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Review on Carbon Nanotube Reinforced Composites and their Applications

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Abstract: *Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the different fields of science and medicine. Nanotechnology is a multidisciplinary branch on engineering involving study of materials at a length scale of 1-100nm. It involves synthesis, imaging, modeling and manipulating materials at this length scale. The nanomaterial field includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions. Carbon nanotubes are one of the most researched nanomaterials because of their excellent mechanical, electrical and thermal properties.*

It consists of carbon atoms covalently bonded in a cylindrical crystalline lattice. Carbon nanotubes can be single-walled or multi-walled based on its diameter. CNTs are well-suited for virtually any application requiring high strength, durability, electrical conductivity, thermal conductivity and lightweight properties compared to conventional materials.

Carbon nanotube enabled nanocomposites have received much attention as a highly attractive alternative to conventional composite materials due to their properties and range of applications.

In this review paper, the different types of materials used for making of carbon nanotubes along with their process of manufacturing have been collected from various research papers and a brief review is presented. The various applications of carbon nanotubes are also mentioned in this paper.

Keywords: *reinforcements, Aluminium matrix, ceramic matrix, polymer matrix, powder metallurgy, chemical vapour deposition.*

I. INTRODUCTION

A composite is a material which is made from two or more materials and has properties much superior compared to the individual material. Nano-composites are prepared by reinforcing a nano-particle in a base matrix. The reinforced particles are called filler particles. Carbon Nanotubes (CNT) are generally rolled up graphene sheets. They may be single-walled CNT or multi-walled CNT. CNTs are formed by the sp^2 bond between carbon atoms.

Their properties like high strength, low weight and also being superior conductors of heat and electricity has drawn interest over the years. This was first discovered by Sumio Iijima[16] who published a ground breaking paper “Helical microtubules of graphitic carbon” reporting the discovery of multi-walled CNT.

Since then successful attempts have been made in fabricating CNT reinforced composites. A lot of research has been done in processing CNT reinforced metal matrix composites. Very less composites of CNT-ceramic reinforcements have been processed till now due to the limited use of ceramics for engineering applications. Polymers are easy to fabricate as they do not require high temperatures.

These composites are now easily available and are used extensively for engineering applications. A lot of research is also being done in this field. There are a few challenges faced in the fabrication of CNT reinforced composites. One of the major challenges of processing CNT polymer composites is controlling the structure of CNTs. They are not consistent in their properties and aspect ratio. CNTs are easily agglomerated and to control their orientation is difficult. It is difficult to break the agglomerated CNT's for dispersion. The common problem faced during processing of CNT metal matrix and polymer matrix is the uniform dispersion of CNT's.

This will result in the poor mechanical properties of the resultant composites. Researchers started the use of functional groups for better interaction of CNTs and polymer molecules. Achieving interfacial bond between CNT and the base metal is also an important factor.

CNT-metal matrix composites which require a certain amount of heat and elevated temperatures may damage the CNTs. Densification of the composites is also a challenge faced during the fabrication of CNTs. These composites are successfully being used in Automotive sector and aerospace fields extensively. There are a few bio medical applications related to the CNT reinforced composites.

II. CARBON NANOTUBE REINFORCED METAL MATRIX COMPOSITES

The numerous applications of Aluminium metal in the field of science and Engineering has fuelled researchers to constantly improve its properties. A promising way seemed to be reinforcing Aluminium with a nano material. Reinforcing other materials with Aluminium as base metal offers a promising enhancement of its properties. There has been a lot of research in reinforcing CNTs into Aluminium metal matrix. This proved to be a great leap in improving the properties of Aluminium. Aluminium is extensively used in the field of Aerospace and Automobile sector. It's light weight property when combined with CNT will improve its strength and hardness.

The reinforcement of CNT into Aluminium matrix offers a great enhancement to the original properties of the metal. CNTs triggered an interest among researchers because of the high ratio of strength to weight of CNTs. CNT reinforced Al matrix can be prepared by various methods which include powder metallurgy, melting and solidification, thermal spray, Electrochemical and various other blending methods. Even though researchers have been successful in fabricating CNT reinforced metal matrix, they still face few challenges. It is a great deal to achieve homogeneous dispersion of CNT within the metal matrix. Sometimes the composites show insufficient bonding at the interface of CNT and metal. Of these the major challenge being the difficulty in aligning the CNTs within the metal matrix. Various methods used in the processing of CNT reinforced aluminium metal matrix composites are discussed below.

A. Ball Milling Method

It is performed using a planetary ball mill. The metal powder along with CNT and some heavy balls (made of steel) are filled into the mixing jars. The mixing jars rotate around their own axis. The CNTs get fabricated into the metal matrix by the impact energy sometimes lead to strong chemical reactions due to the high mechanical energy induced to it.

V Balasubramanian[1] et al have prepared CNT-Al composite using Multi-wall CNT of 2 vol%. They observed an enhancement in the mechanical properties when the milling time was reduced from 6 hours to 3 hours and carrying out annealing at 500 C for 10 hours. They observed an enhancement of tensile strength by 21%. Extrusion was also found to promote the direction of alignment of the CNTs within the metal matrix. In this process the nano-structure of the metal was retained compared with the un-milled Al.

Esawai[2] et al of the balls. This method generally produces a homogeneous distribution of reinforcement phase into the matrix. This process can

have processed CNT and pure Al by planetary ball milling and subsequent extrusion process. Their results show a decrease in the mechanical properties compared to un-reinforced Al. This is because of agglomeration of CNTs. There was only a marginal improvement in the mechanical properties but beyond 5 wt% there was agglomeration of CNTs within the metal matrix.

B. Spark Plasma Sintering (SPS) Method

In this method a Graphite die is filled with a powder material. An uni-axial pressure is applied via two graphite punches. Then the sample is heated by pulsed electric DC. This process is conducted under vacuum or inert gas atmosphere. This is generally employed for processing CNT-Al composites. In this process there will be formation of Al₄C₃ which can be controlled by the quantity of CNT.

Zhang[3] et al has processed a sample of CNT (multi-walled)-Al composite by ball milling and subsequent SPS. Their results depict an ideal amount of CNT to be around 0.5 vol%. The results of Young's modulus (YS) and Ultimate tensile strength (UTS) show an increment from pure alloy. These values decreased as the amount of CNT increased beyond 0.5 vol%. This may be attributed to the non-homogeneous dispersion of CNT within the Al matrix.

C. Thermal Spraying Method

This process is employed for the deposition of CNT within finely prepared metal matrix substrate in the form of spray deposit with the help of heat. Heat is generated using a spraying gun.

Laha[9] et al has prepared CNT-Al composite by plasma spraying process. The CNT was ball milled to provide homogeneous mixing. Then the CNT powder was sprayed over the metal matrix. The CNTs were successfully retained in the composite. His results showed that the practical density of the composite was higher than the theoretical density. The hardness of the composite also increased with the CNT content compared with Al.

Keshri[13] et al again prepared the CNT-Al composite by spraying 1.5wt% CNT on Al₂O₃ at room temperature and few elevated temperatures. They showed that the fracture toughness increased by 24%. Wear resistance improved by 12% when the spraying was done at room temperature.

D. Powder Metallurgy Method

In powder metallurgy, the metal powder is mixed with the CNT and compressed to form the finished product. It is then heated below the melting temperature of the metal and this process is termed as Sintering.

Elsayd[11] et al have processed a CNT-Al composite using powder metallurgy. The Al powder and CNTs were allowed to mix well and then compacted at 560 MPa using a single acting uni-axial hydraulic press. Then the sample was sintered at 600 C for 3 hours in vacuum. Wet-mixing allowed a homogeneous distribution of CNT within the matrix. They observed no solid state reaction between CNT and Al after sintering. Both the hardness and compressive strength increased compared to the un-reinforced Al. There was an increase of co-efficient of friction by 26% of the composite compared to un-reinforced Al.

E. H. High Pressure die Casting (HPDC) and Cyclic Extrusion (CE)

This process involves injection of molten metal at high speed and high pressure. Cyclic extrusion involves ramming the composite for a definite number of times. Fleischer[12] et al. have summarised the tensile properties of un-reinforced Al and reinforced Al. They confirmed that HPDC is the most efficient way of CNT injection into molten metal. Their results show an increased YS and UTS compared to pure Al. CNTs dispersion within the matrix depended on various factors such as die temperature, melt temperature, gate form and plunger velocity. Turbulent flow in the die increases the efficiency of CNT dispersion. There was no relation as such established between the number of extrusions and mechanical properties. A minimum of 10 cycles was required for a perfect nano and micro level dispersion of CNT.

F. Rheocasting and Squeeze Casting

In this process the base metal is turned into molten state and then the filler metal is added to the molten metal. This mixture is further squeezed for solidification. Elshalakany[10] et al have prepared a composite using an Al alloy (A356) and MW CNT. The alloy was first melted at 660 C in a graphite crucible. Then the CNTs were added into the molten alloy. The mixture was passed into a pre-heated low carbon steel mould and immediately pressed for solidification. The ideal amount of CNTs from their results was found to be 1.5 wt% CNT. There was a uniform distribution of CNTs within the alloy matrix and there was agglomeration of CNT to be found. Additionally, there was an increase in the grain size. As a result there was a significant improvement in the YS and UTS of the casting.

G. High Pressure Torsion Method

In this process high torsion is used to process the composite and this process needs no subsequent heat treatment. This process creates severe plastic deformation which induces heavy strain in the materials. This helps in producing a refined grain structure. Tokunaga[4] et al have used Aluminium powder of diameter 75 μm and single-walled CNT for processing their composite using high pressure torsion. This process was carried out at room temperature and a pressure of 2.5 GPa was used. They were successful in achieving 98% of the theoretical density for their composite. Since there was no need for sintering, they could prevent the formation of Al_4C_3 . They have achieved tensile strength of more than 200 MPa with reasonable ductility. They also reported a decrease in the grain size which was due to the obstruction of Alumina to the dislocation motion.

III. CARBON NANOTUBE REINFORCED POLYMER MATRIX

The high intrinsic conductivity of CNT has triggered researchers to process high conductivity polymer composites by reinforcing with CNTs. A polymer composite is a multi-phase material where one phase has one, two or three dimensions in different polymer matrices. They are known to have high mechanical strength, stiffness and resistance to corrosion. One of the amazing property of polymers is they are light weight. CNT reinforced polymer matrix can be fabricated at low temperatures or even at room temperature. This is considered to be a major advantage compared to the fabrication of CNT-metal matrix composites which require relatively higher temperatures. The challenges faced during the fabrication of CNT-polymer matrix is the agglomeration of the CNT. We have to break the van der Waals forces among the molecules. Besides this the uniform dispersion of CNT within the polymer is also a concern. Various methods of processing CNTs reinforced polymers are:

A. Stereolithography Method

In this process the composite is prepared by printing each layer. This process uses a laser beam. When the laser beam strikes the liquid photopolymer it hardens. A recoater blade moves all over the photopolymer and recoates the second layer. This continues till all the layers are filled. Then the printed object is raised and the liquid photopolymer is drained.

Sandoval[5] et al have prepared CNT-polymer composite using this process. They used MWCNT with epoxy polymer. They prepared 0.5 wt% CNT-polymer composite. The use of MWCNT resulted in remarkable increase in UTS, fracture strength and hardness. Similarly Zhang[6] et al have performed the above process using Acrylic ester photopolymer and MWCNT's. The resultant composite was a radar absorbing material.

B. Solution Processing Method

This is the most common method of fabricating CNT-polymer composites. This process involves mixing of CNT in a suitable solvent. This is then mixed with the polymer. The mixing of CNT with a solvent helps in uniform dispersion of CNTs within the polymer. Thermoplastics and thermoset plastics can be prepared using this method. The mixing of CNTs within the polymer is done by magnetic stirring, shear mixing or ultrasonication. The removal of the solvent after the composite is formed is a drawback of this process.

C. Melt Processing Method

This process involves melting the polymer to form viscous fluid and then adding the CNT with high shear and elongational force to help break the agglomeration of CNT and hence provide a uniform dispersion. This process is generally carried out using a twin-screw. Li Qui[7] et al have prepared polyamide-MWCNT composite using this process. They prepared the composite using a twin-screw extruder.

The temperature was maintained around 260 C. The rotational speed of the twin screw was 45 rpm. The composite under study had 1 wt% of CNT. They found that the dispersion of CNT within the polymer was very low. Amine functionalization has improved the dispersion of CNTs. The nano-hardness and elastic modulus of amine modified CNT had no change.

D. In-situ Polymerization Method

Again this technique can be used for both thermoset and thermoplastic materials. In this process the CNT are dispersed in the monomer and then the reinforced monomer is polymerized. Polymerization is initiated by an increase in temperature or by adding a chemical solvent or by adding another monomer. This process is preferred to melt processing when the CNT is unstable to high temperatures.

E. Electro Spinning Method

This process favours the control of orientation of CNT's. This process uses a high voltage current which is supplied to the polymeric solution. Charge is induced on the layer. Mutual charge repulsion lead to development of force opposite to the surface tension. A jet of polymer solution is drawn with the help of current.

IV. CARBON NANOTUBE REINFORCED CERAMIC MATRIX COMPOSITES

CNT-ceramic composites are attractive due to their high strength and stiffness. Their brittle nature of ceramics does not find vast applications.

Due to their amorphous nature, they do not have the ability to obstruct the crack propagation. Other properties like thermal shock resistance, hardness and insulation seem useful for few applications in gas turbines. CNT's have been successfully reinforced into silica, Alumina and others. These composites are fabricated using the techniques which are similar to the ones used for polymer composites.

A. Chemical Vapour Deposition

Thermal decomposition of hydrocarbon takes place in presence of a metal catalyst. Metals such as Co, Fe and Ni are used as metal catalyst for CNT growth. Then the ceramic material is used as buffer layer and enhance their catalytic properties in CNT growth. The reinforcement formed in this method is found to be highly dense. Xia[8] et al have prepared CNT-ceramic composite using MWCNT and alumina. They used Co and Ni as catalyst. They found that the composite was able to deflect crack at CNT-alumina interface. The CNT dispersion was found to be of the highest order.

B. Powder Processing Method

Powder processing is carried out by mixing CNT and ceramic powder in a liquid solution. Then the mixing is followed by ultrasonication or ball milling and finally densified by hot pressing. Alumina, silicon nitride, borosilicate glass have been processed with CNT using this technique.

V. APPLICATIONS

- 1) *Automotive Industry:* The commercialization of polymer nanocomposites started in the year 1991 when Toyota Motor Co. first introduced nylon-6/clay nanocomposites in the market to produce timing belt covers as a part of the engine for their Camry cars. Fuel lines in automobiles are made of nano clay carbon nanotubes in fuel pumps, fuel filter housing and fuel filler pockets. CNT-polymer based composites are finding applications in manufacturing tyres of high performance and grip and subsequently improve the overall efficiency of the vehicle. The thermal properties of MWCNT are used as coolant in radiators of automobiles. S.Chougule[15] et al has performed an experimental study to show the heat transfer enhancement using MWCNT and water with varying composition. He showed that there was an increase in the thermal performance of nanocoolant over water. He also established that the thermal efficiency of the coolant increased with the increase in the concentration of CNT. This is due to the enhanced thermal property of CNTs.
- 2) *Aerospace Engineering:* Large industrial components such as aircraft wings are often made of CNT composites. NASA computer modelling analysis has shown that composites using carbon nanotube reinforcements could lead to a 30% reduction in the total mass of a launch vehicle. They are also testing the tensile properties of a CNT composite tank over that of conventional carbon fiber epoxy composites. Balasubramanian[14] et al have shown the ideal composition and ratio of the composite material for use in shielding of electrical circuits of space vehicles from radiations of outer space. CNT's can also be used for satellites and spacecrafts for reducing weight. CNT can be used as propellant for chemical propulsion systems. CNT polymer matrix composite being chemically stable is fire resistance. This property finds its application in aircraft body, housing of many components, crew suit, heat shrinkage tubing, cockpit and many. This property of the nanocomposite is also viewed as a disadvantage. This cannot be used in components which work on thermal signals.
- 3) *Biomedical Application:* CNT's have recently gained substantial interest for their potential applications in tissue engineering due to their large ratio of surface area to volume and unique microstructure. The subcutaneous tissue reactions and bone tissue reactions were evaluated for the alumina ceramic and CNT-alumina composite. After 4 weeks, thin fibrous capsules attached to alumina ceramic had been formed and the initial inflammatory reaction had disappeared.

VI. CONCLUSION

I have reviewed and summarised the various processing methods and applications of CNT composites. Studies show that many researchers are successful in synthesizing CNT composites using various processing methods. Few of the CNT composites have also been commercialized.

In the present age, research is going on extensively on CNT reinforced functionally graded materials (FGM). They were initially used as thermal barriers for aerospace applications and fusion reactors. CNT reinforced FGM materials show more thermal stability and mechanical properties such as strength, toughness and hardness.

The use of advanced composites started in the year 1959 with the development of Optimum Pitch Blade for the XCH-47 twin rotor helicopter of Vertol Aircraft Corporation.

The overall challenges faced in processing CNT composites are the difficulty of dispersing the CNT in the matrix, an ideal amount of CNT should be reinforced beyond which the properties do not enhance, insufficient bonding at the interface and difficulty in aligning the CNT's. Many have published productive works in over-coming these challenges. We can open a wide range of applications of CNT composites if they can be produced commercially.

Thermal spraying can be concluded as the most convenient and economical method of processing for CNT reinforced metal matrix composites. Powder processing is best compared with other techniques for processing CNT reinforced polymer or ceramic matrix composites.

Also the polymer nanocomposites are the future of packaging industry. There are many on-going efforts in fabrication of silica nanocomposites and clay nanocomposites. Nanomaterials are the future of most of the engineering materials. They are also proven to be sustainable and eco-friendly. If these materials are successfully commercialized on a large scale they will find a huge number of applications in various fields.

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