composite systems fabrication utilizing conventional powder metallurgy (P/M) routes, they have not exhibited any significant benefits in properties characteristic of traditional metal-matrix composites (MMCs) [12]. This is due in part because the carbon nanotube (CNT) material variously agglomerates, and is difficult to disperse in the metal matrix as a consequence of poor wetting, or related interfacial phenomena or integrity issues.

Investigations have shown that it is extremely difficult for the mechanical stirring method to distribute and disperse nano-scale particles uniformly in metal melts due to their large surface-to-volume

ratio and their low wettability in metal melts, which easily induce agglomeration and clustering. Recent studies show that a high-intensity ultrasonic waves with strong micro-scale transient cavitations and acoustic streaming were successfully used to introduce, distribute and disperse nanoparticles into Mg alloy melts and Al matrices, thus making the production of cast high-performance nano-sized particles reinforced matrix composite promising [16].

In the present study, explosive-shock consolidation was employed as a novel approach in creating a 2-phase monolith from mixtures of varying volume fractions of multiwalled carbon nanotube (MWCNT) aggregates with micron-size (~150 μm) aluminum powder. These 2-phase composites were of special interest because the MWCNT aggregates consisted of as-manufactured mixtures of tubes and various sizes of multi-concentric fullerenes (with diameters ranging from ~ 2 to 40 nm), and it was not clear that these aggregates could themselves be consolidated into a contiguous phase region, and whether this regime would be bonded, monolithically, to the consolidated aluminum particle regime.

Chapter 2: Background

2.1 Metal Matrix Composites

The interest in MMCs is due to their generally superior mechanical properties compared to typical alloys. Composite materials generally consist of two parts. The major part or bulk of a composite is the matrix, while the second part consists of a reinforcement material. This material is chemically different from the matrix and there exists a distinct interface between the two materials. They should also have properties that are unattainable by any of the individual constituents. What makes composite materials attractive is the possibility to be able to tailor the properties according to the needs of a specific design. MMCs are fabricated to take advantage of the properties of all the materials used in making the composite [17].

Metal matrix composites have certain advantages over the more widely used polymer matrix composites because MMCs usually exhibit higher strength, toughness, elastic modulus, higher thermal and electrical conductivity and are more stable at higher temperatures. Advantages over the un-reinforced metal include higher strength to weight ratios, increased wear resistance, and higher hardness [1]. Possible applications of MMCs include several moving automobile parts, such as pistons and connecting rods, and aerospace components [18].

Metals or alloys usually employed as matrices include aluminum, magnesium, copper, titanium, titanium aluminides, nickel, nickel aluminides, nickel-based superalloys, and various alloys of iron, but the aluminum matrix alloy composites are the only ones that have become widely available. The reinforcements in these types of composites are divided into five categories: fibers (continuous or discontinuous), whiskers, particles and wires. Most of these are ceramics (Al_2O_3, SiC) and graphite (carbon fibers) [1].The potential applications for these materials can be easily recognized by the significant increase in properties (table 2.1). These properties include high modulus and strength, high strength to weight ratios, higher stiffness-to-density ratios and wear resistance. This investigation will deal with Al based MMCs which are known for their low density, wide alloy range, heat treat capabilities, and processing flexibility. MMC composites reinforcements, manufacturing techniques, and mechanical properties have been recently reviewed [9, 10].

Table 2.1: Comparison between properties of a conventional Al alloy and a MMC with the same Al alloy as the matrix [19].

Material	Tensile Strength (MPa)	Abrasive Resistance (Volume loss, mm^3)	Wear Resistance (Volume loss, mm^3)
A356 – T6	228	0.575	0.18
A359/SiC/20p –T6	340	0.202	0.023

2.1.1 Literature Review

It was mentioned in the introduction that there are certain advantages of MMCs over the monolith, among them is enhanced strength. The increased strength noted in the composites is a result of microstructural differences brought about by the introduction of reinforcement. Lloyd and Chawla have listed the possible strengthening mechanisms suggested by various researchers. They include Orowan looping/strengthening, grain and substructure strengthening, quench strengthening, as well as work hardening [20, 21]. Dai et al. and Sarkar have reported that in a more general sense, there are two divisions of strengthening: direct (load transfer) and indirect (matrix strengthening) [22, 23]. Those discussed by Lloyd and Chawla are considered indirect strengthening mechanisms whereas load transfer is considered direct. Sarkar states that the distinction between transfer and matrix strengthening is that transfer (direct) theories consider shape and volume fraction of particle reinforcement and matrix strengthening considers particle size and volume fraction. A combination of all this factors usually contributes to the strengthening of the composite [23].

It is widely accepted that a major strengthening mechanism in metals is due to an increase in dislocation density. Strength can be correlated to the ease or difficulty of dislocation movement. As dislocations meet effective barriers, which hinders their motion, strength is increased. Countless investigations have demonstrated a correlation between strength of a material and dislocation density. Likewise, strengthening through a reduction in grain and subgrain or cell size has also been demonstrated. This concept of strengthening by increasing dislocation density, reducing grain and cell size applies to MMCs as well and has been studied by many scientists. Ma and Tjong have stated that a reduction in size of the particulate reinforcement increases the strength of the composite possibly related to the smaller spacing between particles for a given volume fraction [24]. A good correlation between microstructural changes (increasing dislocation density and reduction of subgrain size) in the matrix and

the changes in yield stress of MMCs has been observed by Arsenault et al. in Al/Sic composites produced by powder metallurgy process. The data obtained indicates the dislocation density increases with an increase in volume fraction, and the density decreases with particle size [25].

Refinement of grains in MMCs has not been as critical to strengthening of MMCs as the introduction of dislocations to the matrix. Arsenault et al. have shown the effect of particle size and volume fraction, dislocation density and cell size in the matrix of a 6061 aluminum alloy reinforced with SiC particles [25]. It was reported that the dislocation density increased with volume fraction while cell size decreased. Likewise, when only particle size was compared, dislocation density decreased with particle size while cell size increased with an increase in particle size. In addition, it was seen that the yield stress of the MMCs increased with particle volume fraction and decreased with particle size. These results were expected since it is known that the highest strengths are obtained with a fine particle size and an optimum particle spacing for a given volume fraction. Another indirect strengthening mechanism in composites, related to dislocation caused by elastic modulus mismatch between the matrix and the particle, is the work hardening mechanism. These dislocations are formed to allow deformation of the material in the presence of geometrical constraints such as brittle particles in a ductile matrix. Such dislocations provide compatibility so that voids or overlapping does not occur in the specimens under load. Taya et al. have reported a similar mechanism which they refer to as back stress that results from particles resisting plastic flow of the matrix [26].

According to Taya et al., the two main strengthening mechanisms in MMCs are: (1) the CTE effect which is the generation or punching of dislocations in the matrix due to a mismatch in the coefficients of thermal expansion (CTE) between the matrix and reinforcement material, and (2) the back stress developed as a result of the reinforcement material resisting the plastic flow of the matrix. These two mechanisms are now accepted as the main strengthening mechanisms and the microstructural evolution between matrix and reinforcement has been reported by many authors. It was found that larger changes in the temperature caused larger punching distances. This idea is put into practice by the strengthening of MMCs through the quenching and subsequent punching of dislocations due to the differences in CTE values [27].

Quench hardening is related to the increased dislocation density, but, in this case, caused by the difference in CTEs, which cause internal stresses that are generated near the particle/matrix interface with temperature change. If these stresses are sufficiently high, dislocations are produced [28].An explanation is that during cooling the matrix contracts more than the reinforcement. As these thermal stresses exceed matrix flow stress, mobile dislocations in the microplastic zone, around the renforcement, move away from the particle/matrix interface. A conclusion reached is that the extra

dislocations n the material were generated by the presence of reinforcements and that the increased strength was brought about by increased dislocation density as well as other factors such as those previously mentioned [25].

MMCs offer significant improvements in mechanical properties over their monolithic counterparts. These improvements are highly dependent on (a) the ability to transfer stresses from the matrix to the reinforcing materials, (b) the volume fraction, size, and distribution of reinforcements, (c) enhanced dislocation density and interactions, (d) precipitation in the matrix and at interfaces, and (e) the overall strengthening of each individual component of the composite [29].The need for lightweight and high strength structural materials is always high in the aerospace, automotive, and similar industries. This tremendous demand for such materials has prompted continuous studies to give a better understanding of the mechanical properties of different and new types of MMCs .

2.1.2 Processing of MMCs.

A multitude of fabrication techniques have been developed for metal matrix composites. These many processes can be classified as solid-state, liquid-state and deposition processes. Powder metallurgy *(*P/M) is the most widespread method in solid-state processes. P/M is typically used for high melting point matrices because the process avoids segregation effects and brittle reaction product formation which frequently occurs in liquid state processes [9].

Liquid phase methods include squeeze casting and squeeze infiltration, spray deposition, compocasting, and in-situ composites. In liquid-state processes, infiltration processes are where the reinforcements form a preform which is infiltrated by the matrix melt. Other liquid-state processes such as stir-casting use a dispersion process where the reinforcements are particles stirred into the liquid alloy. Process variables and matrices are monitored to avoid negative reaction with particles. Commercially, liquid phase processing has demonstrated the more attractive economic results.

Deposition processes spray droplets of molten metal together with the reinforcing phase which are then collected on a substrate where the composite solidification is completed. This technique is currently limited to use with discontinuous reinforcements and the final product must be obtained by extrusion, rolling or forging. Very fine grain sizes and low segregation in the matrix microstructure are the main advantages; however the limited usage coupled by high costs decreases the effectiveness of this method.

In order to achieve the best mechanical properties, the reinforcements and the matrix are required to be physically and chemically compatible. However during the fabrication process, the reinforcement and the matrix often react, and create some potentially detrimental effect such as: 1) chemical reaction at

reinforcement and matrix interface; 2) dissolution of the reinforcement in the matrix; 3) constituting segregation and/or precipitation of the matrix in the interface; 4) thermal induced defaults (residual stresses, porosities). At elevated fabrication temperatures these interactions occur more readily. So it may be best to predetermine an arrangement of reinforcement and matrix pairs, which can be based on experimental method.

2.1.3 New type of composites with CNTs

There is much interest in producing metal matrix nanocomposites that incorporate nanoparticles and nanotubes for structural applications, as these materials exhibit even greater improvements in their physical, mechanical and tribological properties as compared to composites with micron-sized reinforcements. The discovery of carbon nanotubes has provided us with a material that exhibits exceptional material properties that are a consequence of their structural perfection and strong carbon–carbon bonds. These are promising candidates as reinforcements for composites because of their attractive mechanical properties where the stiffness, strength and resilience exceed any current materials. Carbon nanotubes are theoretically one of the strongest and stiffest materials with a calculated tensile strength of ~200 giga Pascal and modulus of more than 1-4 tera Pascal for a single walled nanotube (SWNT) [30]. If the mechanical properties of SWNT could be effectively incorporated into a matrix, composites with lightweight, exceptional strength and stiffness can be achieved.

In the recent decade, various fabrication attempts and much growth have been made by researchers wishing to take advantage of the exceptional mechanical properties of CNT reinforced composite materials. Polymers, ceramics and metals have been tried out as matrices [11, 31]. The primary success has been in polymers reinforced with carbon nanotubes. Within this success lies the motivation to further investigate the potential use of the exceptional properties of CNTs in metal matrix composites which will incorporate high strength to weight ratio characteristics for engineered structural applications. Metal composites reinforced with CNTs could find wide applications in aerospace, automotive and sports industry replacing conventional materials.

CARBON NANOTUBES

Transparent diamond and black graphite are the two basic forms in which carbon exists as a solid Figure 2.1. Diamond exhibits a very stable configuration characterized by each carbon atom having four nearest neighbors arranged in a tetrahedron. Graphite carbon has atoms which are arranged in a hexagonal array of graphene layers where each carbon atom has three nearest neighbors (Fig. 2.1). The bonding in the plane of layers is then very strong while the bonding between layers is relatively weak due to van der Waals forces. In 1985 [32] a new type of carbon form, the fullerenes, were discovered by Kroto et al. These fullerenes are cage-like structures of carbon atoms comprising pentagonal and hexagonal faces in the surface of the cage. The C_{60} molecule was the first cage-like structure discovered and consists of 60 carbon atoms. Similar cage-like forms with different number of atoms have been observed (Fig.2.2).

Afterwards in 1991, S.Iijima [34] discovered the carbon nanotubes. Carbon nanotubes can be viewed as long and slender fullerenes where the walls of the tubes are sheets of graphene layers of hexagonal structure rolled into cylinders (Fig. 2.2). Carbon nanotubes can be divided into two main types that can have high structural perfection: single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). The SWNT is defined by its honeycomb lattice structure representing a layer of rolled up graphene held together by strong sp^2 bonds. Multi-wall nanotubes consist of an array of single-wall nanotubes that are concentrically nested.

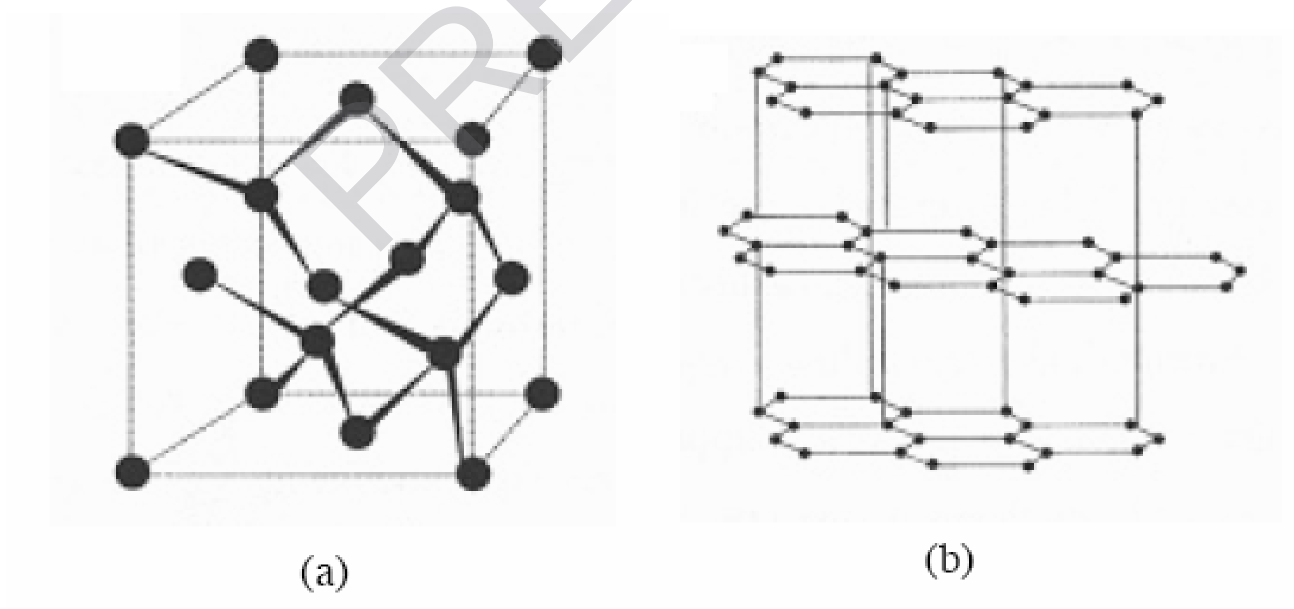
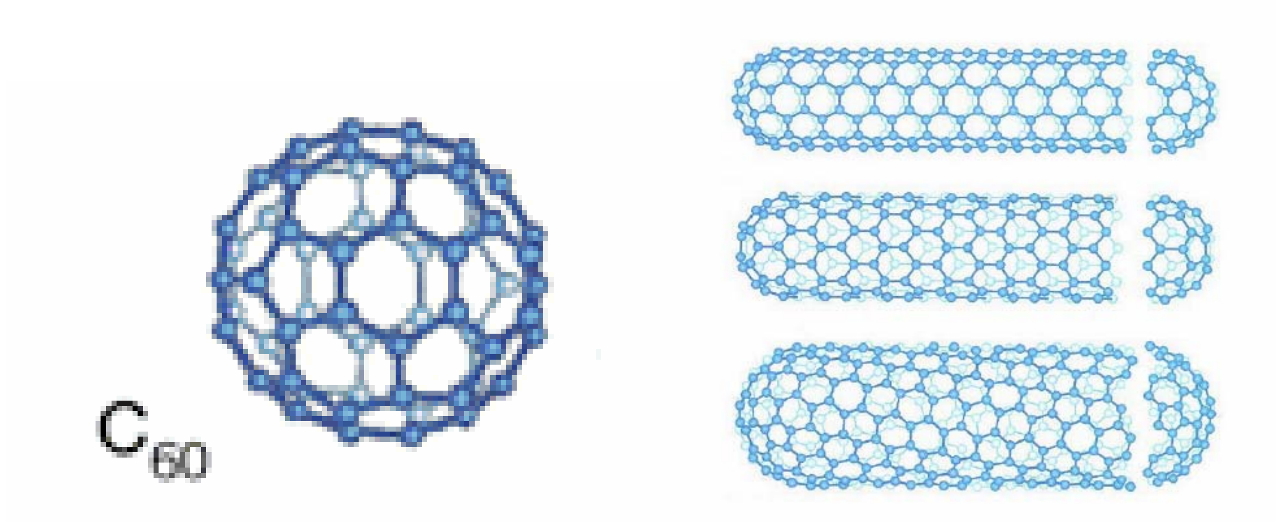


Figure 2.1 Structure of (a) diamond and (b) graphite [33].



(a) **(b)**

Figure 2.2: Structure of (a) C-60 fullerene (b) single-walled carbon nanotubes [33].

2.2.1 Properties of carbon nanotubes

The remarkable mechanical properties of carbon nanotubes, such as structural perfection, small size, low density, high stiffness and high strength along with the superior physical properties, such as thermal conductivity about twice as high as diamond and the electric current carrying capacity 1000 times higher than copper wires. [35] These exceptional properties of carbon nanotubes make them ideal as novel reinforcement fibers for composite materials. As a result of their unique atomic structure, carbon nanotubes exhibit remarkable electronic, thermal, magnetic and field emitting properties. In vacuum, carbon nanotubes are thermally stable up to 2800 °C [36]. However it is the mechanical strength and low mass density properties of nanotubes that are of interest to the author. They share many of the strength properties of their molecular cousin, the diamond. This stiffness in material, which is measured in terms of its Young's modulus (the rate of change of stress with applied strain) coupled with the lightness of carbon nanotubes, gives them great potential in applications such as aerospace. Many researchers have reported mechanical properties of carbon nanotubes which are unparalleled by any previously existing materials. Below is a summary of these exceptional properties compared with those for other structural materials.

Table 2.2: Properties of CNTs compared to other structural materials [30]

Material	Elastic modulus (GPa)	Yield strength (GPa)	Density (g/cm3)	Strain (%)
SWCNT	1210	4	65.0	1.4
MWCNT	1260	1.5	2.7	1.8
IM-7 / 977-3 (graphite fiber)	152	1.2	2.1	1.6
Titanium	103	15	0.9	4.5
Aluminum (2024)	69	16	0.5	2.7
Steel (1050)	207	9	0.8	7.8

2.2.2 Advantages and challenges of using CNTs in MMCs

Incorporation of carbon nanotubes into a metal matrix could potentially provide structural materials of lightweight composites with exceptionally increased Young's modulus and strength. This indicates that this new type of materials could meet higher requirements in mechanical properties demanded for some applications. Because of their high aspect ratio, high modulus, and strength, nanotubes are promising reinforcement in metal matrix composites. On the other hand, by retaining the same level of mechanical properties, less material would be required; for instance, the walls of parts could be thinner. This could consequently lead to energy saving.

Although it has been the no defect description of SWCNTs that has probably sparked an interest in developing NMCs, the high aspect ratio of nanotubes promises an increase in the load transfer. The concentric nanotubes that compose the multi-walled carbon nanotubes are held together by secondary, van der Waals forces. It is the sliding properties of multi-walled carbon nanotubes that may aid them as ideal elements that can be exploited in reinforcement composites [37].

Also simulations show that carbon nanotubes are remarkably resilient, sustaining extreme strain with no sign of brittleness or plasticity [38]. The tremendous resilience of CNT in sustaining bending to large angles and restraightening without damage is distinctively different from the plastic deformation of metals and brittle fracture of carbon fibers at much lower strain when subjected to the same type of deformation. When exposed to great axial compressive forces, nanotubes have been seen in electron

microscope images to form bends, twists, kinks, and finally buckle then to relax elastically when the distorting forces are removed [39]. These tubes however do not break under the compressive loads. This distinct behavior is illustrated in Figure 2.3. When tested under great axial compression, it has been found that nanotubes behave consistent with the Euler limit. The Euler limit specifies the point at which a straight tube will buckle. Since the deformation in a nanotube is elastic, the tube returns to its original shape when the load is removed [40].

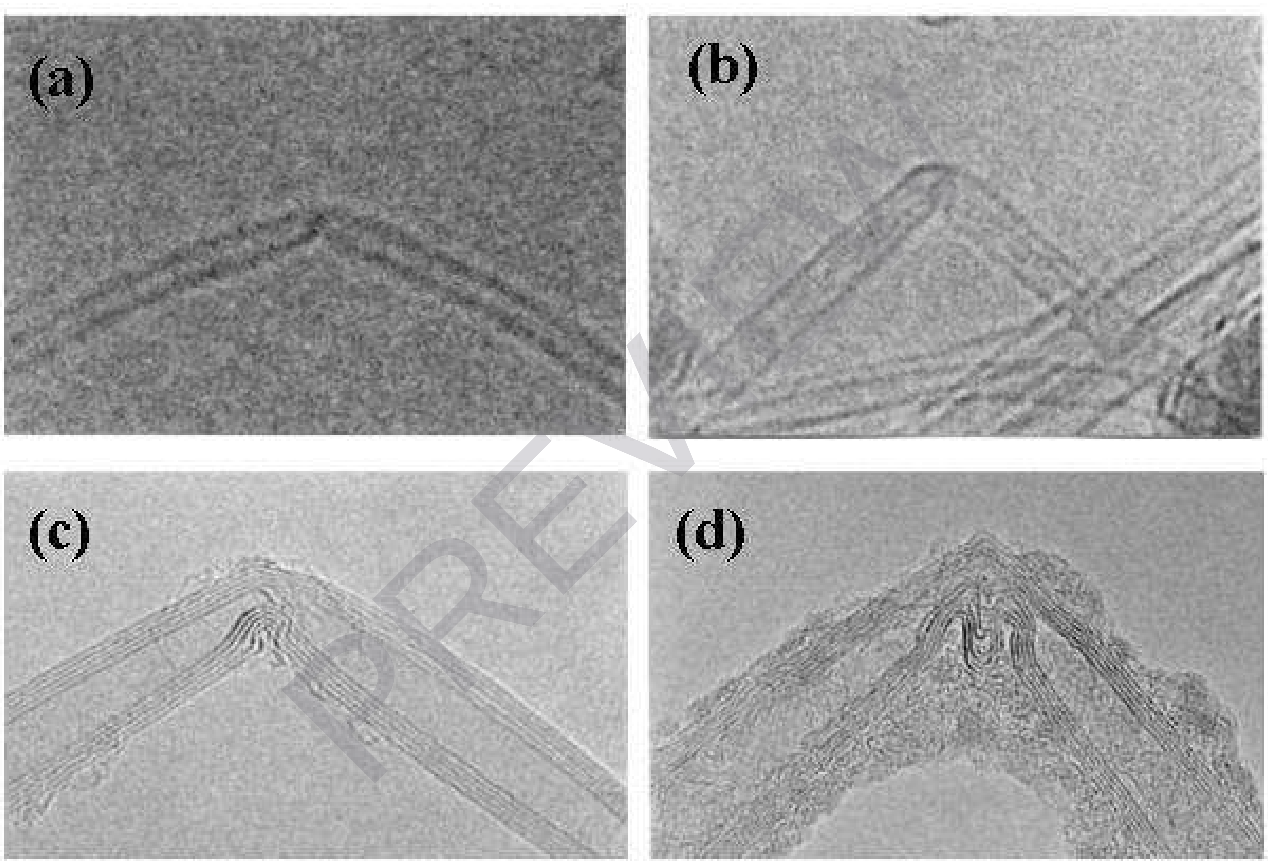


Figure 2.3: The demonstrated bending of CNTs [40]

2.2.3 Technical Challenges of Nanotube Based Nanocomposites

Research findings in nanotube-based composites have indicated that there is potential for carbon nanotubes as a reinforcement in composite applications. These finding have also identified some critical challenges that must be overcome before their full potential is realized. In order to take full advantages