

Carbon nanotube reinforced metal matrix composites – a review

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This review summarises the research work carried out in the field of carbon nanotube (CNT) metal matrix composites (MMCs). Much research has been undertaken in utilising CNTs as reinforcement for composite material. However, CNT-reinforced MMCs have received the least attention. These composites are being projected for use in structural applications for their high specific strength as well as functional materials for their exciting thermal and electrical characteristics. The present review focuses on the critical issues of CNT-reinforced MMCs that include processing techniques, nanotube dispersion, interface, strengthening mechanisms and mechanical properties. Processing techniques used for synthesis of the composites have been critically reviewed with an objective to achieve homogeneous distribution of carbon nanotubes in the matrix. The mechanical property improvements achieved by addition of CNTs in various metal matrix systems are summarised. The factors determining strengthening achieved by CNT reinforcement are elucidated as are the structural and chemical stability of CNTs in different metal matrixes and the importance of the CNT/metal interface has been reviewed. The importance of CNT dispersion and its quantification is highlighted. Carbon nanotube reinforced MMCs as functional materials are summarised. Future work that needs attention is addressed.

Keywords: Carbon nanotubes, Metal matrix composites, Dispersion, Processing, Interfacial phenomena, Mechanical properties, Strengthening, Thermal properties

Introduction

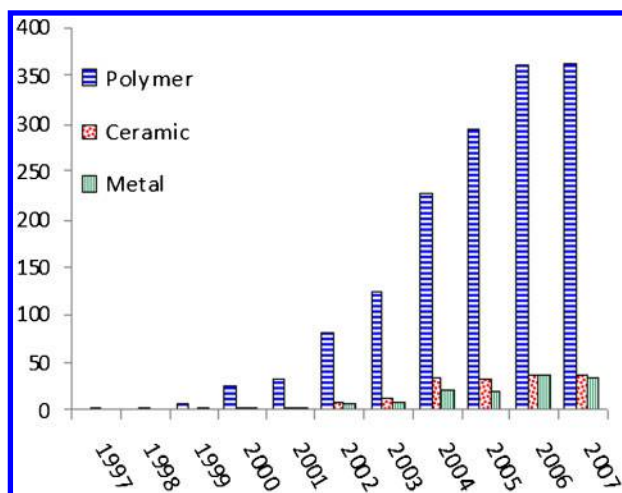
The need for lightweight, high strength materials has been recognised since the invention of the airplane. As the strength and stiffness of a material increases, the dimensions, and consequently, the mass, of the material required for a certain load bearing application is reduced. This leads to several advantages in the case of aircraft and automobiles such as increase in payload and improvement of the fuel efficiency. With global oil resources on a decline, increase in the fuel efficiency of engines has become highly desirable. The inadequacy of metals and alloys in providing both strength and stiffness to a structure has led to the development of metal matrix composites (MMCs), whereupon the strength and ductility is provided by the metal matrix and the strength and/or stiffness is provided by the reinforcement that is either a ceramic or high stiffness metal based particulate or fibre. Metal matrix composites can be designed to possess qualities such as low coefficient of thermal expansion and high thermal conductivity which make them suitable for use in electronic packaging applications. Metal matrix composites today

are extensively used in automobile and aerospace applications.¹⁻⁴

In 1960, Roger Bacon⁵ demonstrated the formation of graphite whiskers (diameter ranging between fractions of a micrometre to a couple of micrometres) that were flexible and had a tensile strength of up to 20 GPa. Subsequent research led to development of processes for large scale production of these fibres by carbonisation of Rayon, poly-acrylonitrile (PAN), or pitch. Manufacture of carbon fibres of high strength in the 1960s and 1970s made them the first choice for the manufacture of advanced composites for use in rocket nozzle exit cones, missile nose tips, re-entry heat shields, packaging and thermal management. Since 1970, carbon fibre reinforced composites have been extensively used in a wide array of applications such as aircraft brakes, space structures, military and commercial planes, lithium batteries, sporting goods and structural reinforcement in construction. Research in the field of carbon was revolutionised by the discovery of carbon nanotubes (CNTs) by Iijima⁶ in 1991. Although CNTs might have been synthesised in 1960 by Bacon,⁵ it took the genius of Iijima to realise that they are tubes made by rolling a graphene sheet onto itself. A multiwalled carbon nanotube (MWCNT) is made up of many single walled carbon nanotubes (SWCNT) arranged in a concentric manner. Unless otherwise specified, CNT in this work refers to MWCNTs. Experiments and simulations showed that CNTs have extraordinary mechanical

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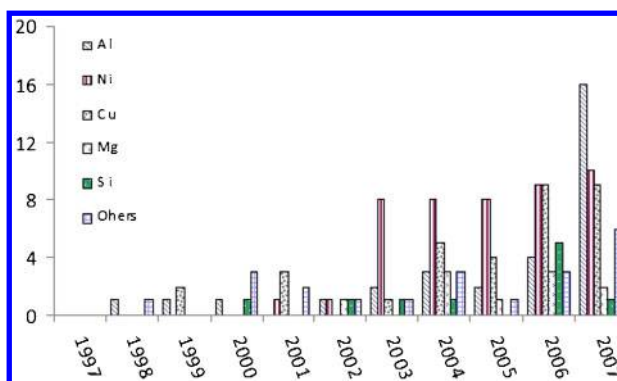
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1 Number of publications on polymer/ceramic/metal matrix-CNT composites during 1997–2008 (Source: www.scopus.com)

properties over carbon fibres, e.g. stiffness up to 1000 GPa, strength of the order of 100 GPa (Refs. 7–11) and thermal conductivity of up to $6000 \text{ W m}^{-1} \text{ K}^{-1}$.^{12,13} These investigations showed that CNTs were the strongest fibres known to mankind that possess exceptional properties.

Since the last decade, a number of investigations have been carried out using CNT as reinforcement in different materials, namely polymer, ceramic and metals. Figure 1 shows the number of journal articles published on CNT-reinforced composites in the last decade. It can be clearly seen that majority of the research has been carried out on reinforcement of polymers by CNT. This can be attributed primarily to the relative ease of polymer processing, which often does not require high temperatures for consolidation as needed for metals and ceramic matrixes. Studies on CNT reinforcement of ceramic matrix are few as compared to those on polymer matrix, whereas those on CNT-reinforced MMCs are even fewer. This is quite surprising considering the fact that most of the structural materials used in today's world are metals. Figure 2 plots the number of publications on various CNT-reinforced metal matrix systems for each year. It is clearly observed that there has been an increase in the number of publications on that topic since 2003. These articles address various aspects, such as processing, microstructure, modelling of mechanical properties and the chemical interaction of CNTs with metals. Several review papers have been published on polymer-CNT composites,^{14–21} whereas for ceramic matrix composite there are only few of such publications available.^{21–24} But there is not a single review article which deals with only CNT-reinforced MMCs. Hence, a systematic study of the efforts towards development of CNT-reinforced MMCs was found necessary for the following reasons. First, it will provide a summary of the work performed to date and a critical analysis of the success achieved in this area. Second, it will serve as a guideline for future researchers that are new to the subject. The purpose of this article is to review the studies on CNT-reinforced MMCs in order to have a clear picture on the state of the art of this field, and to highlight the immense possibilities of research and development in this area.

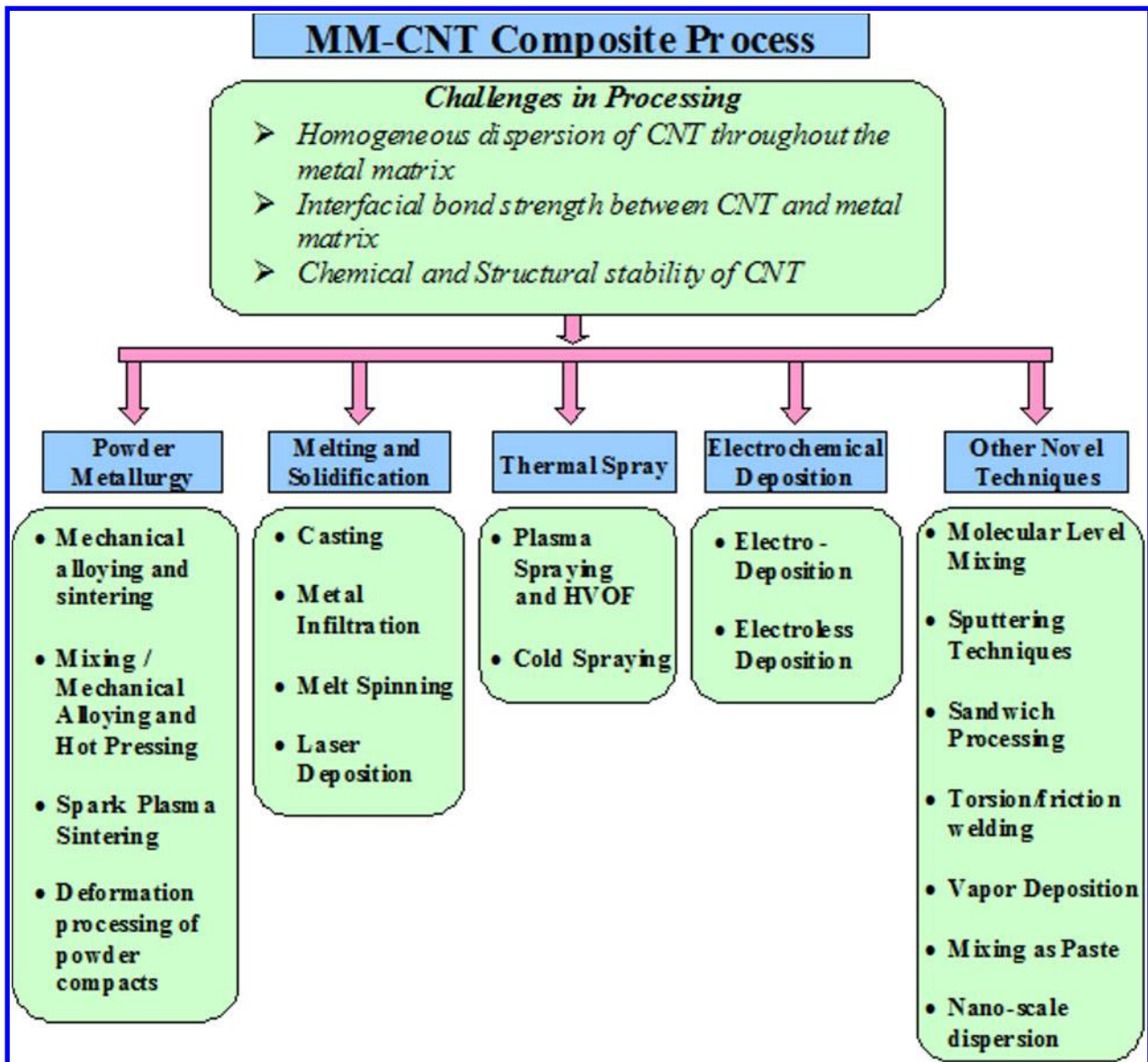


2 Number of publications on different metal matrix-CNT composites during 1997–2008 (Source: www.scopus.com)

The following is an outline of this review article. The section on 'Processing techniques' discusses the processes that have been applied for the fabrication of CNT-reinforced composites. Strengthening mechanisms and applicability of micromechanical models in estimation of properties at nanoscale is discussed in the section on 'Strengthening mechanisms in CNT composites'. Mechanical properties of CNT-reinforced MMCs studied to date have been summarised in the section on 'Mechanical properties of different MM-CNT systems'. An important requirement during MMC fabrication is the chemical stability of the reinforcement and matrix-reinforcement interfacial reaction. The section on 'Interfacial phenomena in CNT-reinforced MMCs' reviews the interfacial reaction and stability of CNTs in various metal systems. Along with chemical stability it is also required that the CNTs be distributed homogeneously to achieve uniform properties of the composite. The disperse behaviour of CNTs in the metal matrix is discussed in the section on 'Dispersion of CNTs in a metal matrix'. The section on 'Other properties affected by CNT reinforcement in metals' summarises the effect of CNTs on other properties, i.e. electrical, thermal, hydrogen storage and catalytic properties which been of considerable interest. Finally, the section on 'Potential applications of CNT-reinforced metal matrix composites' outlines the summary, scope and directions for future research, based on the discussion in previous sections.

Processing techniques

Carbon nanotube reinforced metal matrix (MM-CNT) composites are prepared through a variety of processing techniques. Figure 3 shows the various processes that have been adopted for synthesis of CNT-reinforced MMCs. Powder metallurgy is the most popular and widely applied technique for preparing MM-CNT composites. Electrodeposition and electroless deposition are the second most important techniques for deposition of thin coatings of MM-CNT composites as well as for deposition of metals on to CNTs. For low-melting-point metals such as Mg and bulk metallic glasses, melting and solidification is a viable route. Apart from these techniques, scattered efforts have been made on indigenous methods for preparing MM-CNT composites. Following subsections will present all of these processing techniques.



3 List of different processing routes for MM-CNT composites

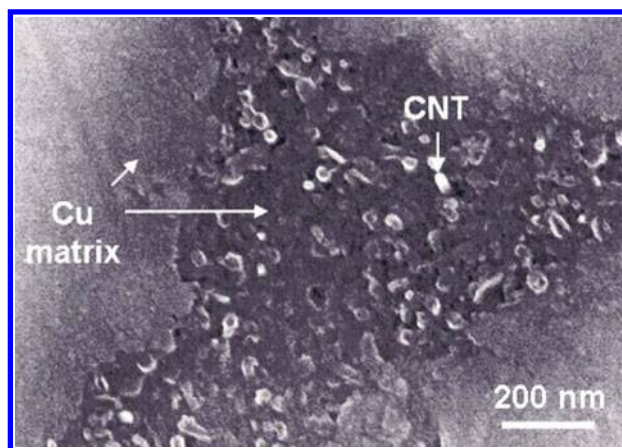
Powder metallurgy route

Most of the studies on Al-CNT and approximately half of the research work on Cu-CNT composites have been carried out using the powder metallurgy method. A few researchers have also prepared CNT composites based on Mg, Ni, Ti, Ag, Sn, and intermetallics through this route. The basic process steps consist of mixing CNTs with metal powder by grinding or mechanical alloying, followed by consolidation by compaction and sintering, cold isostatic pressing, hot isostatic pressing, or spark plasma sintering. In most of these works, the composite compacts were subjected to post-sintering deformation processes such as rolling, equi-channel angular processing, extrusion, etc. Irrespective of the process steps, the main focus was on obtaining good reinforcement, by achieving homogeneous dispersion of CNT in the metal matrix and good bonding at the metal/CNT interface. Different variations of powder metallurgy techniques are discussed briefly in the following sub-sections.

Mechanical alloying and sintering

Some of the MM-CNT composites prepared using this technique are Cu-CNT,^{25,26} Al-CNT,²⁷ W-Cu-CNT,²⁸

Mg-CNT²⁹ and Ag-CNT.³⁰ In some cases,^{31–35} only mechanical alloying was used to prepare composite powder particle as the final product. Realising that the most critical issues in processing of CNT-reinforced MMCs are (i) dispersion of CNTs and (ii) interfacial bond strength between CNT and the matrix, many researchers have adopted modified steps in their approaches. In the preparation of Cu-CNT composites^{25,26} through mixing, compaction and sintering route, CNTs were coated with Ni using electroless deposition to achieve good interfacial bond strength. Density of the composites was comparable up to 8 wt-%CNT addition beyond which it decreased drastically due to agglomeration,^{26,27} No interfacial product formation was observed. In order to obtain homogeneous dispersion of CNTs, He *et al.*²⁷ have grown CNT by chemical vapour deposition (CVD) process on Al powders which were then compacted and sintered at 913 K to obtain Al-5 wt-%CNT composite of high relative density of 96%, and homogeneous dispersion of CNTs. Carbon nanotube pullouts and bridges, revealed at fracture surface were responsible for increased hardness (4.8 times) and tensile strength (2.8 times)



4 Image (SEM) showing Cu-CNT (5 vol.-%) composite processed through SPS of ball milled Cu-CNT powders⁴⁶ (Reproduced with permission from Elsevier)

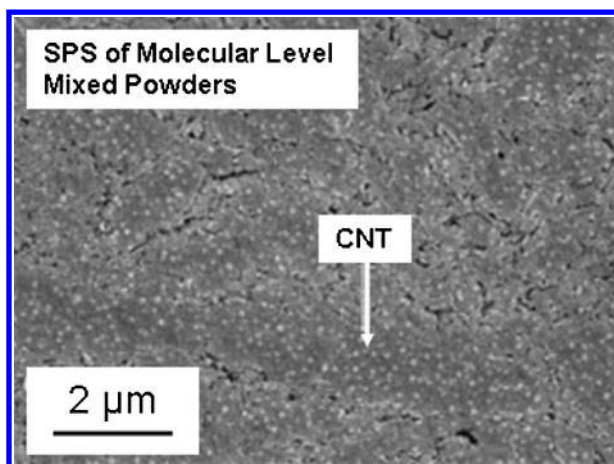
over pure Al. Yang *et al.*²⁹ have achieved homogeneous distribution of CNT in Mg matrix by mechanical mixing of the powders in an alcohol and acid mixture followed by sintering at 823 K. In order to enhance adhesive bonding at the surface, CNTs have also been treated by acid to roughen the surface through oxidation and used in Ag matrix composite.³⁰ Carbon nanotubes were shortened in length due to this treatment, but no damage to the wall was reported. Morsi and Esawi^{34,35} have used ball milling to disperse CNTs in Al matrix. Milling for up to 48 h lead to good dispersion of CNTs but resulted in formation of large spheres (>1 mm) due to cold welding.

Mixing/mechanical alloying and hot pressing

Instead of sintering, some researchers have used hot pressing consolidation of powder mixtures. Researchers have found hot pressing method to be inappropriate for fabricating Al-CNT composites as it results in clustering of CNTs.^{36,37} For achieving better dispersion in the Cu matrix, CNTs were electroless coated by Ni before hot pressing at 1373 K,³⁸ which ultimately resulted in improved mechanical and wear properties for the composite. Kuzumaki *et al.*³⁹ have optimised milling time for mechanical mixing at 5 h to avoid damage to CNTs and fabricated Ti-CNT composite by hot pressing. Mg-CNT composites⁴⁰ and Fe₃Al-CNT composites synthesised via hot-pressing⁴¹ have shown improved mechanical properties (hardness, compressive strength and bend strength) due to uniform distribution of CNTs. The enhancement in the mechanical properties was attributed to grain growth inhibition caused by interlocking nanotubes.⁴¹ Hot pressing route has also been explored for processing CNT-reinforced Ti-based bulk metallic glass (BMG) composite.^{42,43} Addition of CNT has been shown to increase in the glass transition and crystallisation temperature in this composite which further assisted in decreasing the required cooling rate for glass formation, thus assisting BMG formation.

Spark plasma sintering

Spark plasma sintering (SPS), a comparatively new and novel sintering technique, has also been explored by some researchers for synthesising CNT-MMCs. In this process, a pulsed direct current is passed through a die and the powder, producing rapid heating and thus greatly enhancing the sintering rate.⁴⁴ Efficient



5 Image (SEM) of Cu-CNT (5 vol.-%) composite fabricated by SPS from molecular level mixed composite powders, showing homogeneous distribution of CNTs⁴⁷ (Reproduced with permission from Wiley Interscience)

densification of powder can be achieved in this process through spark impact pressure, joule heating and electrical field diffusion. This method is, generally, suitable for consolidation of nano powders, without allowing sufficient time for grain growth. Most of the studies using SPS have been carried out in Cu-CNT⁴⁵⁻⁴⁸ and in Al-CNT systems.⁴⁹

Kim *et al.*⁴⁵ were the first to report SPS of Cu-CNT composites; these were fabricated at 1023 K and 40 MPa with better dispersion and improved density (97–98.5%). Sintered microstructure consisted of dual zones of CNT free matrix and CNT rich grain boundary regions as seen in Fig. 4.⁴⁷ Further rolling was performed on the composite to deform and align the CNT rich regions resulting in improved properties. Spark plasma sintering of Cu-CNT nanocomposite powder, produced by molecular level mixing process (described in the section on ‘Sputtering techniques’), helps further improvement in density (~99%) and mechanical properties.^{48,49} Figure 5 shows homogeneous dispersion of CNTs in the Cu matrix achieved in this study.⁴⁹ Enhancement in mechanical strength by 129% with addition of 5 vol.-%CNT has been reported for Al-CNT composite synthesised by SPS followed by hot extrusion of powders prepared by a nanoscale dispersion method (described in the section on ‘Nanoscale dispersion (NSD)’).⁵⁰ Good dispersion and alignment of CNTs in the matrix as well as formation of Al₄C₃ at the CNT/matrix interface were the prime reasons for improvement in mechanical properties.⁵⁰ Spark plasma sintering has also been explored for synthesis of CNT-reinforced Ni–Ti based shape memory alloys⁵⁰ and Fe₃Al-CNT composites⁵¹ with enhanced mechanical properties. In all the above-mentioned studies, SPS, being a high-temperature and high-pressure process, resulted in good densification and mechanical properties. However, at the processing conditions of SPS, CNTs may have been damaged or may have reacted with the matrix material. These issues are yet to be elucidated properly.

Deformation processing of powder compacts

Some researchers have explored the possibility of deformation of powder compacts to achieve better density and distribution/alignment of CNTs in the MMC.

However, the approach has been mainly confined to Cu-CNT^{46,52–56} and Al-CNT^{57–64} composites. Kuzumaki *et al.*⁵⁷ have synthesised Al-CNT composite through hot extrusion of powder compacts, at 873 K. It was found that the CNTs were aligned along the extrusion direction and were strong enough to withstand the extrusion load. However, inhomogeneous distribution of CNTs in the fractured surfaces of the composites suggested poor dispersion of CNTs in the matrix.

Rolling seemed to be a better option than extrusion for Cu-CNT composites in terms of alignment of CNT clusters in the matrix.^{46,52,56} Good reinforcement of the composites was confirmed from the appearance of bridging and pullout on the fracture surface.⁵³ Improvement in wear resistance and coefficient of friction was also observed in rolled samples.⁶⁵

Equal-channel angular processing was employed to successfully synthesise Cu-CNT composites from powder compacts,^{53–55} with CNT content varying between 1 and 5 vol.-%. Increasing number of passes in Equal-channel angular processing has been claimed to break the CNT agglomerates to form better dispersion of CNTs in the matrix (though not supported by micrographs) and thus enhancement of mechanical strength of the composite. Equal-channel angular processing, being a severe plastic deformation technique, is expected to induce high amount of deformation to the constituent phases, thus damaging the CNTs.^{54–56}

Al-CNT-MMCs have also been extensively synthesised using deformation routes. Deng and co-workers have performed a series of systematic studies on Al-CNT (1 and 2 wt.-%) composites, synthesised through hot extrusion (733 K, extrusion ratio of 25:1) of cold isostatic pressing and hot pressed compacts.^{59–62,66} High temperature processes result in Al₄C₃ formation at CNT/matrix interface. A relative density of ~99% and bridging and pullout in the fracture surface was observed in the Al-1 wt.-%CNT composites while Al-2 wt.-%CNT showed agglomerates and interface debonding. Rolling of ball milled powders enclosed in a can have shown to result in poor composite properties.⁶³ Recently, Al-CNT composites with significant improvement in properties have been fabricated by hot extrusion of compacts prepared from ball milled powder mixtures.^{49,64,65} The enhancement has been credited to the fibre reinforcement and Al₄C₃ precipitation.⁴⁹ A few studies have found that weak interfacial bonding between matrix and CNT to be the hindrance for further enhancement in mechanical strength.^{50,66} But no assessment of damage due to severe milling on CNT has been made.^{50,66,67}

Mg-CNT composites have also been processed by hot extrusion (623 K, 20:1 ratio) of sintered pellets.^{67,68} Homogeneous dispersion of CNTs was reported while damage, interfacial reaction or alignment of CNTs, were not studied. Nai *et al.*^{69,70} have conducted studies on cold extruded (20:1 ratio) Sn–Cu–Ag lead free solder alloy, reinforced up to 0.7 wt.-%CNTs. Although these studies did not throw light on the distribution of CNTs, Kumar *et al.*⁷¹ have observed segregation of CNTs at the corner of the grains, in the same alloy system containing 1 wt.-%CNT. Nai *et al.* also reported decrease in density and CTE, and increases in hardness and wettability of the composites at soldering surfaces, with increasing CNT content.⁷²

The issues of utmost importance in powder processing of CNT-MMC are dispersion and interfacial bonding of CNTs in the matrix. The solution to tackle these challenges is to introduce efficient mixing steps and/or shorter sintering time. Thus, ball milling of the initial powder mixture became almost common for all processing routes. However, benefits obtained through ball milling can easily be lost in consolidation stages. Spark plasma sintering and post-sintering deformation looks promising for consolidation. Although short sintering time of SPS effectively reduces agglomeration time of CNTs, clusters formed in the previous processing steps (mixing, compaction) could be carried over in this step. Post-sintering deformation has been found to avoid this problem. Heavy deformation breaks CNT clusters and result into more homogeneous dispersion of CNTs. However, this process also can lead to damage and fracture of CNTs and formation of interfacial products. Future studies need to be directed at important CNT-MMC systems to prepare industry-acceptable process maps under powder metallurgy approach.

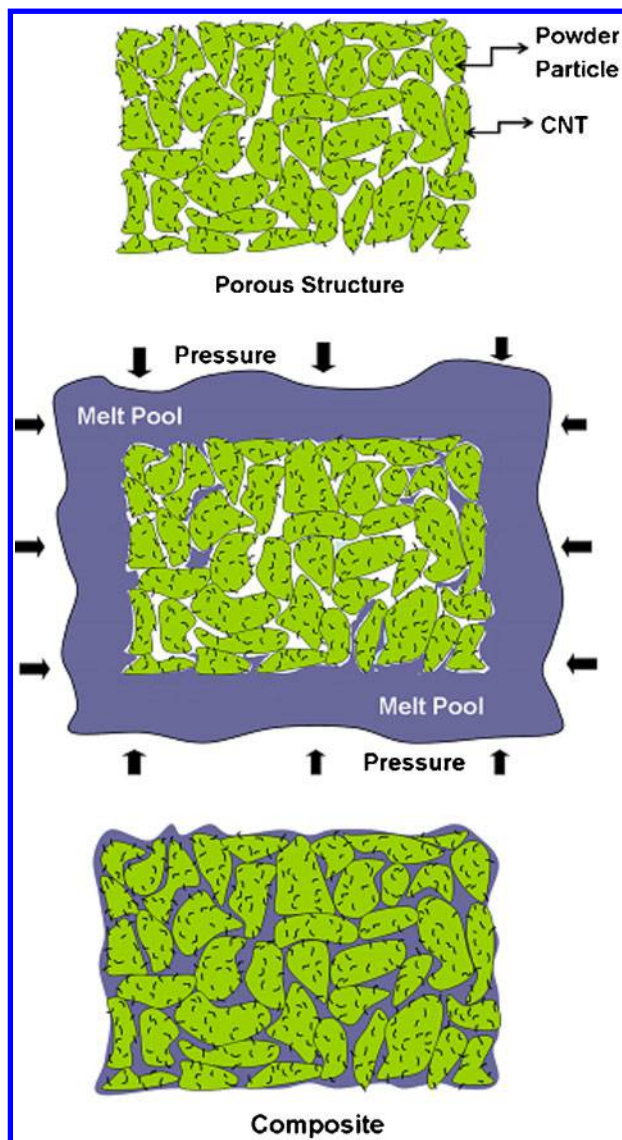
Melting and solidification route

Melting and solidification, the most conventional processing techniques for MMCs, has also been utilised for synthesising CNT-reinforced composites. A few studies are available that employ melting and solidification route for preparing MM-CNT composites due to the requirement of high temperature for melting. The process may cause damage to CNTs or formation of chemical reaction product at the CNT/metal interface. Therefore, this route is mainly favoured for composites having low melting point matrix. Another limitation is that suspended CNTs tend to form clusters due to surface tension forces.

Casting

Bian and co-workers were the first to synthesise CNT-reinforced Zr-based bulk metallic glass by this route.^{72,73} Pre-alloyed powders, mixed with CNTs and compacted into cylinders, were melted and cast to form **Zr-BMG-10 vol.-%CNT composite** rods. Increase in crystallinity of the matrix has been attributed to ZrC formation at the CNT matrix interface as well as depletion of Zr from amorphous matrix. Enhancement of hardness, inspite of increasing crystallinity, has been claimed due to CNT reinforcement. The composite has excellent acoustic wave absorption ability that has been attributed to a large amount of interfaces caused by CNT reinforcement.^{74,75}

Mg, being a low melting point metal, has been suitably processed through melting and casting route.^{74–77} The CNTs were Ni plated in some cases for better wettability with the matrix⁷⁶ which resulted in mechanical property enhancement with only 0.67 wt.-%CNT addition. Goh *et al.*^{77,78} have hot extruded (623 K) the cast billet to result in better reinforcement of CNTs in the matrix, but there is no mention about the distribution of CNTs or interfacial characteristics. The study showed that the number of cycles to failure under fatigue decreases with increasing CNT content; the reason being the presence of voids at the CNT matrix interface, making the reinforcement weaker.⁷⁹



6 Schematic of metal infiltration technique

Metal infiltration

The main idea of melt infiltration technique is to prepare a porous solid structure with dispersed CNTs and then infiltrating liquid metal into the pores and solidify to prepare a composite structure. Figure 6 explains the technique schematically. This technique has a higher chance to have uniform distribution of CNTs, but at the same time proper filling up of the pores, to make a good and dense composite structure, becomes a critical step. Also there is a probability of movement and thus agglomeration of CNTs due to high pressure application during infiltration. Yang and Schaller²⁹ have used infiltration technique to prepare Mg-CNT composite. Carbon nanotubes were grown by CVD on a structure made by Al_2O_3 fibres and then the same was infiltrated with molten Mg under pressurised gas. This study reported improvement in the high temperature (500 K) shear modulus by 20%. Al-CNT composite has been synthesised by Zhou *et al.*⁷⁹ through infiltration of a porous preform made by pressing a ball milled mixture of Al, Mg powders and CNTs at 1073 K for 5 h. Good reinforcement was evinced by embedded CNTs at the fracture surface, which improved hardness and wear resistance of the composite. Due to the high

temperature, there is all possibility for the preform to get fully molten resulting in clustering of CNTs. Uniform distribution of CNT has been claimed, but energy dispersive spectrometry does not have enough resolution to distinguish between dispersed and clustered CNTs.⁸⁰ In a recent study, Uozumi *et al.*⁷⁸ have explored the possibilities of squeeze casting to fabricate CNT-reinforced Al and Mg alloy composite with good dispersion of CNTs and without pores.

Melt spinning

Melt spinning involves pouring a molten alloy drop by drop on to a rotating Cu wheel. The droplets are converted into ribbons which are amorphous due to the high cooling rates. CNT- $\text{Fe}_{82}\text{P}_{18}$ -bulk metallic glass composite ribbons of 40 μm thickness have been prepared in this manner.⁸⁰ Retention of undamaged CNTs and amorphous nature of the composite has been reported, but no comments have been made on reinforcement, dispersion and interface nature of CNTs in the matrix.

Laser deposition

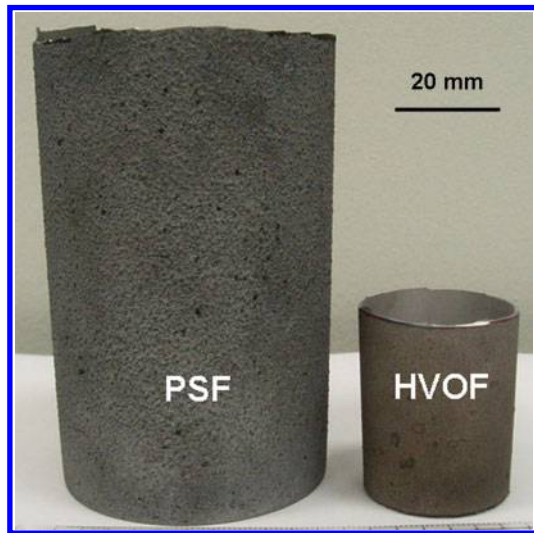
Only one study by Hwang *et al.*⁸¹ reports about Ni-10 vol.-%CNT composite processed through laser deposition technique after roller mixing of CNT and Ni powder. Although the process incurs very high temperatures, still CNTs were retained. But, they have reported increase in defect density and graphitisation of CNTs, which is quite reasonable considering the high processing temperature. The study claims wetting of CNT by Ni and no interfacial compound formation but no evidence has been provided.

In summary, the main issue for better performance of the composite is the dispersion and reinforcement of the CNTs. The reinforcement, again, is dependent on the interfacial wettability of CNTs with matrix and any chemical reaction occurring at the interface. Melting route has a high chance of CNT agglomeration in the melt pool. Infiltration and rapid solidification techniques are suitable to reduce CNT agglomeration. But, rapid solidification can largely be used for preparing composites of amorphous matrix. For infiltration technique, the criticality lies in infiltration and closure of the pores. Unfortunately, none of the reported studies addressed issues of interfacial compound formation and its effect on reinforcement. Wetting of CNTs by molten metal matrix is another critical issue. Finally, melting technique should ideally produce much dense composite than powder metallurgy technique. But none of the addressed densification, neither have they provided any comparison regarding the same.

Thermal spray

Plasma spraying and high velocity oxy-fuel (HVOF) spraying

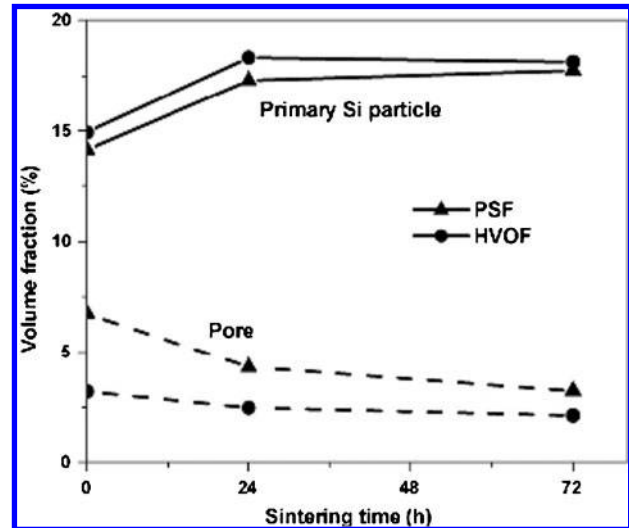
Our research group has pioneered thermal spray techniques for synthesis of Al-CNT composites. Thermal spraying can be defined as the spraying of molten or semi-molten particles onto a substrate to form a coating/deposit by way of impact and solidification. Thermal spraying methods offer the advantage of large cooling rates as high as 10^8 K s^{-1} during solidification which often result in the formation/retention of nanocrystalline structure in the coatings.⁸²⁻⁸⁴ Based on the heat source, thermal spray processes can be classified into flame



7 Free standing structures of Al-23 wt-%Si alloy containing 10 wt-%CNT produced by plasma spray forming (PSF) and HVOF

spraying, plasma spraying, high velocity oxy-fuel (HVOF) spraying or cold spraying. In plasma spraying, the heat source is a plasma created by the ionisation of an inert gas by an arc struck between a tungsten cathode and concentric copper anode (DC plasma spraying) or by high frequency radio waves (RF plasma spraying).⁸⁵ Powders injected into the plasma (temperature $\approx 10\,000$ – $15\,000$ K) absorb the heat as well as gain kinetic energy and are projected at high velocities onto the substrate to form coating. Particle velocities can reach up to 1000 m s^{-1} in plasma spraying. In HVOF, the source of heat is high pressure combustion of a fuel-oxygen mixture. The fuel can be gaseous such as propylene, methane, propane or hydrogen, or liquid such as kerosene. The velocities of the particles are considerably higher (up to 1500 m s^{-1}) in the case of HVOF, leading to the formation of dense coatings. Thermal spraying can also be used for near net shaping of bulk nanocrystalline components. By spraying on rotating mandrels of complex geometries, parts with intricate shapes can be generated. The faster rate of deposition and the fabrication of components having shape close to the final shape offers tremendous advantages by way of savings in the machining costs.

To the best of our knowledge, all of the work on thermal spraying of CNT-reinforced MMCs has been carried out only by our research group. Plasma spraying,^{86–89} HVOF spraying^{87,88} and cold spraying⁹⁰ have been successfully demonstrated for the fabrication of CNT-reinforced MMC and ceramic coatings.^{91–93} Laha *et al.* have studied the feasibility of spraying CNTs with Al powders to form composite coatings.⁸⁶ Successful retention of undamaged CNTs in plasma sprayed aluminium coatings was reported. Laha *et al.* have also fabricated bulk free standing cylindrical structures of CNT-reinforced Al-23 wt-%Si alloy using plasma spray forming (PSF) and HVOF.⁸⁷ These cylinders were prepared by spraying on a rotating 6061 aluminium mandrel. The thickness of the PSF and HVOF cylinders were 0.64 and 1.24 mm respectively (Fig. 7). The thickness of the cylinders was limited due to the fact that the flowability for blended (Al + CNT) powders was not good and lead to clogging of powder feed pipes. High velocity oxy-fuel resulted in a higher density



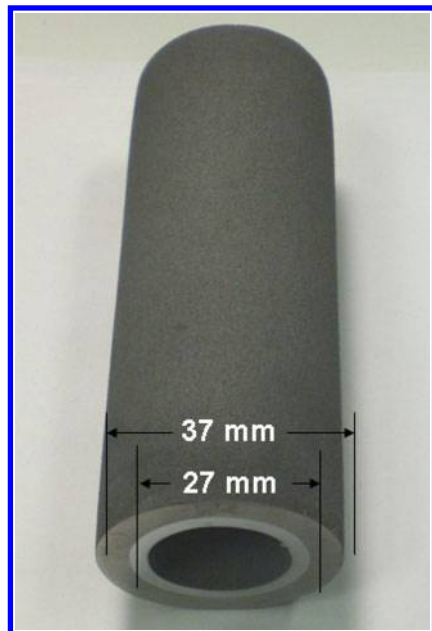
8 Variation of pore volume fraction and primary Si content with time of sintering of Al-23 wt-%Si composite containing 10 wt-%CNTs⁹⁵ (Reproduced with permission from Elsevier)

coating (2.54 g cm^{-3}) compared to PSF (2.45 g cm^{-3}) because the higher velocities of the particles during HVOF lead to better compaction. Elastic modulus and hardness were found to be higher for the HVOF coating compared to that of the PSF which was attributed to the lower degree of porosity and higher dislocation density in HVOF coatings.⁸⁷ Interfacial phenomenon in the PSF composite was studied and will be discussed in detail in the section on 'Interfacial phenomena in CNT-reinforced MMCs'. It was shown that 2–5 nm layer of SiC is formed at the interface of the CNTs in the case of Al-23 wt-%Si alloy.⁹⁴ Sintering of the HVOF and PSF composites in an argon atmosphere at 400°C for up to 72 h resulted in densification and increase in the size and fraction of primary silicon as shown in Fig. 8.⁹⁵ No noticeable effect on the interfacial carbide morphology was observed.

Recently, we succeeded in synthesising bulk Al-CNT nanocomposite cylinders with improved CNT dispersion up to 5 mm thick by using spray dried powders.⁸⁹ Use of spray drying resulted in good flowability and dispersion of CNTs in microsized Al-12 wt-%Si powders. Increase in the powder flowability enables longer spray times and fabrication of thicker components. Figure 9 shows a picture of a 5 mm thick cylinder having a length of 100 mm of Al-12 wt-%Si composite reinforced with 10 wt-%CNTs. The uniformity of colour in Fig. 9 suggests that CNTs are uniformly distributed. The microstructure of the composite was found to be two phase with a matrix containing uniform distribution of CNTs and CNT rich clusters. Figure 10 shows the SEM images of the fracture surface of Al-12 wt-%Si composite reinforced with 5 wt-%CNTs. It can be seen that the CNTs are uniformly distributed within the splats and pull out phenomena is observed with a degree of alignment that could lead to strengthening. Al_4C_3 formation was observed in the case of the Al-12 wt-%Si-CNT composite while in our previous study SiC formation occurred in an Al-23 wt-%Si-CNT composite.⁹⁴

Cold spraying

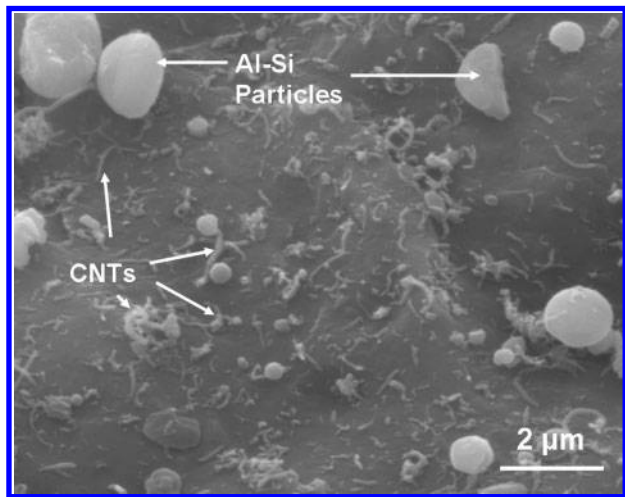
Cold spraying is a relatively new process in which particles are accelerated to very high velocities at low



9 Plasma sprayed cylinder 5 mm in thickness of Al-12 wt-%Si alloy with 10 wt-%CNTs

temperature (200–500°C) and made to impact on a substrate. The particles undergo severe plastic deformation on impact and form splats that stick to each other. Since the temperature of the particles is below the melting point, oxidation and phase transformations can be avoided. Cold spraying was shown to be successful in the fabrication of CNT-reinforced aluminium composites coatings.⁹⁰ Spray dried Al-12 wt-%Si agglomerates containing 5 wt-%CNT were mixed with pure aluminium powder and sprayed onto a 6061 substrate. Coatings up to 0.5 mm thick and containing 0.5 wt-% and 1 wt-%CNTs were produced. Uniform distribution of CNTs was obtained on the fracture surface as shown in Fig. 11. Three types of deformation phenomena for cold sprayed CNTs were observed which were kink formation, necking fracture and peeling of graphite layer due to shear.

Thermal spray provides an efficient way of incorporating CNTs into coatings and bulk components. Addition of CNTs could lead to improvement in the wear resistance and thermal conductivity of the coatings. Also possibilities of rapid prototyping exist with thermal spray methods.



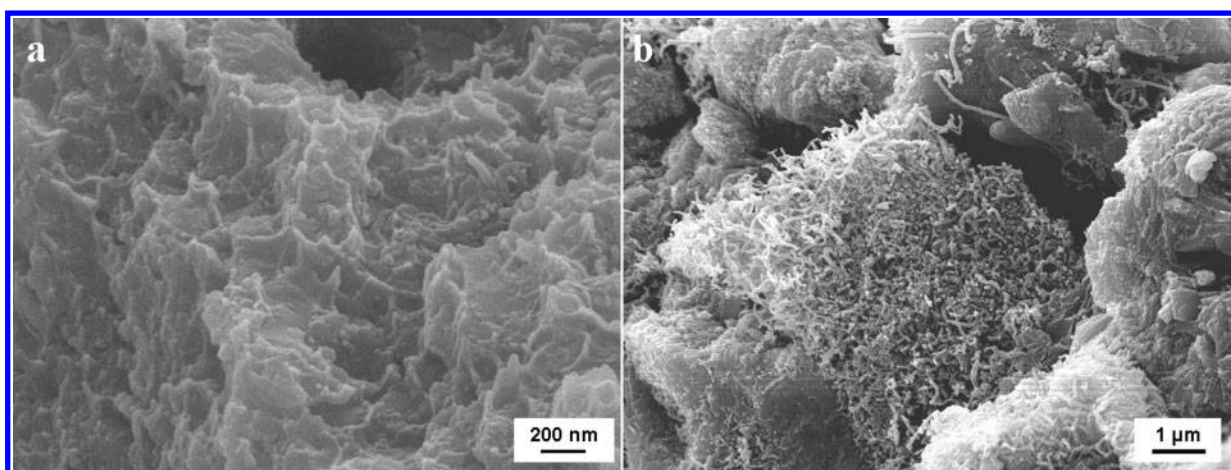
11 Image (SEM) of fracture surface of cold-sprayed aluminium composite containing 0.5 wt-%CNTs showing uniform distribution of CNTs

Electrochemical route

In terms of number of publications on MM-CNT composites, electrochemical deposition is the second most popular route after powder metallurgy techniques. The main difference between the two is that the electrochemical method is primarily used for formation of thin composite coatings with a reported thickness of 20 to 180 μm,⁹⁶ though some of the studies on electrochemical deposition do not report coating thickness. This technique has also been used for coating CNTs with metals to produce one-dimensional (1D) composites, the projected application for which includes, but is not limited to, different types of nano-sensors, electrodes, inter-connects and magnetic recorder head in computer applications. Both electrodeposition and electroless deposition have been used for MM-CNT fabrication. Electro deposition requires the traditional electrochemical cells in which composite film is deposited by current flow between anode and cathode. The second technique, known as electroless plating, does not require any external energy source. This is basically a chemical process, in which thermochemical decomposition of metallic salts takes place in the bath to release metallic ions that forms composite with CNTs.

Electrodeposition

Electrodeposition technique has been reported as a processing route for mainly Ni-CNT⁹⁶⁻¹¹³ and



10 Image (SEM) of fracture surface of a Al-5 wt-%CNT coatings showing pull out and b Al-10 wt-%CNT showing CNT cluster

Cu-CNT^{114–117} composites. The first ever report on electrochemical deposition of an MM-CNT composite coating was by Chen *et al.*⁹⁹ on co-deposition of a Ni-14 vol.-%CNT composite coating from an electrolytic bath at a current density of 15 A dm⁻² and CNT concentration of 2 g L⁻¹. It was found that the CNT content increased with an increase in CNT concentration of the electrolyte, current density and agitation rate of the bath.^{99,100} Guo *et al.*¹¹⁰ have shown that pulse deposition produces smoother surfaces, and that the CNT content of the Ni-CNT-composite coating increases with increasing pulse frequency and reverse ratio.

In the case of co-deposition of CNTs and metals, uniform dispersion of CNTs in the bath and good suspension is the key factor for getting coatings with homogeneous CNT distribution. This is challenging because CNTs have a natural tendency for agglomeration. Ultrasonication and magnetic stirring have been used to keep the CNTs in suspension. Arai *et al.* have added polyacrylic acid to the bath to keep the CNTs in suspension.^{102,106,108} Ball milling of CNTs has been used to decrease their aspect ratio to help them being dispersed in the bath.^{97,100,104} Acid cleaning and adding surfactants has also improved suspension of CNTs.^{101,103} Metal ions deposit on CNT surfaces by absorbing electrons^{109,118} and hence the large surface area provided by CNTs serves as a mechanism for reduction of the grain size of electrodeposited coatings. Shi and co-workers¹⁰³ have reported a 250% reduction in grain size (42 to 17 nm) of Ni-Co co-deposited coatings. Guo *et al.*¹¹⁰ have shown increase in the microhardness of Ni-CNT composite coating by AC-deposition with an increasing pulse reverse ratio and current density up to 8 A dm⁻² of the bath.

Cu-CNT composite coatings and 1D structures have also been prepared by electro deposition.^{114–116} Cu nanoclusters were deposited on CNTs dispersed on glassy carbon for glucose sensing applications.¹¹⁶ Another processing approach is filling the voids of aligned arrays of CNTs, used as cathode, with Cu by electrodeposition.¹¹⁷ Composites with up to 40 vol.-%CNT were produced having lower thermal resistance and electrical resistivity than unreinforced matrix making them suitable for interconnect and thermal management applications.¹¹⁷

Electroless deposition

Electroless deposition is basically a chemical technique in which a metal or its alloy is decomposed by catalytic action and deposited onto a surface without application of any current. This technique is mostly developed and employed for Ni-P or Ni-B alloys.^{25,119–136} There are only a few studies on Co-CNT,²⁷ Ni-Fe-P alloy¹³⁷ and Ni-Cu-P alloy.¹³⁶ The very first report of electroless deposition technique was by Chen and co workers¹²³ on a Co-CNT system to prepare 1D nanostructures for magnetic recording. Maintaining the suspension and uniform dispersion of CNTs in the bath is a challenge in the case of electroless plating too. Agitation of the bath during processing and ball milling of the CNTs before mixing in the bath have been proposed as a solution for improved CNT dispersion.^{120,121,124,128} The mechanism of deposition in electroless process is based on thermochemistry of the system. Hence, the bath temperature and pH value plays a very critical role in the coating composition and morphology. Most of the studies on

Ni-P-CNT composites have used a pH value in the range of 4.5–5 whereas the temperature was between 353 and 361 K.^{122,124–127,131–135} Some of the studies have tried to correlate the concentration of CNT in the coating with that in the bath.^{125,129,131,136} The bath compositions were optimised to obtain a maximum CNT concentration. Increasing beyond the optimised bath composition resulted in reduction in CNT content of the coating due to agglomeration of CNTs in the bath. Uniformly distributed and deeply embedded CNTs were reported in some of the studies,^{127,128,131,136} while some studies report presence of CNT-clusters.¹²⁹ Other than coatings, synthesis of 1D composites of CNT coated with Co¹²³ and Ni and Ni-alloys^{121,130} by electroless deposition technique have also been reported.

As is evident from the above discussion, electro-deposition techniques have been developed by several workers and optimised for producing uniform composite coatings. This process is unique and most suitable for producing 1D MM-CNT composites. The problem of maintaining uniform dispersion and suspension of CNTs in the bath is the main challenge in the process. There is usually a critical concentration of CNTs that can be dispersed in the bath and addition beyond which it does not affect the CNT content of the coating. These processes are suitable for fabrication of thin coatings only. A lot of research has been carried out in the Ni-CNT system while development of the process for other MM-CNT systems requires further work.

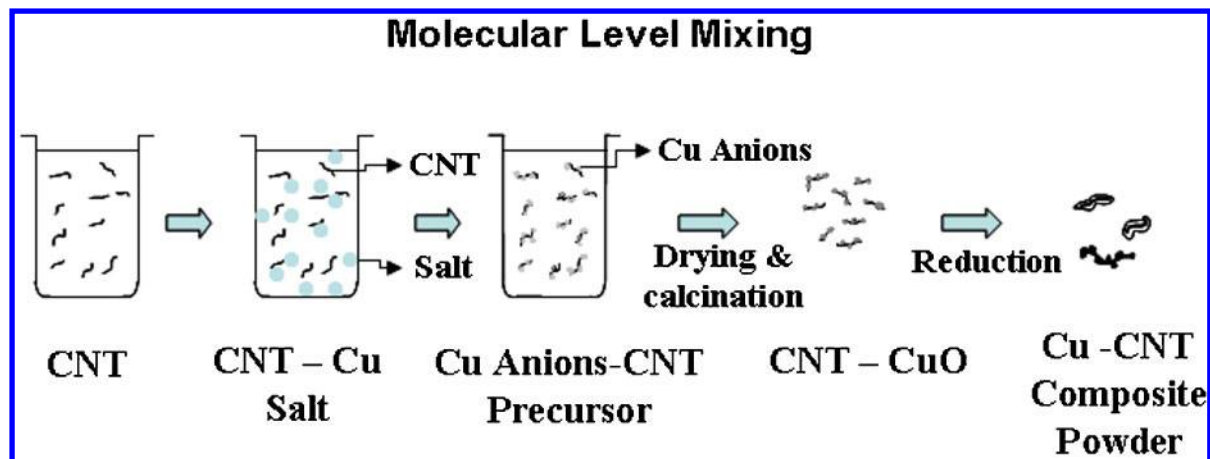
Other novel routes

There are a few studies that have explored unique processing routes. Some of these routes are improvisation of the conventional processes whereas others are indigenous and novel techniques to process MM-CNT composites.

Molecular level mixing

Most of the studies in this method are related to Cu-CNT Composites,^{47,48,138–140} except one that deals with Sb and SnSb_{0.5} matrix composites.¹⁴¹ This method is capable of producing composite particles or 1D nanostructure of CNT coated with metal. The process requires CNTs to be acid treated and functionalised before introducing them into the metal-salt bath, thus aiding the CNT suspension and surface metal deposition on their surface. Subsequently, the bath is sonicated to prepare a CNT-metal ion precursor which goes through drying, calcinations, and a reduction process, in series, to produce metal-CNT composite powder.⁴⁷ Figure 12 explains the process schematically. Some researchers have used reducing agents directly in the bath to avoid the separate step of reduction.^{138,139,141}

Chen *et al.*¹⁴¹ synthesised Sb/SbSn_{0.5}-CNT nanocomposite for anode application in Li-ion batteries. They were able to form a semi-continuous layer of metal on CNTs. The nanocomposites, after drying, formed a web of coated CNTs with some metal particles entangled in it. The majority of the studies have used molecular level mixing technique for producing nanocomposite powders to be used for bulk processing through the powder metallurgy route.^{47,48,139,140} The aim is to obtain good dispersion and better bonding of CNTs with matrix in the final composite structure. Ping *et al.*¹³⁸ have employed molecular level mixing to produce Cu-CNT composite in order to prevent agglomeration of Cu nano particles by



12 Schematic of molecular-level mixing process

coating them on CNTs. Thus they claim to provide more surface area of Cu nanoparticles to be used for catalytic performance in the thermal decomposition of ammonium perchlorate. Molecular level mixing has shown a capability to improve distribution and interfacial bond strength of CNT with metal matrix. Still, there are only few studies of this technique and the technique needs to be explored for other systems.

Sputtering techniques

Only two reports are available on the formation of metal-CNT composite by sputtering technique.^{142,143} Huang *et al.*¹⁴² have tried to deposit several metals on CNT bundles. Au, Ag and Cu form an array of nanocrystals of ~ 10 Å size on the surface of CNTs, whereas Ti, Zr and Mo forms nanowires at the grooves of the CNT bundles. This difference in morphology has been explained in terms of interactions between carbon and respective metal atoms. Particle formation in Au, Ag and Cu indicates a weak interaction of those metals with C, whereas strong interaction of C with Ti, Mo and Zr helps them in forming elongated islands. Ci *et al.*¹⁴³ have sputtered Al at the bottom surface of vertically grown CNTs detached from the quartz surface. Subsequent annealing in the temperature range of 723–1223 K leads to Al_4C_3 formation. It was shown that carbide formed at defect sites and amorphous regions of CNTs. The information available on sputtering technique for processing of MM-CNT composite is scanty.

Sandwich processing

Researchers have tried to prepare MM-CNT composites by putting alternate layers of CNT and metal like a sandwich structure and then consolidating by applying severe pressure.^{144,145} Li *et al.*¹⁴⁴ have arranged 20 layers of 10 μm Cu foil with alternate CNT layers of 450 nm thickness and cold rolled the assembly with intermittent annealing steps to form a Cu-CNT composite. They have reported good bonding between CNT and Cu, and improvement of Young's modulus by $13 \pm 5\%$ by addition of 3.1 vol.-%CNTs. But no image of the cross-section of the composite has been provided to show the bonding between Cu layers. The authors also have not reported about possible damage to the CNTs, due to severe plastic deformation. Salas *et al.*¹⁴⁵ have explored shock wave consolidation of alternate layers of Al powder and CNTs to produce composite with 2 and 5 wt.-%CNT content. The process turned out to be unsuccessful in terms of dispersion of CNTs in the

matrix, as the CNTs agglomerated at grain boundaries and triple points of the matrix. The tendency of agglomeration increases with CNT content. This has resulted in deterioration of the mechanical properties of the composite. Sandwich processing could become popular technique because of its ease of processing.

Torsion/friction welding

The studies under this category required applied torsion or frictional force to weld CNT and metal together to form MM-CNT composite.^{146–148} Tokunaga *et al.*¹⁴⁶ have severely deformed ultrasonicated mixtures of Al powder and CNT under a torsion force of 2.5 GPa and rotation speed of 1 rev min^{-1} . They could produce Al–5 wt.-%CNT composite of 98% theoretical density. They have also reported a decrease in grain size by 80% which has been attributed to the presence of CNTs in the matrix, thereby causing constrained movement of dislocation towards the grain boundary and subsequent annihilation. Morisada and co-workers¹⁴⁷ have adopted a similar process for producing Mg-alloy-CNT composite. They have put CNTs in a groove of a bulk piece of Mg alloy and then applied frictional force inside the groove with a probe rotating at 1500 rev min^{-1} with various travel speeds. The authors mentioned about CNTs embedded in a metal matrix and grain refinement, but no quantification on decrease in grain size was provided. Dispersion of CNTs increased with decrease in travel speed of the tool which is obvious because it increased the mixing time.

Vapour deposition

Few research groups have used physical/chemical vapour deposition (PVD/CVD) techniques for processing 1D or particulate type of MM-CNT composites.^{27,149–152} Zhang *et al.*¹⁴⁹ coated CNTs by tungsten through PVD of a W filament heated to 2473 K in an H_2 environment. They obtained a non-uniform coating formation. Shu *et al.*¹⁵⁰ and Kim *et al.*¹⁵¹ have reported processing of a Si-CNT composite, to be used as Li-ion battery anode, by CVD technique. Both the studies have grown CVD on Si particles using Ni as catalyst. Carbon nanotubes form a cage such as structure entangling the Si particles with voids in the composite. These voids are required to accommodate the shape and size change of Si particles during battery cycles, without creating stress in the structure. Wang *et al.*¹⁵³ have produced Si-coated CNT composites by decomposition of silane (SiH_4) in order to increase thermal stability of CNTs. Ishihara and co-workers¹⁵² have produced Si particles coated

with nanotubes by chemical decomposition and vapour deposition of tetramethyl silane $[(\text{CH}_3)_4\text{Si}]$. They have used Ni/Si catalyst for the deposition. They reported producing a composite with high H_2 storage capacity but failed to explain the mechanism behind it. The process route is also not very clear. Chemical vapour deposition process has also been used to produce Al-CNT composite powder by growing CNT on Al particle using Ni catalyst. He *et al.*²⁷ have used this composite particle with 5 wt-%CNT to prepare bulk composite structure through the powder metallurgy route. They reported obtaining a 3% higher density in these composites in comparison to the composites made of just an Al and CNT powder mixture. Hardness and tensile strength of these composites have also increased by 200 and 180% respectively, over the composite made with blended powders.

Mixing as paste

There are a few studies that have reported production of an MM-CNT paste/mixture, which may not be classified as composites in a real sense. A paste of Cu particles and CNTs, mostly in mineral oil, was made to be used as biosensors.¹⁵⁴⁻¹⁵⁷ All these composites are reported to have increased sensitivity, stability and reproducibility.

Nano-scale dispersion (NSD)

This method utilises natural rubber (NR) to improve dispersion of CNTs in metallic powder.¹⁵⁸ A preform of CNT in NR and CNTs and metal mixture in NR are stacked alternatively. The stacks are compression molded into slabs at 80°C into slabs which are subsequently heated in a N_2 atmosphere at 800°C. This treatment burns off the rubber and melts the Al incorporating the CNTs into the composite in a dispersed manner. A sevenfold increase in compressive yield strength was reported by addition of 1.6 vol.-%CNTs. In another study,⁴⁹ NSD process was used to produce precursor Al powder on which CNTs were distributed uniformly. This powder was subjected to spark plasma sintering followed by hot extrusion for synthesising 5 vol.-%CNT composites that have a tensile strength (194 MPa) twice that of pure aluminium.

As has been seen from the discussion on processing, the main objective is to achieve homogeneous dispersion and good reinforcement of CNTs in the matrix. Electrochemical deposition techniques are the best for achieving the same, but, the main limitation of those techniques is that they can produce thin coatings and not free standing bulk composite structures. Casting techniques are suitable for only low-melting-point materials or amorphous structures though uniform dispersion of CNTs in the melt pool is still a challenge. Powder metallurgy is, by far, the most widely used and feasible route for preparing MM-CNT composites, but it needs immediate attention to both the dispersion and reinforcement issues. Molecular level mixing technique and CVD method have shown promising improvement in preparation of starting powder for the powder metallurgy route. If they are combined with SPS technique for sintering, MM-CNT composites with better mechanical properties may be produced. But, these techniques are still in their nascent stage and further studies are required to explore their possibilities as suitable methods for preparing MM-CNT composites. Thermal spray methods such as plasma spraying and

HVOF have been shown to produce CNT-reinforced coatings and near-net-shaped structures. During high impact, CNTs were shown to support processes such as cold spraying and explosive shock-wave consolidation. Thermal spray methods offer the advantages of rapid solidification and rapid prototyping for bulk composite fabrication as compared to extrusion or casting.

Strengthening mechanisms in CNT composites

The objective of adding of fibrous reinforcements such as CNTs is twofold: (i) to increase the tensile strength, and (ii) to increase the elastic modulus of the composite. Both of these effects are due to the fact that the CNTs have a higher stiffness and strength compared to the metal matrix. The mechanisms for enhancement of mechanical properties will be discussed below.

Tensile strength of CNT composites

Understanding the strengthening mechanisms in fibre reinforced composite materials has been a focus of research for almost 50 years now. The shear lag models¹⁵⁹ used in the case of conventional fibre reinforced composites have also been applied to CNT composites. The stress is transferred to the fibre (σ_f) via the interface and is related to the shear stress (τ_{mf}) between the fibre and matrix given by

$$\frac{l_f}{D_f} = \frac{\sigma_f}{2\tau_{mf}} \quad (1)$$

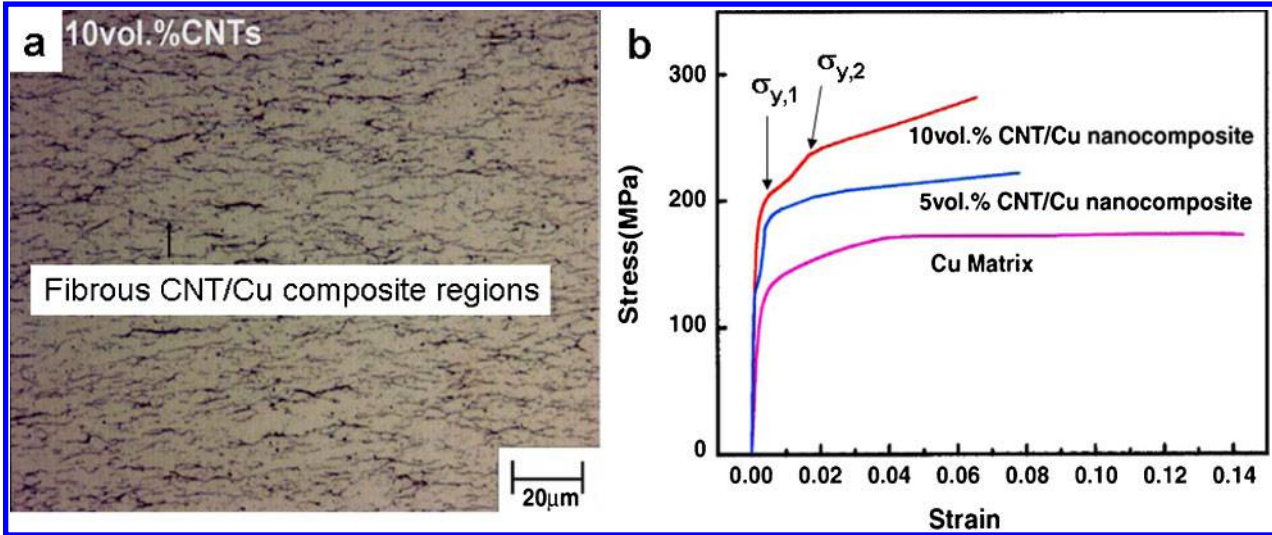
where l_f and D_f are the length and diameter of the CNT respectively. Carbon nanotubes with a larger aspect ratio will assist larger load transfer and hence efficient utilisation of reinforcement. For a critical length l_c , the value of σ_f becomes equal to the fracture strength of CNTs. For nanotube lengths $l < l_c$, the fracture strength of the composite (denoted by superscript Frac) is given as

$$\sigma_c^{\text{Frac}} = V_f \sigma_f^{\text{Frac}} \left(\frac{l}{2l_c} \right) + V_m \sigma_m^{\text{Frac}} \quad (2)$$

Choi *et al.*⁶⁴ found this relation to hold good for Al-CNT composites prepared by extrusion of ball milled powders. Coleman *et al.*¹⁸ reviewed the strengthening models for CNT composites. In the case of MM-CNT composites, reaction with the metal matrix might lead to an interfacial carbide product. The stress transfer to the CNT is then affected by the shear strength of the carbide phase. When the stress exceeds this value, the fracture occurs along the carbide layer leading to fibre pull out phenomena. Coleman *et al.* have derived the strength of the composite in the presence of an interfacial layer as follows¹⁶⁰

$$\sigma_c = (1 + 2b/D)[\sigma_{\text{Shear}}l/D - (1 + 2b/D)\sigma_m]V_f + \sigma_m \quad (3)$$

where σ_{Shear} is the shear strength of the interface and b is the width of the interfacial layer and D is the diameter of CNT. Laha *et al.*¹⁶¹ have found that the value of strength calculated by this formula (226 MPa) is quite large compared to experimentally measured value (83.1 MPa) which is due to reasons such as porosity, uniformity of interfacial product, and clustering of CNTs which are not considered in the model. Kim *et al.* have observed elongated clusters of CNT in the



13 a microstructure of CNT-Cu composites produced by spark plasma sintering and cold rolling⁴⁶ and b stress-strain curves showing two stage yielding process (reproduced with permission from Elsevier)

microstructure of Cu-CNT composites produced by spark plasma sintering of ball milled powders followed by cold rolling.⁴⁶ The stress-strain curve of the composite showed a two stage yielding process. Figure 13a shows the microstructure and Fig. 13b shows the corresponding stress strain curve. The first ($\sigma_{y,1}$) was matrix yielding and second ($\sigma_{y,2}$) yield strength was CNT cluster yielding and both could be modelled by the following equations

$$\sigma_{y,1} = \frac{V_f \sigma_m}{2} S_{eff} + \sigma_m \quad (4)$$

where $S_{eff} = S \cos^2 \theta + \left(\frac{3\pi-4}{3\pi}\right) \left(1 + \frac{1}{S}\right) \sin^2 \theta$ is the effective aspect ratio of an elongated CNT cluster oriented at an angle θ to the loading direction. The average S_{eff} is given as

$$S_{eff}^{Av} = \int_0^{\pi/2} S_{eff}(\theta) F(\theta) (2\pi \sin \theta) d\theta \quad (5)$$

where $F(\theta)$ is the probability distribution function of the misorientation of the CNT/Cu clusters which was obtained by image analysis. The second yield stress is given as

$$\sigma_{y,2} = \sigma_{y,1} (1 - V_f) + \sigma_f V_f \quad (6)$$

Yeh *et al.*¹⁶² have shown that a modified Halpin-Tsai equations fits the properties of phenolic-based composites well which could be used for MMC-CNT composites too

$$\sigma_c = \frac{1 + \xi \eta V_f}{1 - \eta V_f} \sigma_m, \text{ where } \eta = \frac{\alpha(\sigma_f/\sigma_m) - 1}{\alpha(\sigma_f/\sigma_m) + \xi}$$

The coefficients ξ and α can be determined and are influenced by the degree of dispersion of the CNTs in the matrix. The properties of the CNT composites are also affected by nanotube waviness as suggested by some finite element method simulations.¹⁶³ Strengthening due to dislocation generation by thermal expansion mismatch and precipitate strengthening by Orowan looping mechanism has been suggested as a mechanism of strengthening in Al-CNT composites⁵⁸ although observation of such mechanisms have not been made yet. But

the most important factor in achieving the predicted theoretical strengths is uniform dispersion of CNTs in the matrix.⁴⁷

Elastic modulus of CNT composites

Improvement in the elastic modulus of the composite is a result of the large tensile modulus of 350–970 GPa of CNTs.¹¹ Most of the research has also been carried out on polymer CNT composites which can be applied to metal matrixes. Various micromechanical models have been proposed to predict the elastic modulus of composite materials and they have been applied to CNT composites also.^{18,164–166} Some of the most commonly used models are discussed below. In the equations that follow, E stands for elastic modulus, σ stands for yield strength, V stands for volume fraction, k stands for bulk modulus, μ stands for rigidity modulus, ν stands for Poisson's ratio and the subscript m corresponds to matrix while f corresponds to fibre (CNT).

Combined Voigt-Reuss model

The elastic modulus for randomly oriented fibre composites is given by

$$E = \frac{3}{8} E_{||} + \frac{5}{8} E_{\perp} \quad (7)$$

where $E_{||} = V_f E_f + (1 - V_f) E_m$ is the longitudinal modulus (along the direction of the fibres) and $E_{\perp} = \frac{E_f E_m}{E_f(1 - V_f) + E_m V_f}$ is the transverse modulus (along the direction normal to the fibres).

Cox model

Elastic modulus of the composite according to this model is given by^{164,167}

$$E = \frac{1}{5} \eta_L E_f V_f + E_m (1 - V_f) \quad (8)$$

where $\eta_L = 1 - \frac{\tanh(\beta s)}{\beta s}$, $s = \frac{2l}{r}$ and $\beta = \frac{2\pi E_m}{E_f(1 + \nu_m) \ln(1/V_f)}$ where l and r are the length and radius of the fibre reinforcement.

Halpin-Tsai equations

Qian *et al.*¹⁶⁸ have used the Halpin-Tsai equations¹⁶⁹ to obtain the elastic modulus of randomly oriented fibre

composites as follows

$$E = \frac{3}{8} \left[\frac{1 + (2l/D)\eta_L V_f}{1 - \eta_L V_f} \right] + \frac{5}{8} \left[\frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right] \quad (9)$$

where $\eta_L = \frac{E_f/E_m - 1}{E_f/E_m + 2l/D}$, $\eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2}$ and l and D represent the length and diameter of the CNT respectively. Halpin-Tsai equations have been found to closely predict mechanical property in the case of small CNT concentrations in polymer and metal matrix CNT composites.^{18,90,162}

Hashin-Strikman model

This model based on variational principles^{170,171} provides the upper and lower bounds for the elastic modulus of a composite. It is independent of the shape of the particle. Laha *et al.*⁸⁷ found that experimental elastic modulus for Al-CNT composites prepared by PSF and HVOF and sintered for various times ranged between the upper and lower bounds.

Modified Eshelby model

Chen *et al.*¹⁷² have used modified Eshelby model to relate the properties in CNT composites to the volume fraction of CNTs as well as porosity. The longitudinal elastic modulus value is given by the formula

$$E_{11} = E_m \epsilon_{11}^m (\epsilon_{11}^m + V_f \epsilon_{11}^{CNT})^{-1} \quad (10)$$

The values predicted by the model were higher than those observed experimentally, the discrepancy attributed to the poor bonding between CNT and matrix.

Dispersion based model

All the above equations assume that the CNTs are distributed uniformly which is seldom the case, especially at large concentrations. Recently, Villoria and Miravete¹⁷³ have developed a model to take into account clustering phenomena in CNT composites. They have developed a model to compute the properties of CNT clusters which could be applied to any type of fibre reinforcement where clustering is present. The overall properties of the composite are obtained by considering it as a dilute suspension of the clusters (properties with subscript dsc) in the matrix

$$k_{dsc} = k_m + \frac{(k_{Cluster} - k_m)c_c}{1 + \frac{k_{Cluster} - k_m}{k_m + 4\mu_m/3}} \quad (11)$$

$$\mu_{dsc} = \mu_m \left[1 - \frac{15(1 - v_m) \left(1 - \frac{\mu_{Cluster}}{\mu_m} \right) c_c}{7 - 5v_m + 2(4 - 5v_m) \frac{\mu_{Cluster}}{\mu_m}} \right] \quad (12)$$

where c_c refers to the volume fraction of clusters which is related to the overall CNT fraction by $V_f = c_f c_c$, c_f being the CNT concentration in of a cluster. This model has been shown to predict the values more accurately compared to Cox model in the case of epoxy CNT composites.¹⁷³

Mechanical properties of different MM-CNT systems

The critical issues in mechanical properties in MM-CNT composites are the homogeneous distribution of CNTs in the metal matrix, and the interfacial reaction and bonding to the matrix, to work as an effective

reinforcement. That is why the processing techniques were also discussed critically in the light of these phenomena. In the following sections, brief reports, specific to different MM-CNT systems, on improved mechanical properties are presented, with a highlight on the significant achievements and their probable mechanisms. Figure 14 shows the percentage enhancement in mechanical property of MM-CNT systems as a function of CNT content. The non-linearity in the trend with CNT content owes to the variance in the microstructural features, defects, flaws and porosity level caused by processing. The variance is further aggravated by the difficulty in measuring the mechanical properties of CNT-reinforced composites caused by difficulties of preparing mechanical testing samples.

Aluminium-CNT composites

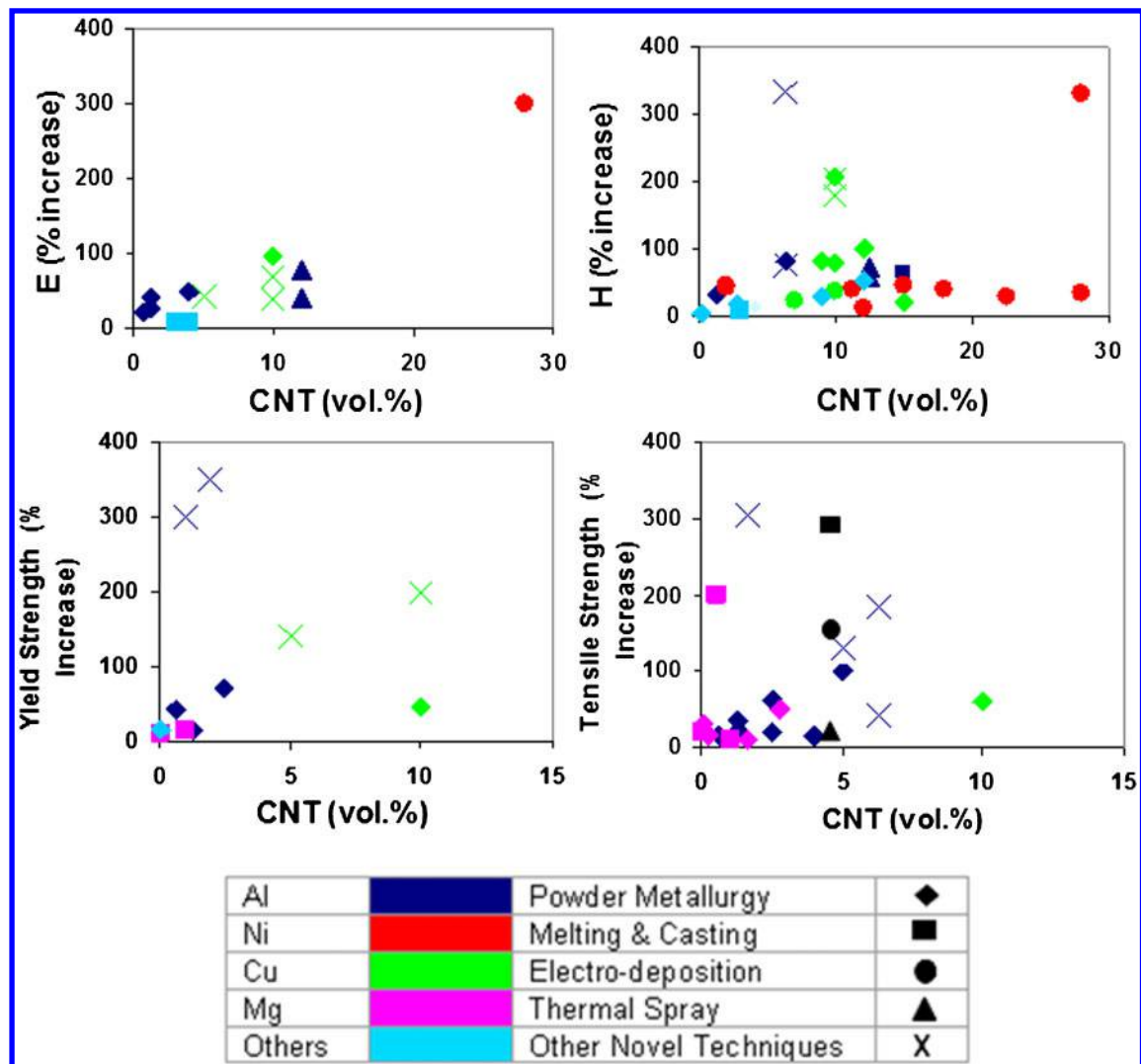
Kuzumaki *et al.*⁵⁷ were the first researchers to show a 100% increase in the tensile strength with 10 vol.-% CNT addition. Researchers have tried to incorporate 1–6.5 vol.-%CNTs into a free standing Al-CNT composite structure by the powder metallurgy route^{37,63} accompanied by SPS⁶⁰ and/or hot deformation.^{59–61,86,88,145,146,148,158,174} A maximum of 129% increase in the tensile strength has been reported with the addition of 5 vol.-%CNT addition.⁶⁰ On the contrary, Salas *et al.*¹⁴⁵ have reported deterioration in hardness in a shock-wave-consolidated Al-5 vol.-%CNT composite. Agglomeration of CNTs in the matrix and weak interface bonding led to deterioration in the properties.

Carbon nanotube reinforcement to composite coatings prepared by Laha *et al.*^{86,87,161} using thermal spraying methods, have been shown to improve the hardness by 72%, elastic modulus by 78%, marginal improvement in tensile strength and 46% decrease in ductility with 10 wt.-%CNT content. Sintering (673 K, 72 h) of the sprayed coating has been reported to further increase the elastic modulus of the composite coating by 80%, which has been attributed to reduction in porosity and to residual stress.⁹⁵ Al-12 vol.-%CNT composite produced by plasma spray processing shows ~40% increase in elastic modulus and CNT addition has been reported to increase the elastic recovery of the composite.⁸⁹ Carbon nanotube reinforced Al composite fabricated by cold spraying has been shown to behave heterogeneously with respect to mechanical properties, and no quantification on enhancement of the strength has been provided as a result of CNT addition.⁹⁰

Noguchi *et al.*¹⁵⁸ have reported a 350% increase in the compressive yield strength with 1.6 vol.-%CNT addition, which, is due to a very homogeneous distribution of CNTs obtained by the nano-scale dispersion method. He *et al.*²⁷ have also emphasised homogeneous distribution and good interfacial bonding of CNTs growing them directly on Al powder through the CVD method before compacting and sintering them. They also have achieved 333% increase in hardness and 184% increase in tensile strength with 6.5 vol.-%CNT addition.²⁷ Hence, it is clear that homogeneous distribution of CNTs and strong bonding with the matrix are the main means to control the mechanical properties of the MM-CNT composites.

Copper-CNT composites

Reports on Cu-CNT systems deal with improvement in mechanical as well as electrical properties. Powder metallurgy technique, comprising of compaction and



14 Improvement in mechanical properties of different MM-CNT composites as a function of CNT content, classified according to processing routes employed

sintering, helps increasing the hardness up to 20% with 15 vol.-%CNT addition.^{52,56} Carbon nanotube reinforcement coated with Ni improved bonding with the Cu matrix and resulting in about 80–100% increase in the hardness for 9–12 vol.-%CNT addition.^{25,175,176} Spark plasma sintering of Cu-10 vol.-%CNT composite has improved the hardness by 79% with a further improvement up to 207% resulted from rolling of the SPS composite. This improvement is attributed to better dispersion and reinforcement induced by SPS and rolling.^{45,46}

Molecular level mixing has also been employed to prepare composite powder with better dispersion of CNTs in Cu. An improvement of 200% in the yield strength and 70% in the elastic modulus was obtained using SPS of molecular-level-mixed-powder.⁴⁷ Cu-CNT composite, processed by cold rolling of sandwiched layers of metal and SWCNT shows an 8% improvement in tensile strength and a 12.8% increase in elastic modulus.¹⁴⁴ The improvement is not very great, but the processing route has a capability to be a very popular one, due to its ease if further improvement in properties is possible.

Nickel-CNT composites

Except for a very few, all of the studies on Ni/Ni-alloy-CNT composites films/coatings have been processed

through electrochemical or electroless deposition techniques. Hence, most of the studies report the hardness value as a measure of mechanical properties. Some of these studies do not mention CNT content of the coatings. This makes it difficult to compare the improvement in mechanical properties among different studies. C.S. Chen *et al.*¹²⁸ and X. Chen *et al.*¹²² have reported the maximum improvement in the hardness by 68% for the composite coating deposited by electroless technique. Deng and co-workers have reported improvement of hardness of the electroless composite coating by 44% with addition of 2 vol.-%CNT.^{129,133} On the contrary, Chen *et al.*¹²⁴ have reported an improvement in hardness with addition of 11% with 12 vol.-%CNT addition. This might have been caused by agglomeration of CNT in the bath due to increase in its concentration. Shen *et al.*^{134,135} observed an extraordinary 300% improvement in the hardness and elastic modulus of Ni-CNT composite coating prepared by electroless deposition technique for microelectromechanical system (MEMS) application. The improvement in mechanical properties is attributable to the acid oxidative method used for surface modification of the CNTs that keep them dispersed and suspended uniformly in the bath and in the coating.

A few researchers have also prepared a free standing Ni-CNT composite structure using electrochemical co-deposition technique and have measured its tensile strength. Sun *et al.*¹⁰⁹ achieved a significant increase in the ultimate tensile strength of 320% for SWCNT and 270% for MWCNT addition in electrodeposited Ni Films. However, this study did not mention the CNT content. Jeon *et al.*¹⁷⁷ have also achieved a lesser improvement in properties, because of CNT agglomeration in the bath in the absence of ultrasonic agitation. Hence, for both the Ni-CNT system and electrodeposition technique also, the main key to improvement of mechanical properties is the uniform dispersion of CNTs in the bath and in the coating.

Magnesium-CNT composites

The number of reports on Mg-CNT composite is fewer as compared to those on Al, Cu and Ni-CNT composites. Some of these studies are restricted to the effect of CNT addition on hydrogen storage properties of the composite.³³ Li *et al.*⁷⁴ have reported a maximum of 150% increase in the tensile strength of the Mg-CNT composite with 0.55 vol.-%CNT prepared through the melting-and-casting route. Such a high increase in mechanical properties is attributable to Ni-coating on CNTs before addition, which helps in improving wetting with the matrix. Morisada *et al.*¹⁴⁷ have prepared Mg-CNT composites through friction-stir welding, and reported a 90% increase in hardness, though the CNT concentration and its gradient were not mentioned. Goh *et al.* have reported a 15% increase in yield strength for 1 vol.-%CNT composite prepared through casting route.⁷⁵ They have also studied the fatigue behaviour of Mg-CNT composite and found out that CNT addition decreases the number of cycles to failure.⁷⁷ A recent study on Mg-0.1 wt.-%CNT composite through casting route resulted in a 36% increase in the compressive strength.¹⁷⁸ There are too few studies on Mg-CNT composites to make any significant comment on the effect of the processing route or CNT content on the improvement in the mechanical properties.

Other metals/alloys-CNT

Carbon nanotubes have also been used as reinforcement for few other metals, alloys, intermetallics and BMG. These are scattered efforts and hence will be discussed together in the following paragraphs.

Ti-CNT composite, produced by powder metallurgy, shows 450% improvement in the hardness and 65% increase in elastic modulus, though the CNT content of the composite was not mentioned.³⁹ Zeng and colleagues also have observed 200% increase in the hardness of Ti-Ni shape memory alloy with 4.5 wt.-%CNT addition.¹⁷⁹

Researchers have also used CNTs as reinforcement in BMGs. Ti-based BMG-CNT composites, processed by powder metallurgy, have shown a 53% increase in hardness,^{42,43} but reinforcing Zr-based BMG with CNT has not been proven to be so successful. Such composites, prepared by melting-and-casting technique, show ~10% improvement in hardness and elastic modulus.^{72,73} Based on these few studies, superiority of the powder metallurgy route over the casting route for BMG-CNT composites cannot be inferred conclusively.

Nai *et al.*^{69,70} have attempted to improve the mechanical properties of Sn-based soldering alloys using addition of a mere 0.04 wt.-%CNT addition, fabricated

through sintering and extrusion. A marginal increase in the hardness was observed, while a 31% improvement in tensile strength was reported. Kumar *et al.*⁷¹ have achieved a 50% increase in tensile strength for their soldering alloy with only a 0.01 wt.-%SWCNT content. Better mechanical properties of SWCNT might be a probable cause to achieve larger improvement in mechanical properties in the latter case.

A single study on compacted, sintered and repressed Ag-CNT composites resulted in a maximum of 27% increase in hardness with 9 vol.-%CNT addition.³⁰ Lowering of mechanical properties at even higher concentration of CNTs has been explained in terms of agglomeration of CNTs. Carbon nanotubes have also been used as reinforcement for intermetallics. Pang and co-workers have reported 30 and 11% increase in hardness and compressive strength respectively, of Fe₃Al intermetallic, with 3 wt.-%CNT addition through powder metallurgy.^{41,51}

To summarise, as seen from the plots of the mechanical properties versus CNT content of composites in Fig. 14, novel techniques seem to be more successful in improving the mechanical properties of the composites because of improved dispersion and interface bonding. There is no direct correlation between CNT content and an improvement in mechanical properties because of the presence of defects induced by various processing techniques and a lack of uniformity in mechanical testing methods.

Interfacial phenomena in CNT-reinforced MMCs

Interfacial phenomena and chemical stability of the CNTs in the metal matrix are critical for several reasons. The fibre-matrix stress transfer¹⁸⁰ and the interfacial strength¹⁸¹ play an important role in strengthening. The applied stress is transferred to the high strength fibre through the interfacial layer, so that a strong interface would make the composite very strong but at the expense of ductility of the composite. A weak interface would lead to lower strength and inefficient utilisation of fibre properties by facilitating pullout phenomena at low loads due to interface failure. Wetting of the fibre by the liquid metal is essential. Non-wetting will lead to poor interfacial bonding. Interfacial reactions leading to formation of an interfacial phase can improve wetting if the liquid has a lower contact angle with the phase forming due to the reaction. A lot of work has been carried in reinforcing aluminium matrix with carbon fibres. Interfacial reactions and degree of wetting of the fibres have been shown to affect the properties of the composite.¹⁸²⁻¹⁸⁴ Formation of aluminium carbide (Al₄C₃) has been observed at the interface in liquid metal infiltrated aluminium silicon alloy composites reinforced with carbon fibres containing 7 (Ref. 185) and 13 wt.-% Si (Ref. 186). Vidal-Setif *et al.* have shown reduction in strength and premature failure of 75 vol.-% carbon fibre reinforced A357 alloy due to formation of Al₄C₃ and presence of brittle Si particles.¹⁸⁷ Formation of Al₄C₃ needs to be avoided. However, there have been reports of improvement of the properties of Al-SiC_p composites due to limited amounts of Al₄C₃.¹⁸⁸ In the case of CNT-reinforced aluminium composites, Kwon *et al.* suggest that the Al₄C₃ helps in load transfer by

pinning the CNTs to the matrix.⁴⁹ The extent and nature of chemical reactions can be changed by either by controlling the chemistry of the matrix¹⁸⁹ or by using coatings on reinforcements.^{190,191}

Because of their perfect structure, CNTs are expected to be quite stable chemically compared to carbon fibres. Unless otherwise specified, CNT in this section refers to MWCNT. It is obvious that reaction of SWCNTs with metal leading to carbide formation would lead to destruction of the tubular structure. Comparison of the intensity of the (111) peak of the XRD pattern of cobalt, after a 10 h annealing treatment with various forms of carbon at 1000°C shows that the chemical interaction of layered graphite was the lowest followed by SWCNT, MWCNT and activated carbon respectively.¹⁹² Layered graphite has perfect structure of sp^2 hybridised carbon atoms arranged in ABABAB... stacking sequence which would make it less reactive chemically. Defects in activated carbon and in CNTs provide sites for chemical reactions to occur. Reaction of CNT with metal matrixes leading to carbide formation have been observed by many researchers. In fact, Dal *et al.* have utilised reactions between volatile oxides/halides with CNTs as a means of synthesis of various carbide nanorods, namely TiC, NbC, Fe₃C, SiC and BC_x.¹⁹³ Shi *et al.* have synthesised WC-CNT composites by reduction and carbonisation of WO₃ precursors produced after a molecular level mixing followed by calcination.¹⁹⁴ Kuzumaki *et al.* have observed formation of TiC in hot pressed Ti-CNT composites.³⁹ Ci *et al.* have shown the formation of Al₄C₃ on annealing CNTs (upon which aluminium was deposited by magnetic sputtering process) at temperatures above the melting point of aluminium.¹⁴³ It was found that carbide formed at amorphous areas of CNT via incomplete graphitisation. The small size and amount of Al₄C₃ formed was due to the smaller availability of defective sites and amorphous carbon. The formation of carbide also depends on the processing techniques. Some researchers have reported no formation of Al₄C₃ in the case of solid state processes such as extrusion.⁶⁴ In our research group, we have shown formation of SiC due to reaction between Al–23 wt-%Si alloy and CNTs⁹⁴ while Al₄C₃ is formed when the matrix is Al–11.6 wt-%Si alloy.⁸⁹ Thermodynamic and kinetic analysis of the reactions confirmed the above observations.¹⁹⁵ A study on chemical stability of CNT with temperature in Al (2024 alloy)-CNT composite has been carried out by Deng and co-workers.¹⁹⁶ They found no existence of CNT in the matrix when heated up to 1073 K and XRD results show that CNT fully converts to Al₄C₃. Figure 15 shows the TEM images of CNT matrix interfaces in various composites. Different interfacial carbides may result in significantly different mechanical properties of the composites since the shear strength of the carbides determines the stress that could be transferred to the CNTs.

An important aspect of composite fabrication is wetting of the reinforcement by the liquid alloy. Wetting is related to the surface energies of the interacting species by the Young's equation and the Young–Dupre relation given below

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}} \quad (13)$$

$$W_A = \gamma_{LV}(1 + \cos \theta) \quad (14)$$

here θ is the contact angle and γ_{SV} , γ_{LS} and γ_{LV} are the solid/vapour, solid/liquid and liquid/vapour surface energies and W_A is the work of adhesion between the liquid and the substrate. Carbide nucleation and growth were discussed by Landry *et al.*¹⁹⁷ and they were applied to Al–23 wt-%Si composites reinforced with CNTs by Laha *et al.*⁹⁴ The critical thickness for carbide nucleation is given by the equation

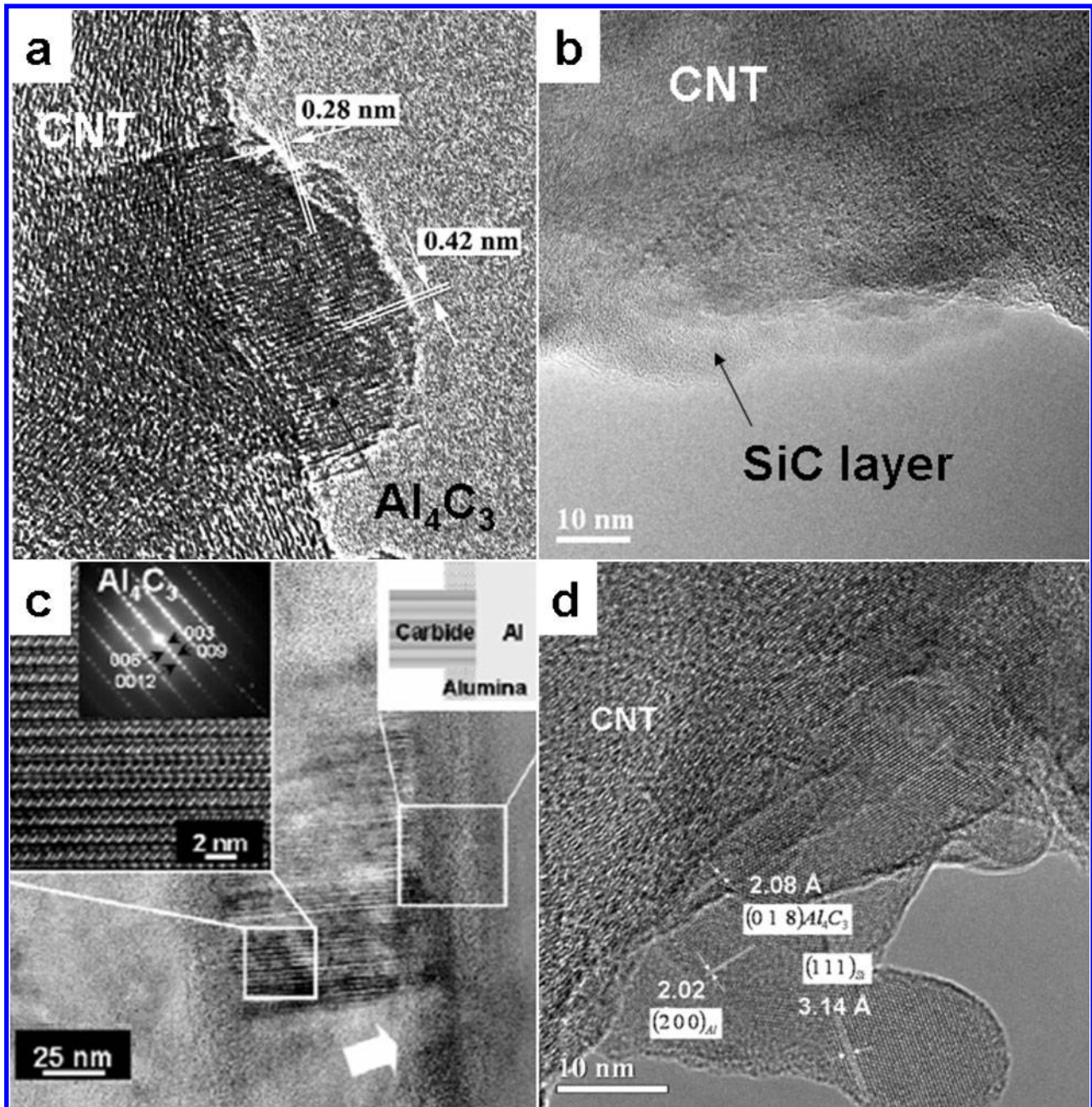
$$t_{\text{crit}} = -V_M \frac{\Delta\gamma}{\Delta G^f} \quad (15)$$

here, V_M is the molar volume of the carbide formed, ΔG^f is the free energy of formation per mole of carbide and $\Delta\gamma = \gamma_{MC/CNT} + \gamma_{MC/Alloy} - \gamma_{Alloy/CNT}$ is the increase in total surface energy as a result of formation of new interfaces. MC stands for metal carbide. When carbide thickness reaches t_{crit} , further growth is energetically favourable. This might result in a decrease in contact angle and an improvement in wetting. Smaller t_{crit} values therefore indicate easy formation of carbide as well as better wetting. The surface tension of CNTs (γ_{SV}) is 45.3 mJ m⁻², which is similar to that of the carbon fibre.¹⁹⁸ It has been shown that a liquid with surface tension between 100 and 200 mN m⁻¹ results in good wetting with CNT.^{199,200} Molten aluminium silicon alloys have a surface tension of ~800 mN m⁻¹. Hence, it is expected that the wetting between Al–Si alloys and CNTs will be poor. It has been experimentally observed in sessile drop experiments by Landry and co-workers that Al–Si alloys do not wet graphite in the beginning and exhibit a large contact angle of ~160°. ^{197,201} Al₄C₃ and SiC formation reduces contact angles to 45 and 38° respectively.²⁰² Hence, formation of interfacial carbides favours wetting that will promote infiltration of liquid melt into CNT performs. The reaction at the triple point between liquid alloy and CNT leads to formation of carbide and subsequent spreading of metal. Minimal reaction of CNT is desirable in order that efficient stress transfer can occur without much damage to the CNT structure.

Dispersion of CNTs in a metal matrix

Uniform dispersion of CNTs has been the main challenge in CNT-reinforced composites be they polymer, ceramic or metal matrix. This is due to the fact that CNTs have tremendous surface area of up to 200 m² g⁻¹, which leads to formation of clusters due to van der Waals forces. The elastic modulus, strength and thermal properties of a composite are related to the volume fraction of the reinforcement added. Hence, a homogeneous distribution of reinforcement is essential as it translates into homogeneous properties of the composite. Clustering leads to concentration of reinforcement at certain points and this could lead to worsening of overall mechanical properties.

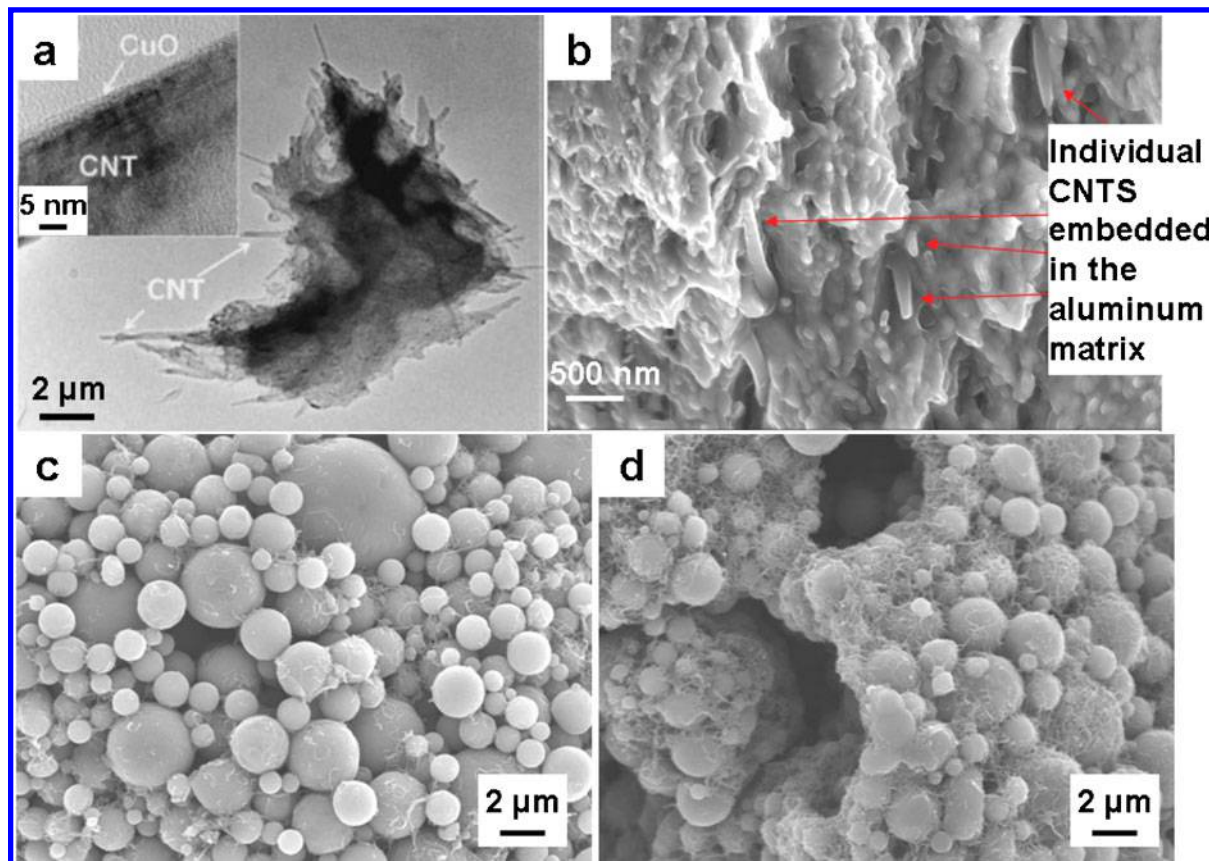
Most of the early research on fabrication of CNT composites used blending for adding CNTs to metals.^{26,30,86} Blending by mixing is not effective in dispersing the CNTs. Several researchers have observed that mechanical properties (wear, hardness, tensile strength) deteriorate for composites made by blending of larger concentration of CNTs.^{26,30,56,70} The



15 Images (TEM) of CNT/matrix interface from various composite systems, namely *a* annealed Al-deposited on CNT showing Al_4C_3 ,¹⁴³ *b* SiC layer in Al-23 wt-%Si composite containing 10 wt-%CNT,⁹⁴ *c* Al_4C_3 in composites obtained by hot extrusion of spark plasma sintered samples⁴⁹ and *d* Al_4C_3 in plasma sprayed Al-11.6 wt-%CNT composite having 10 wt-%CNT (reproduced with permission from Elsevier)

worsening in the properties is due to the inability to obtain uniform distribution of CNTs at large volume fractions. Several methods have been developed to uniformly distribute the CNTs in metal matrixes. Noguchi *et al.* have suggested an NSD process which results in uniform dispersion of CNTs on Al powder.¹⁵⁸ A sevenfold increase in the compressive yield strength was observed for 1.6 vol.-% CNT addition. Esawi *et al.* have shown that excellent dispersion of CNTs in Al powders can be achieved by ball milling.³⁵ However, large particles up to 1 mm in diameter resulted from the milling action. Choi *et al.* used hot extrusion for consolidating ball milled powders and aligning the CNTs in the extrusion direction.⁶⁴ Cha *et al.* have developed a novel molecular-level mixing method for dispersing CNTs.⁴⁷ He *et al.*²⁷ have used the CVD

method to grow CNTs on Al powders which were then used to fabricate a 5 vol.-% composite by pressing and sintering. Our research group have shown that spray drying can be used to uniformly disperse CNTs in microsized Al-Si powders.⁸⁹ Spray drying also led to increased flowability which enabled fabrication of bulk composite cylinders up to 5 mm in thickness by plasma spray forming. Figure 16 shows the images of the powders obtained by the various techniques and uniform distribution of CNTs. The methods suggested above have their own drawbacks. The NSD process leads to good dispersion of CNTs on the particle surface, so that the level of dispersion is dependent on the particle size used. Ball milling leads to excellent dispersion but might result in the damage to CNTs. Molecular-level-mixing methods might lead to oxide



16 *a* image (TEM) of CuO/CNT powder prepared by molecular level mixing method,⁴⁷ *b* image (SEM) of the fracture surface of Al/CNT powder prepared by ball milling for 48 h,³⁵ and image (SEM) of spray dried Al-Si agglomerates containing *c* 5 wt-%CNT and *d* 10 wt-%CNT (reproduced with permission from Wiley Interscience and Elsevier)

impurities because of incomplete reduction of the powders. While the quality of dispersion is important, the processes used should also be amenable to bulk production of powders.

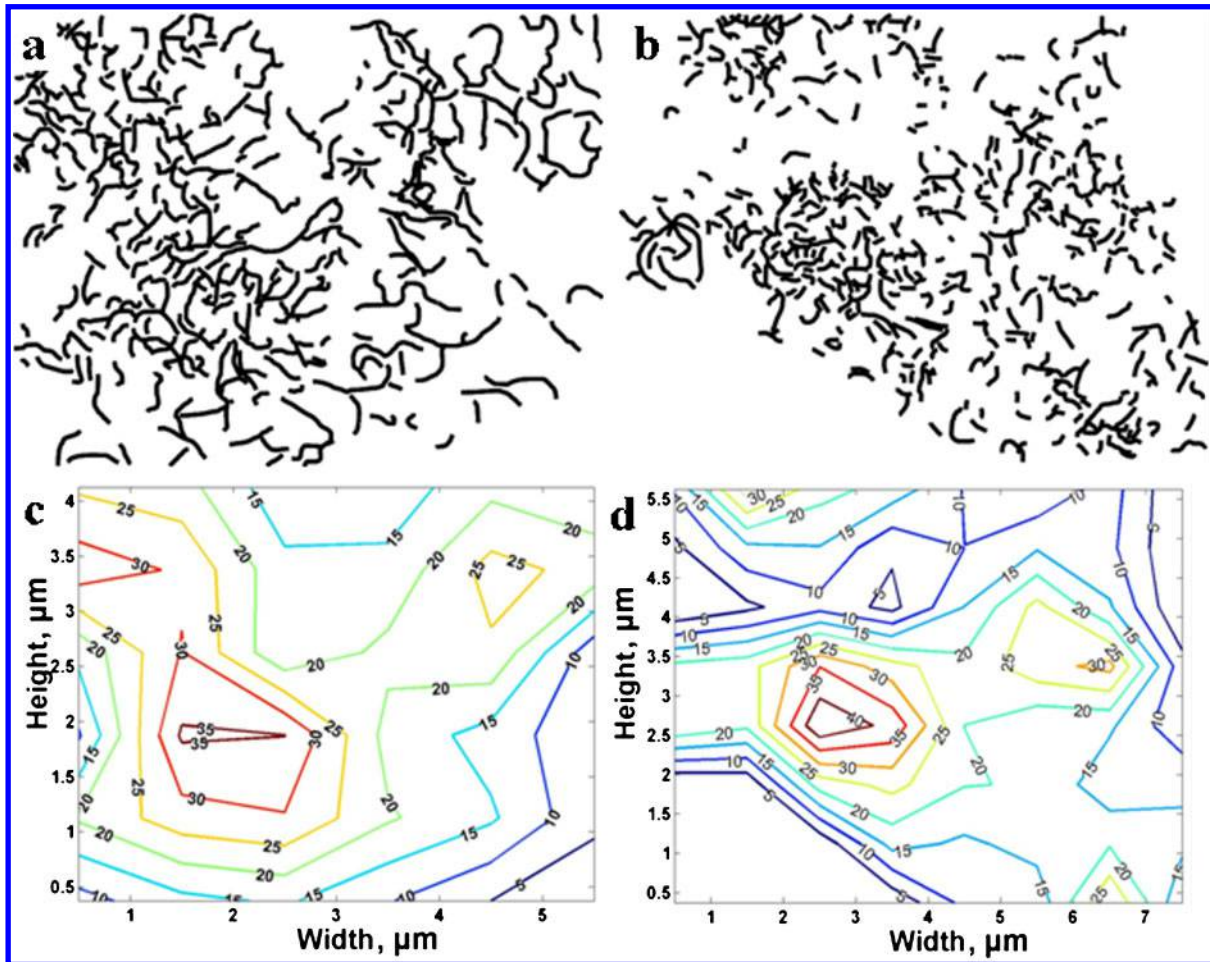
Quantification of the degree or quality of CNT reinforcement is important. It helps in comparing various microstructures and the effectiveness of various methods for dispersion of CNTs in composites. Dirichlet tessellation has been used in the quantification as well as to study the effect of dispersion in composite materials.^{166,203,204} However, there has been hardly any study in the quantification of dispersion in carbon nanotube composites. The majority of the researchers mention uniform CNT dispersion in the composites which is based on visual examination of the microstructure. Recently, Luo and Koo proposed a method based on the statistical distribution of horizontal and vertical separation distances between the peripheries of the particles/carbon fibres in a cross-sectional image of the composite.²⁰⁵ A log-normal distribution was found to fit the distribution obtained. Two parameters, $D_{0.1}$ and $D_{0.2}$, were defined representing the probability that the values lied between $\mu \pm 0.1\mu$ and $\mu \pm 0.2\mu$ of the values respectively, μ being the average distance. The larger the values of $D_{0.1}$ and $D_{0.2}$ the better the distribution, since it meant uniform separation of the filler materials. Recently, Pegel *et al.*²⁰⁶ have used spatial statistics on TEM images of polymer CNT composites to study the variation of the area fraction of CNTs as a function of radius of the nanotubes. They showed that the variation of the area and spherical contact distribution function

converged to 100% faster in case of clustered CNT configurations.

Our research group has suggested a simple method to quantify the spatial distribution of CNTs in nanocomposites.²⁰⁷ Figure 17 shows the binary images of CNT distribution (*a* and *b*) gathered from actual SEM images of fracture surfaces and the contour plot of the variation of the CNT content along the micrograph (*c* and *d*) for 5 wt-% and 10 wt-%CNT containing coatings, respectively, obtained by plasma spraying. From the plot of the variation of the maximum area fraction of CNT in a cell versus the number of divisions carried out, a dispersion parameter is derived. From the distribution of distance between the centres of nearest neighbours (obtained using Delaunay triangulation) a clustering parameter was also derived. A larger dispersion parameter and smaller clustering parameter indicates good quality of CNT dispersion in the micrograph.²⁰⁷ This approach was used for correlating the elastic modulus values obtained by nanoindentation with the microstructure in the case of cold sprayed Al-CNT composite coatings.⁹⁰ Use of the above methods is very useful in differentiating processes based on their ability to disperse CNTs in the microstructure.

Other properties affected by CNT reinforcement in metals

Several researchers have studied the effect of CNT in MMCs on properties other than mechanical ones. Non-mechanical properties that have been investigated most are electrical, thermal and wear properties. Few



17 *a* and *b* binary schematic images of SEM micrographs, *c* and *d* plot of CNT distribution in Fig. 17*a* and *b* with contours showing areas of same CNT fraction

other properties, such as corrosion resistance, sensing capability, etc. were also investigated. Following subsections will describe the effects of CNT reinforcement on these properties.

Electrical and Electronic Properties

Owing to excellent electrical properties, evinced by the current carrying density of $\sim 4 \times 10^9$ A cm⁻² (three orders of magnitude higher than Cu or Al),²⁰⁸ CNTs have been used as reinforcement to metals for enhancement of electrical properties. Al-12.5 vol.-%CNT composite prepared by powder metallurgy³⁶ displayed increased electrical resistivity by 66%. The authors have also reported an abrupt drop in resistivity to almost zero at 80 K, though no suitable explanation for this behaviour was provided. A recent study by Yang *et al.*¹¹¹ showed at up to 10 wt.-% SWCNT addition, that the electrical resistivity of Cu-CNT composites remains same as that of pure Cu. The observation by Feng *et al.*³⁰ for Ag-CNT composites also showed a marginal increase in the electrical resistivity at up to 10 vol.-%CNT addition. The sharp increase in the electrical property beyond 10 vol.-%CNT is attributed to the increase in interfacial area and strain in the matrix due to presence of CNT clusters, both of which hinders electron transfer through the composite.

Few research groups have studied the suitability of MM-CNT composites in different electrical applications. Shen and co-workers^{134,135} have found the Ni-P-CNT composite to be a better choice for MEMS

application because of their favourable E/ρ ratio which provides the best combination of strength and power efficiency. Ni-CNT composites have also shown their capability to be used as field emission displays, showing uniform images with improved quality.¹³² Chai *et al.*¹¹⁵ have used arrays of CNTs as the matrixes to fill Cu in the channels and thus form a Cu-CNT composite for the interconnect applications. Few studies have reported use of Si-CNT composites as the anode materials for Li-ion batteries, but CNT addition in Si was not related to improvement in electrical properties. Carbon nanotubes were added to obtain a porous yet strong structure that can accommodate the volume change of Si during charging and discharging cycles.^{150,151,209}

Thermal properties

Carbon nanotubes are known to have very high thermal conductivity²⁸ of 1812 ± 300 W m⁻¹ K⁻¹ and very low coefficient of thermal expansion⁶² (CTE) ~ 0 . Hence, MM-CNT composites have a great potential to be used for thermal management. Tang and co-workers²¹⁰ reported 63% decrease in CTE with 15 vol.-%CNT addition to Al matrix. Further increase in CNT content increases CTE, which has been attributed to the agglomeration of CNTs. Deng *et al.*⁶² have obtained 12% reduction in CTE with 1.28 vol.-%CNT addition in Al, which has been attributed to the larger surface area of CNTs that creates larger interface and thus restricts thermal expansion of the metal matrix. Goh *et al.*⁷⁷ have shown the gradual decrease in CTE of

the Mg matrix composite with CNT addition up to 0.30 wt-% where the CTE is decreased by 9% of the base material. Increase in the thermal conductivity of Ni-0.7 wt-%CNT composite by 200% with has been attributed excellent dispersion and bonding of CNTs forming defect free interface with matrix by electro-deposition technique. W-Cu alloy also shows 27.8% increase in thermal conductivity with 0.4 wt-%CNT addition.²⁸ But thermal conductivity decreased with further increase in CNT content as the density of the composite decreases due to increase in pore volume.

Thermal resistance is a very critical issue for interconnects and integrated circuits in microprocessors as they require fast heat dissipation for better performance. Ngo *et al.*¹¹⁷ and Chai *et al.*¹¹⁵ have shown decrease in thermal resistance by ~62% when Cu is filled into the voids of CNT arrays. Wang *et al.*²¹¹ have reported that Si coating on CNTs increase their thermal stability by increasing their oxidation starting temperature from 844.2 to 949.3 K.

The improvement in thermal properties of MM-CNT composites largely depend on the distribution of CNTs and their bonding with the matrix. Hence CNT content and the processing route are the two vital factors that determine the thermal properties of the MM-CNT composites.

Wear and friction properties

Wear properties are more critical for coatings and hence most of the wear studies are on Ni-CNT composite coatings formed by electro-deposition techniques.^{99,122} There are few studies on Cu-CNT^{25,48,56,119,175} and Al-CNT⁷⁹ composites. All of these studies have reported a decrease in the coefficient of friction (COF) and increase in the wear resistance with addition of CNTs to the metal matrix. The decrease in the COF has been attributed to the lubricating nature of the MWCNTs caused by the easy sliding of their walls, which are attached by weak van der Waals forces. The improved resistance to wear is attributed to role of CNTs as spacers preventing the rough surfaces of the matrix from contact with the wear pin.

Deng and his group^{129,133} have reported a maximum of 83% decrease in the wear volume for electroless plated Ni-P-CNT composite coating with a 2 vol.-%CNT content, whereas the COF reduced was by 60%. It has been noted that COF continues decreasing with increasing CNT content in the composite but the wear rate starts increasing after a critical concentration is reached.²⁵ This phenomenon can be attributed to the clustering of CNTs in matrix beyond the critical concentration. Clusters provide enough lubrication to lower the frictional coefficient, but cannot resist wear as they are easier to get detached from the surface than homogeneously dispersed nanotubes.

Tu and co-workers^{25,104} have reported a maximum improvement of wear properties in a Cu-CNT composite processed through powder metallurgy technique using Ni-coated CNTs. They have obtained a 91% reduction in COF and a 140% reduction in the wear rate with 16 vol.-%CNT addition. Molecular-level-mixing technique has also helped improving the wear properties of Cu-CNT composite by resulting in a 76.9% decrease in wear loss with 10 vol.-%CNT addition.⁴⁸ Homogeneous CNT dispersion is the prime reason for great improvement in wear properties of the composites. The only report on wear properties of Al-CNT composite

processed through pressureless infiltration technique shows a 22% decrease in COF and a 25% decrease in the wear rate with 20 vol.-%CNT addition.⁷⁹

Carbon nanotube reinforcement plays a major role in improvement of wear resistance and decrease in COF of the MMCs. Effect of CNTs on wear properties of Ni-CNT composites has been studied extensively, but needs further investigations for other MM-CNT systems to optimise the relationship between the CNT content and its wear resistance.

Corrosion properties

Most of the corrosion studies are performed on electrodeposited Ni-CNT composite coatings^{32,33,101,110,125,126} with only a single study on Zn-CNT composite coating.²¹² Electrodeposited coatings are more prone to corrosion due to the presence of pores and voids. All the studies have shown an increase in the corrosion resistance of the composite coatings with CNT addition. Yang *et al.*^{125,126} have reported increase in pitting potential by 24% with 5 wt.-%CNT addition, whereas Chen and colleagues¹⁰¹ have reported a 75% increase in the same without mentioning CNT content. Chen *et al.*¹⁰³ have also measured the corrosion rate of the composites to be 5 times lower than the Ni coating. Praveen *et al.*²¹² have reported the service life of Zn-CNT composites to be more than double of that of only Zn coating. All these studies indicate the improvement in corrosion resistance due to two reasons. First, the chemical inertness of the CNTs that helps forming a passive layer on the coating surface. Second, CNTs help filling up voids and pores of electrodeposited coatings leaving no place for initiation of localised corrosion. Apart from these, Yang *et al.*¹²⁵ have also reported that CNTs in the Ni matrix hinder growth of corrosion pits.

Hydrogen storage properties

Hydrogen-storage capacity has been studied for MM-CNT composites by very few researchers. Chen *et al.*³³ reported the effect of CNT content on the hydrogen storage capacity of Mg-CNT composites. Mg-CNT composites have a better hydrogen-storage capacity and absorption-desorption rate than other hydrogen-storage materials. At higher temperatures, composite with 5 wt.-%CNT shows better hydrogen-storage capacity than 20 wt.-%CNT, attributable to the breakage and amorphous carbon content of the CNTs in the latter. However, Huang and co-workers³² did not observe any improvement in hydrogen storage capacity of Mg-based composites with addition of CNT over carbon black and graphite. Ishihara *et al.*¹⁵² have reported large hydrogen storage capacity of Si-CNT composite material formed by chemical vapour deposition of tetramethylsilane. Research on the hydrogen storage capacity of metal matrix CNT composites is at an early stage with very little available information.

Applications as sensors and catalysts

A special class of MM-CNT composites is used as sensors or catalysts. These composites are basically a paste of metallic nano-particles with CNTs in liquid medium, either used directly as electrodes or dried as a film to be used as electrodes in sensor devices. Such mixture is usually termed as 'aggregates', but they have been reported as composites and hence been included in this review. All of such reported systems are Cu-CNT

composites, where the paste is prepared mostly using mineral oil and used for the detection of carbohydrates,^{213,214} glucose,¹¹⁴ amino acids and albumins,^{154,156} trinitrotoluene¹⁵⁷ and ammonia.¹⁵⁵ These studies have reported better sensitivity, reproducibility, reduced response time and better stability of the sensors with CNT addition. Male *et al.*²¹³ have reported a 400% increase in the sensitivity for carbohydrate detection using CNTs with Cu nanoparticles in the sensor electrode. Kang and co-workers¹¹⁴ have reported similar observations for glucose sensors and have explained the behaviour in terms of an increase in the available electro-active surface area due to presence of CNTs, which prevents Cu nanoparticles from agglomeration.

Capability of CNTs as reinforcement in metals to improve the composite performance, in terms of properties other than mechanical strength, has not gained a very significant attention till date. Still, quite a fair number of studies show improvement in wear resistance, electrical and thermal conductivity and decrease in coefficient of thermal expansion in composite as a function of CNT addition. Exploration of the effect of CNT addition on other properties, such as corrosion resistance, hydrogen storage, etc., are still at a very early stage, but preliminary evidence shows a bright prospectus that will foster further research in the field of metal matrix-CNT composites for various applications.

Potential applications of CNT-reinforced metal matrix composites

Carbon nanotube reinforced MMCs are at a research stage. To the authors best knowledge there are **no commercial applications** or commercial products based on CNT-reinforced MMCs available **till now**. However, there are several potential applications for these composites. These applications have been summarised in Table 1. Carbon nanotubes have better strength and stiffness than carbon fibres and hence have the potential in replacing carbon fibre reinforced MMCs in various applications. Overcoming the challenges in processing, as described in the previous sections, will result in efficient use of the mechanical properties and will result in the strongest MMCs known to mankind.

Summary and scope for future studies

It can be gauged from the increasing number of publications in the area of CNT-reinforced MMCs that

the interest on this topic has been increasing in the last six years. This could be partially attributed to the reduced prices and availability of better quality of CNTs. Carbon nanotubes containing MMCs are being developed and projected for diverse applications in various fields of engineering ranging from structural applications, such as load-bearing members or tribological coatings to functional applications, such as thermal management in electronic packaging, hydrogen storage and catalysis. There has been success in the use of CNT-reinforced aluminium composites in fabrication of microelectromechanical system (MEMS), as in the case of high-frequency resonators for which a large elastic modulus is required. Improvement in strength and stiffness has been observed in most metal systems and lowering of the coefficient of friction and the wear rates have been observed by addition of CNTs in Ni- and Cu-based composites. However, it has also been observed that at higher CNT, loading properties tend to degrade. This is due to the inability of most of the process to homogeneously distribute CNTs or to obtain dense components at high CNT content. We have seen that the conventional routes of fabrications such as powder metallurgy, mechanical alloying and sintering, extrusion, hot pressing and electro- and electroless deposition have been applied for synthesising CNT-reinforced MMCs with some success. Novel methods have been designed for obtaining better dispersion of the CNTs such as molecular level mixing, nanoscale dispersion and spark plasma sintering which although successful, are on a laboratory scale. Thermal spray processes have been successfully utilised for synthesising MM-CNT coatings at a large scale.

The CNT/metal interface is very important in the strengthening of the composite. Improper bonding could lead to inefficient load transfer to the CNTs. The mechanical properties have been seen to vary a lot more than those predicted by micromechanical models for bulk composite materials, since they are dependent on many other factors such as interfacial bonding and load transfer, curvature of the CNTs and clustering phenomena.

There is a lot of scope for further work in this field. The challenge remains to disperse the ultra fine CNTs uniformly in the microstructure when bulk manufacturing processes are applied. Alignment of CNTs and its effect on properties needs to be studied. Variation in the concentration of CNTs would lead to variation in mechanical and thermo-physical properties which would

Table 1 Potential applications of CNT-reinforced metal matrix composites in various industries

Industry	Application	Property desired
Automobile industry	Break shoes , cylinder liners , piston rings , gears	High strength, wear resistance, good thermal conductivity, low density
Aerospace industry	Aircraft brakes , landing gears	Good wear resistance, good thermal conductivity, low density, high strength
Space applications	High gain antenna boom, structural radiators	Low density, high strength, low coefficient of thermal expansion, good electrical conductivity
Sports industry	Light weight bicycles , tennis and badminton rackets	High strength, high elastic modulus
Electronic packaging	Heat sinks for thermal management, solders	High thermal conductivity, low coefficient of thermal expansion, increased strength
MEMS and sensors	Micro-beams, micro-gears	High elastic modulus, high surface area
Battery and energy storage	Anodes and anode coatings, hydrogen storage materials	Large surface area, high current density, reduced response times, increased H ₂ adsorption-desorption rate

not be desirable in large structures. We have seen that there are only a few methods to quantify the level or quality of dispersion of CNTs in the microstructure. Hence, there is a need to develop a universal quantification scheme for the quality of CNT distribution in order to compare various processes for their ability to disperse the CNTs in the microstructure. A good CNT/metal interface has to be engineered by using suitable processing parameters or techniques. The effect of interfacial reactions and carbide formation on the surface of the CNT on the mechanical properties of the CNTs needs to be assessed. This would lead to efficient load transfer and effective utilisation of the strength of the CNTs.

Newer models need to be formulated to take care of the curved nature of CNTs and the presence of clustering to predict mechanical properties. Multi-scale testing techniques need to be developed given the multi-scale structure of these composites. The bulk properties may or may not correspond to the nanoscale mechanical properties. Newer models must bridge the phenomena occurring at the two length scales. Novel processing techniques must be developed keeping this aspect in mind. Models also need to be generated for predicting thermophysical properties, such as thermal conductivity and thermal expansion coefficient of the composites. New application of CNT metal composites need to be explored in MEMS. The biocompatibility of CNTs is still in debate. Also, studies in the future will be required on the probable mechanisms of CNT released from these composites while in use, and the possible health hazards imposed by the composites.

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