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State-of-the-art Review on Carbon Nanotube Reinforced Metal Matrix Composites

Nuno Silvestre

Department of Mechanical Engineering, Instituto Superior Técnico, University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Abstract The unceasing upgrading of techniques and processes to fabricate high purity carbon nanotubes (CNTs) and the improvement of the available techniques to produce high performance matrix materials, have fostered the way to enhance composite materials and their properties, either mechanical, thermal, electrical or magnetic. CNTs reinforcements have been introduced into polymers, ceramics, cement-based materials and metals. Polymers were the first material to be exploited as matrix material being reinforced by CNTs. Up to now other materials have tentatively been investigated for that purpose, including metals. Today, many applications of CNT reinforced composites exist but CNT reinforced metals are still scarce and only found in very specific applications. Several reasons can be identified but the still growing demand for lighter and stronger metals paved the way to more fundamental research on the topic of CNT reinforced metal matrix composites (MMCs). This review describes the state-of-the art in this field and highlights the excellent and promising mechanical, thermal, electrical properties of CNT reinforced MMCs.

Keywords Carbon Nanotube, Metal Matrix Composites, Mechanical Properties, Stiffness, Strength, Ductility

1. Introduction

Since their discovery by Ijiima[1], carbon nanotubes (CNTs) have been considered as an ideal reinforced material to improve the mechanical performance of many materials. CNTs are promising reinforcements for light weight and high strength composites. This is due to their exceptional small diameters and high Young's modulus, high tensile strength and chemical stability. Still, the main obstacle is to obtain a homogenous dispersion of the CNTs in the desired material matrix. Several methods and processes have been developed to improve the dispersion of CNTs in polymer matrices. The state-of-the-art report made by Andrews and Weisenberger[2] on CNT-polymer composites emphasised on the problem of CNT dispersion. Particular focus was given by these authors to interfacial bonding between CNTs and polymer matrices, as well as to potential topics of interest at that time. More recently, Chou et al.[3] examined the recent advancements in the science and technology of CNT-based fibers for polymer composites. Their assessment was made according to the hierarchical structural levels of CNTs used in composites, ranging from 1-D to 2-D to 3-D. At the 1-D level, fibers composed of pure CNTs or CNTs embedded in a polymeric matrix produced by various techniques were reviewed. At the 2-D level, the focuses were on CNT-modified advanced fibers, CNT-modified interlaminar surfaces and highly oriented CNTs in planar form. At the 3-D level, they examined the mechanical and physical properties CNT-polymer composites, CNT-based damage sensing, and textile assemblies of CNTs. The review by Yan et al.[4] focused mainly on functional CNTs and their applications in property enhancement of various polymer composites. Firstly, the general methods for CNT preparation were briefly introduced. Secondly, the functionalization of CNTs, particularly via chemical approaches, was summarized and the application of these functionalized CNTs was discussed. Finally, the interaction of CNTs with various polymers, the formation of CNT-polymer composites, and their property and applications were discussed by Yan et al.[4].

Nowadays, the CNT-reinforced polymer matrix composites are being intensively investigated. However, scarce to moderate research has been conducted to improve the CNT dispersion in metal matrices. Despite the fact that CNTs are an effective reinforcement to improve the mechanical and thermal responses of metal matrix composite (MMCs), very few successful attempts have been made for commercial applications due to the difficulties of incorporating CNTs in metals. It became obvious that segregation of CNTs due to their strong van der Waals forces often produces material defects, decreasing the material properties. Despite CNT reinforced MMCs have received the least attention, they are being thought for use in structural applications because of their high specific strength as well as functional materials for their exciting thermal and electrical

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* Corresponding author:
nsilvestre@ist.utl.pt (Nuno Silvestre)

characteristics. Light MMCs are of great interest due to their potential for reducing CO_2 emission through lightweight design. Using the exceptional properties of CNT in MMCs for macroscopic applications still constitutes a big challenge for the scientific and technological communities.

In order to base these thoughts, let us look at Figure 1. It shows the variation of the number of publications in SCI Web of knowledge per year, since 2000. Each curve corresponds to a different combination of keywords in searched topic: (i) the curve with circles corresponds to “Carbon nanotube and Composite”, (ii) the curve with squares corresponds to “Carbon nanotube and Composite and Polymer”, and (iii) the curve with triangles corresponds to “Carbon nanotube and Composite and Metal”. It is easily seen that the works on CNT-based composites rapidly increased from 81 in 2000 to over 7703 in 2012. The increase rate steadily increased from 2000 to 2007, but from 2007 to 2012 it showed a huge rise mainly due to the advent of nanomaterials. Since 2007, several types of materials fabricated at nanoscale emerged as promising matrices and nanodevices to which CNTs can effectively be added. Figure 1 also shows that the number of publications indexed in ISI Web of Knowledge[5] and focused on CNT-Polymer composites also increased a lot from 2000, with 31 publications, to 2012, with 1593. Regarding the number of publications on CNT-Metal composites, it has also increased since 2000 but to a minor extent: 19 publications in 2000 and 468 in 2012. Figure 2 shows the percentage of publications on CNT-Polymer and CNT-Metal composites with respect to CNT composites. Concerning CNT-Polymer composites, the percentage was more or less uniform till 2007, but then showed a huge drop due to the advent of nano-fabricated materials. It is interesting to note that the percentage of published works on CNT-Metal composites has been decreased since 2000, despite the total number has been increased (Figure 1).

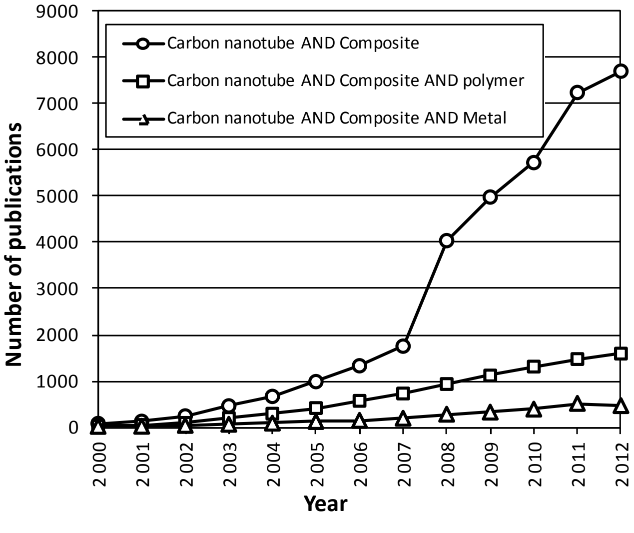

Figure 1. Number of publications indexed in Web of Knowledge per year

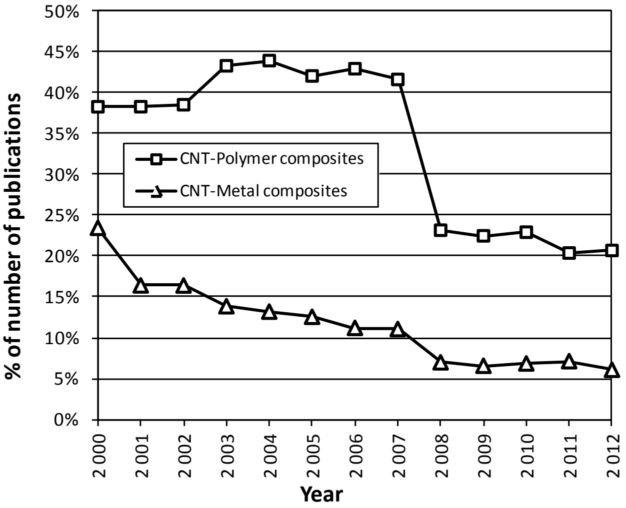

Figure 2. Percentage of the number of publications per year focused on CNT-Polymer and CNT-Metal composites

Since the review by Girot et al[6], few reviews on CNT-reinforced MMCs have been published. In 2004, Curtin et al.[7] reviewed the research on the incorporation of CNTs into ceramic and metal matrices to form composite structures. They emphasised the processing methods, mechanical performance, and prospects for successful applications. They reviewed the literature on the topics of fabrication and properties of ceramic and metal matrix systems. In case of metal matrix materials, they mentioned that enhanced mechanical properties (stiffness, wear, and fatigue resistance) are desirable but a wider range of properties (electrical, magnetic and vibrational) were also investigated. Li et al.[8] studied the behaviour of CNT reinforced light metal composites produced by melt stirring and by high pressure die casting. The light metal composites showed significantly improved mechanical properties already at small CNT contents. The influence of CNT concentration on the composites was also studied by Li et al.[8]. The review by Neubauer et al.[9] gives an overview and summarises the activities related to CNTs and carbon nanofibers used as a reinforcement in metallic matrix materials. They presented the main challenges and the potential with respect to material properties. Bakshi et al.[10] reviewed and summarised the research work carried out in the field of CNT reinforced MMCs. They focused 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 were critically reviewed with an objective to achieve homogeneous distribution of CNTs in the matrix. The mechanical property improvements achieved by addition of CNTs in various metal matrix systems were summarised by Bakshi et al.[10]. Several factors, such as the structural and chemical stability of CNTs in different metal matrices and the importance of the CNT-metal interface were described. The relevance of CNT dispersion and its quantification was also highlighted.

The purpose of this review is to update the state-of-the-art concerning the use of CNTs for reinforcement of MMCs. The recent developments are shown separately by each type of material matrix, in alphabetic order: Aluminium (Al), Cobalt (Co), Copper (Cu), Iron (Fe), Magnesium (Mg), Nickel (Ni) and Titanium (Ti).

2. CNT-Aluminium (Al) Composites

Aluminium is a chemical element in the boron group with symbol Al and atomic number 13. It is a silvery white, soft, ductile metal. Al is the third most abundant element (after oxygen and silicon), and the most abundant metal in the Earth's crust. Al is remarkable for its low density and for its ability to resist corrosion due to the phenomenon of passivation. Structural components made from Al and its alloys are vital to the aerospace industry and are important in other areas of transportation and structural materials. The most useful compounds of Al, at least on a weight basis, are the oxides and sulfates. A sample of Aluminium is shown in Figure 3 and its properties are presented in Table 1.

Figure 3. Aluminium (Al) sample

Table 1. Al properties

Crystal structure	*face-centered cubic*
Magnetic ordering	*paramagnetic*
Electrical resistivity	*(20°C) 28.2 nΩ.m*
Thermal conductivity	$237\ W.m^{-1}.K^{-1}$
Thermal expansion	$(25°C)\ 23.1\ \mu m.m^{-1}.K^{-1}$
Speed of sound	$(r.t.)\ (rolled)\ 5{,}000\ m.s^{-1}$
Young's modulus	*70 GPa*
Shear modulus	*26 GPa*
Bulk modulus	*76 GPa*
Poisson ratio	*0.35*
Mohs hardness	*2.75*
Vickers hardness	*167 MPa*
Brinell hardness	*245 MPa*
Density (near r.t.)	$2.70\ g.cm^{-3}$
Liquid density at m.p.	$2.375\ g.cm^{-3}$
Melting point	*933.5 K, 660.3°C, 1220.6 °F*
Boiling point	*2792 K,2519°C,4566 °F*
Heat of fusion	$10.71\ kJ.mol^{-1}$
Heat of vaporization	$294.0\ kJ.mol^{-1}$
Molar heat capacity	$24.200\ J.mol^{-1}.K^{-1}$

Al matrix is widely used for CNT reinforced MMCs. Since the work by Zhong et al.[11], many achievements have been made in the development of CNT-Al composites. In this review, 24 papers are described and dedicated to this topic[12-35]. Cha et al.[12] proposed a novel process to fabricate CNT-alumina nanocomposites, consisting of a molecular level mixing process and an in situ spark plasma sintering process. The CNT/alumina nanocomposites fabricated by this proposed process showed improved hardness due to a load transfer mechanism of the CNTs and increased fracture toughness arising from the bridging mechanism of CNTs during crack propagation. In order to produce optimized composites, George et al.[13] studied the strength of CNT-Al composites and investigated the relevant strengthening mechanisms involved in CNT-Al composites. Three major mechanisms were analyzed along with experimental procedure for making CNT/Al composites.

Using cold isostatic press and subsequent hot extrusion techniques Deng et al.[14] fabricated 1.0 wt.% carbon nanotube (CNT) reinforced 2024Al matrix composite, measured the mechanical properties of the composite by tensile tests and examined the fracture surfaces using field emission scanning electron microscopy. Their experimental results showed that CNTs are dispersed homogeneously in the composite and that the interfaces of the Al matrix and the CNT bonded well. Deng et al.[15] observed that the tensile strength and the Young's modulus of the composite were enhanced markedly, and the elongation didn’t decrease when compared with the matrix material fabricated under the same process. The extraordinary mechanical properties of CNTs and their pulling-out role in the Al matrix composite are factors that explain this improved behaviour. Deng et al.[15] also investigated the microstructure characteristics and the distribution of CNTs in the Al matrix. They showed that adding a small amount of CNTs to the matrix, the elastic modulus and the tensile strength were increased highly with respect to those of the 2024Al base material. Deng et al.[16] investigated the damping behaviour of 2024Al reinforced with multi-walled CNTs. The damping characteristics of the composite were investigated with frequency of 0.5, 1.0, 5.0, 10, 30 Hz, at a temperature of 25–400 °C. The experimental results showed that the frequency significantly affects the damping capacity of the composite when the temperature is above 230 °C. The damping capacity of the composite with a frequency of 0.5 Hz reached 975×10^{-3}, and the storage modulus is 82.3 GPa when the temperature was 400 °C. This study proved that CNTs can improve highly the damping properties of MMCs at elevated temperature without sacrificing their mechanical strength and stiffness. Deng et al.[17] studied the thermal expansion behaviour of Al composite reinforced with CNTs. The coefficient of thermal expansion of Al matrix composite reinforced with 1.0wt.% multi-wall CNTs fabricated by cold isostatic pressing and hot squeeze technique was measured between 25 and 400°C with a high-precision thermo-mechanical analyzer, and compared with those of pure Al and 2024Al matrix fabricated under the same processing. The results by Deng et al.[17] showed that the coefficient of thermal expansion of the composite reduces in relation to those of pure Al and 2024Al matrix due to the introduction of CNTs. The addition of 1.0wt.% CNTs to 2024Al matrix decreased the coefficient of thermal expansion by as much as 12% and 11% compared with those of pure Al and 2024Al matrix at 50°C, respectively. These evidences indicated that CNT reinforcement of MMC may be a promising material with low coefficient of thermal expansion.

Bakshi et al.[18] prepared multi-walled CNT reinforced Al coatings using cold gas kinetic spraying in order to obtain a good CNT dispersion in micron-sized gas atomized Al–Si eutectic powders. Spray dried powders containing 5 wt.% CNT were blended with pure Al powder to give overall nominal CNT compositions of 0.5 wt.% and 1 wt.% respectively. They showed that the CNTs were uniformly distributed in the matrix. Nanoindentation led to elastic modulus values between 40 and 229 GPa, and this high scatter was attributed to microstructural heterogeneity of the coatings (including pure Al, Al-Si eutectic, porosity and CNTs).

Using hot extrusion of ball-milled powders, Choi et al.[19] fabricated Al matrix composite rods in which tightly bonded multi-walled CNTs were separately dispersed and uniaxially aligned. They showed that the reinforcing efficiency of CNTs in the composites followed the volume fraction rule of discontinuous fibers in the grain size range down to 70 nm.

Pérez-Bustamante et al.[20] produced Al-based nanocomposites reinforced with multi-walled CNTs using mechanical milling followed by pressure-less sintering at 823 K under vacuum. The interface between Al matrix and the multi-walled CNTs was examined using transmission electron microscopy. This work showed that the multi-walled CNTs were not damaged during the preparation of the nanocomposite and that no reaction products were detected after sintering. The mechanical properties of sintered nanocomposites specimens were evaluated by a compression test. The yield stress and the maximum strength obtained were considerably higher than those reported in the literature for pure Al prepared by the same route. The values for yield stress and ultimate strength increased about 100% as the volume fraction of multi-walled CNTs increased from 0 to 0.75 wt.%, for 2h of milling time. They concluded that the milling time and the concentration of CNTs had an important effect on the mechanical properties of the nanocomposite.

In the paper by Esawi and El Borady[21], a powder rolling technique is used to fabricate CNT-reinforced Al strips. The Al-CNT mixtures were blended in either a mixer-shaker at a rotary speed of 46 rpm, or under argon in a planetary mill at a rotary speed of 300 rpm, prior to rolling. The CNT dispersion was shown to be better under the higher energy planetary action. The strength of the rolled strips was evaluated for various wt% CNT samples. The Al-0.5 wt% composite strips exhibited enhanced mechanical properties. The CNT - reinforced Al strips were shown to have numerous attractive applications in the aerospace, automotive and electronics industries. Later, Esawi et al.[22] used planetary ball milling to disperse 2 wt% multi-walled CNT in Al (Al) powder. Despite the success of ball milling in dispersing CNTs in Al powder, it is often accompanied with considerable strain hardening of the Al powder, a fact that might have far reaching implications on the final properties of the composite. Thus, both un-annealed and annealed Al-2 wt% CNT composites were investigated by Esawi et al.[22]. They found that, ball-milled and extruded (un-annealed) samples of Al-2 wt% CNT demonstrated high notch - sensitivity and consistently fractured outside the gauge length during tensile testing. In contrast, extruded samples annealed at 400 and at 500°C for 10 h prior to testing, exhibited more ductile behaviour and no notch sensitivity. Under similar processing conditions, they showed that ball milling for 3 h followed by hot extrusion and annealing at 500°C resulted in enhancements of around 21% in tensile strength compared with pure Al with the same process history. They argued that ball-milling conditions resulted in the creation of a nanostructure in all samples produced, a fact that as proved by means of XRD and TEM analysis. The tensile testing fracture surfaces identified by Esawi et al.[22] showed uniform dispersion and alignment of the CNTs in the Al matrix but also showed that CNTs acted as nucleation sites for void formation during tensile testing. This effect contributed to the observation of CNT pullout due to the poor bond between the CNTs and the matrix. Since the uniform dispersion of CNTs in the Al matrix has been identified as being critical to the pursuit of enhanced properties, ball milling as a mechanical dispersion technique has proved its potential. Esawi et al.[23] used ball milling to disperse up to 5 wt.% CNT in Al matrix and investigated the effect of CNT content on the mechanical properties of the composites. Cold compaction and hot extrusion were used to consolidate the ball-milled Al–CNT mixtures. In comparison with to pure Al, 50% increase in tensile strength and 23% increase in stiffness compared were observed by Esawi et al.[23]. Some carbide formation was observed in the composite containing 5 wt.% CNT. The large aspect ratio of CNTs used by Esawi et al.[23] led to difficulties in CNT dispersion at CNT wt.% greater than 2. Therefore, the expected improvements in mechanical properties with increase in CNT weight content were not fully realized by these authors.

Choi et al.[24] reported a study on the mechanical properties and wear characteristics of ultrafine-grained Al and Al-based composites. In this composite, well dispersed and Al atom-infiltrated multi-walled CNTs formed a strong interface with the matrix by mechanical interlocking. Wear characteristics, varied according to the grain size and the CNT volume, were evaluated by Choi et al.[24] under several combinations of applied load and sliding speed. They reported that strength and wear resistance were significantly enhanced and the coefficient of friction was extremely reduced, for grain size decrease and CNT volume increase. The ultrafine-grained composite containing 4.5 vol. % of CNTs exhibited more than 600 MPa in yield stress and less than 0.1 in the coefficient of friction. Both coefficient of friction and wear rate augmented with increasing load, while they were reduced with increasing the sliding speed. This study demonstrated that CNTs are effective reinforcement for enhancing wear characteristics as well as mechanical properties. Choi et al.[25] produced nanocrystalline Al-Si alloy-based composites containing CNTs using hot rolling ball-milled powders. The grain size was effectively reduced and the Si element was dissolved in the Al matrix during the milling process. Using a thermo-mechanical process, CNTs were gradually dispersed into the Al powders. The composite produced by Choi et al.[25] contained 3 vol.% of CNTs and showed yield strength about 520 MPa and plastic elongation to failure of 5%. Al and Al-based composites containing 4.5 vol.% multi-walled CNTs were fabricated by Choi and Bae[26] using hot-rolling the ball-milled powder. They studied the composite creep behaviour at 523 K and it displayed much enhanced creep resistance at the applied stresses higher than 200 MPa. They also identified a negligible dependency of strain rate on stress for relatively low applied stress region (stresses below 110 MPa). They explained this behaviour due to the fact that diffusional flow of the matrix is significantly restricted by multi-walled CNTs.

Singhal et al.[27] report the fabrication of Al-matrix composites reinforced with amino-functionalized CNTs by means of powder metallurgy process. Functionalization of the CNTs was carried out by ball milling multi-walled CNTs in the presence of ammonium bicarbonate. They found that the mechanical properties of Al-functionalized CNTs composites were much superior to the composites fabricated using non-functionalized or acid functionalized CNTs. Using high-resolution transmission electron microscopy, they attributed the improvement of mechanical properties to (i) homogeneous dispersion of functionalized CNTs in Al matrix, as compared to non-functionalized or acid functionalized CNTs, and (ii) the formation of strong interfacial bonding between functionalized CNTs and Al matrix, leading to efficient load transfer from Al matrix to functionalized CNTs.

Using measurements of grain size and mechanical property changes upon annealing at various temperatures, Lipecka et al.[28] evaluated the effect of CNTs on the thermal stability of ultrafine grained Al alloy processed by the consolidation of nano-powders obtained by mechanical alloying. They found that the grain size of the samples containing CNTs is stable up to high temperatures, and even after annealing at 450 °C, no evident grain growth was observed. This was attributed to the presence of entangled networks of CNTs located at grain boundaries and to the formation of nanoscale particles of carbide Al_4C_3. They also revealed that CNTs decompose at a relatively low temperature (450°C) and form fine Al_4C_3 precipitates. Lipecka et al.[28] revealed that this transformation did not affect the mechanical properties due to the carbide nanoscale size.

Choi et al.[29] investigated the influence of multi-walled CNTs on the strength of Al-based composites with grain sizes ranging from 250 to 65 nm. They found that the composite strength was significantly enhanced by the increase of the CNT volume. The strengthening efficiency of CNTs in ultrafine-grained composites was comparable with that predicted by the discontinuous fiber model. For grain size below 70 nm, the efficiency was half of the theoretical prediction. For nano-grained Al, Choi et al.[29] found that the activities of forest dislocations diminished and dislocations emitted from grain boundaries were dynamically annihilated during the recovery process. This provide weak plastic strain field around CNTs. Their observation gave a basic understanding of the strengthening behaviour of nano-grained MMCs.

Jiang et al.[30] used flake powder metallurgy (flake PM) to achieve uniform distribution of CNTs in CNT-Al composites and realized the potential of CNTs for reinforcement. The structural integrity of the CNTs was maintained in the composites since CNTs were protected from high energy physics force such as ball-milling. They concluded that a strong and ductile CNT-Al composite might be fabricated using this process, leading to tensile strength of 435 MPa and ultimate strain of 6%. These values greatly surpassed the strength values for materials produced by conventional methods. In order to combine high tensile strength and ductile behaviour, CNT/Al nanolaminated composites with alternating layers of Al (400 nm) and CNTs (50 nm) were fabricated by Jiang et al.[31] using flake PM. Compared with conventional homogeneous nanocomposites composed of the same constituents, they found that the final bulk products with high level ordered nanolaminates exhibited both high tensile strength of 375 MPa and high strain of 12%. They attributed this enhancement to the fact that they enabled enhanced dislocation storage capability and two-dimensional alignment of CNTs.

CNT-reinforced Al matrix composite materials were successfully fabricated by Kwon and Leparoux[32] using mechanical ball milling followed by powder hot extrusion processes. Although only a small quantity of CNTs were added to the composite (1 vol%), they found that the Vickers hardness and the tensile strength were significantly enhanced, with an up to three-fold increase relative to that of pure Al. The CNT-Al composites were not only strengthened by the addition of CNTs but also enhanced by several synergistic effects. The nanoindentation stress–strain curve was successfully constructed by setting the effective zero-load and zero-displacement points and was compared with the tensile stress–strain curve. The yield strengths of the Al – CNT composites were obtained from the nanoindentation and tensile tests, and then compared.

Using powder metallurgy followed by 4-pass friction stir processing, Liu et al.[33] fabricated 1.5 vol.% and 4.5 vol.% CNT reinforced 2009Al (CNT-2009Al) composites with homogeneously dispersed CNTs and refined matrix grains. They tested the tensile properties of the composites between 293 and 573 K and the coefficient of thermal expansion from 293 to 473 K. They indicated that load transfer mechanism still takes place at temperatures elevated up to 573 K. Thus, the yield strength of the 1.5 vol.% CNT-2009Al composite at 423–573 K was enhanced compared with the 2009Al matrix. However, for the 4.5 vol.% CNT-2009Al composite, the yield strength at 573 K was even lower than that for the matrix, due to the quicker softening of ultrafine-grained matrix. Compared with the 2009Al matrix, Liu et al.[33] concluded that the coefficient of thermal expansion of the composites was greatly reduced for the zero thermal expansion and high modulus of the CNTs, and well predicted by the Schapery's model.

Yoo et al.[34] studied the behaviour of CNT-reinforced Al composites fabricated through ball milling combined with rolling. The composites exhibited high strength and high strain-hardening ability. During the ball-milling process, CNTs were broken and became low aspect ratio tubes. They observed that the composites had the CNTs (a few dozen nanometers in size) randomly and uniformly dispersed in their grain interiors. They concluded that this type of CNT distribution contributed to work hardening and strengthening by the Orowan mechanism. Yang et al.[35] developed an approach to fabricate CNT-reinforced Al composites. This process allowed well dispersed and deeply embedded CNT reinforcement in the Al powder, forming an effective interface bonding with matrix. They concluded that these CNT-Al composites containing 2.5 wt.% CNTs exhibited ultimate tensile strength of 334 MPa, which was 1.7 times higher than that of unreinforced Al, as well as good ductility of 18% elongation to failure.

3. CNT-Cobalt (Co) Composites

Figure 4. Cobalt (Co) sample

Cobalt is a chemical element with symbol Co and atomic number 27. It is found naturally only in chemically combined form. The free element, produced by reductive smelting, is a hard, lustrous, silver-gray metal. Today, some cobalt is produced specifically from various metallic-lustered ores, e.g. cobaltite (CoAsS), but the main source of the element is as a by-product of copper and nickel mining. Cobalt is used in the preparation of magnetic, wear-resistant and high-strength alloys. Cobalt silicate and cobalt(II) aluminate give a distinctive deep blue color to glass, smalt, ceramics, inks, paints and varnishes. A sample of Cobalt is shown in Figure 4 and its properties are presented in Table 2.

Table 2. Co properties

Crystal structure	*hexagonal close-packed*
Magnetic ordering	*ferromagnetic*
Electrical resistivity	*(20 °C) 62.4 nΩ.m*
Thermal conductivity	*100 W.m*$^{-1}$*.K*$^{-1}$
Thermal expansion	*(25°C) 13.0 µm.m*$^{-1}$*.K*$^{-1}$
Speed of sound	*(20°C) 4720 m.s*$^{-1}$
Young's modulus	*209 GPa*
Shear modulus	*75 GPa*
Bulk modulus	*180 GPa*
Poisson ratio	*0.31*
Mohs hardness	*5.0*
Vickers hardness	*1043 MPa*
Brinell hardness	*700 MPa*
Density (near r.t.)	*8.90 g.cm*$^{-3}$
Liquid density at m.p.	*7.75 g.cm*$^{-3}$
Melting point	*1768 K, 1495°C, 2723 °F*
Boiling point	*3200 K, 2927°C, 5301 °F*
Heat of fusion	*16.06 kJ.mol*$^{-1}$
Heat of vaporization	*377 kJ.mol*$^{-1}$
Molar heat capacity	*24.81 J.mol*$^{-1}$*.K*$^{-1}$

Co matrix is used for CNT reinforced MMCs, but mainly for electrochemical performance in coatings and batteries. In this review, only 2 papers are dedicated to CNT-Co composites[36,37]. Chen et al.[36] demonstrated that cobalt could be plated onto the surfaces of CNTs by electroless plating. In this manner a layer of cobalt is formed as nanoparticles on the suface of the CNTs. It was found that the activation process and low deposition rate were critical for getting better coating. Additionally, the heat-treatment of the coated CNTs was found to be a very effective way of improving the deposited coating layer. The results from the study by Chen et al.[36] demonstrated the technical feasibility of electroless plating for the preparation of a one-dimensional nanoscale composite. Recently, Su et al[37] characterized nanocrystalline Co and CNT-Co coatings produced by different electrodeposition techniques. Nanocrystalline Co and multi-walled CNT-Co coatings were synthesized by direct current and pulse reverse current electrodeposition from aqueous bath containing cobalt sulfate and multi-walled CNTs. Effect of the functionalization of CNTs and electrodeposition techniques on the microstructure and properties of these coatings was evaluated. Their results showed that the incorporations of CNTs, particularly the functionalized CNTs, substantially improve the hardness and the resistance to wear and corrosion of the deposited coatings. The functionalization of CNTs favors the co-deposition of CNTs with Co ions, and then improves the hardness and the corrosion and wear resistance of the produced composite coatings. The differences in friction and wear behaviour of these nanocrystalline Co and CNT-Co coatings as a function of treatment of CNTs or electrodeposition techniques were attributed to their different hardness, microstructures and the corresponding wear mechanisms.

4. CNT-Copper (Cu) Composites

Copper is a chemical element with the symbol Cu and atomic number 29. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; a freshly exposed surface has a reddish-orange color. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys. The main areas where copper is found in humans are liver, muscle and bone. In sufficient concentration, Cu compounds are poisonous to higher organisms and are used as bacteriostatic substances, fungicides and wood preservatives. A sample of Copper is shown in Figure 5 and its properties are presented in Table 3.

Cu matrix has been fairly used for CNT reinforced MMCs. In this review, a total of 9 papers are dedicated to CNT-Cu composites[38-46]. Kim et al.[38] investigated the hardness and wear resistance of CNT-reinforced Cu matrix (CNT-Cu) composites. The nanocomposite was fabricated by molecular level process, which involved suspending CNTs in solvent by surface functionalization, mixing Cu ions with CNT suspension, drying, calcination and reduction. The hardness and sliding wear resistance of CNT-Cu composite were enhanced by two and three times, respectively, compared to those of Cu matrix. They attributed the enhancement of hardness to the effect of homogeneous distribution of CNTs in Cu matrix, good bonding at CNT-Cu interfaces and high relative density of composites. The dispersed CNTs in Cu-matrix composite gave significantly enhanced wear resistance by retarding the peeling of Cu grains during sliding wear process.

Table 3. Cu properties

Crystal structure	*face-centered cubic*
Magnetic ordering	*diamagnetic*
Electrical resistivity	*(20°C) 16.78 nΩm*
Thermal conductivity	*401* $W.m^{-1}.K^{-1}$
Thermal expansion	*(25°C) 16.5* $\mu m.m^{-1}.K^{-1}$
Speed of sound	*(r.t.) (annealed) 3810* $m.s^{-1}$
Young's modulus	*110–128 GPa*
Shear modulus	*48 GPa*
Bulk modulus	*140 GPa*
Poisson ratio	*0.34*
Mohs hardness	*3.0*
Vickers hardness	*369 MPa*
Brinell hardness	*35 HB = 874 MPa*
Density (near r.t.)	*8.96 g.cm−3*
Liquid density at m.p.	*8.02 g.cm−3*
Melting point	*1357.8 K, 1084.6°C, 1984.3 °F*
Boiling point	*2835 K, 2562°C, 4643 °F*
Heat of fusion	*13.26* $kJ.mol^{-1}$
Heat of vaporization	*300.4* $kJ.mol^{-1}$
Molar heat capacity	*24.440* $J.mol^{-1}.K^{-1}$

Figure 5. Copper (Cu) sample

Sun et al.[39] applied molecular dynamics and continuum mechanics to predict the compressive mechanical properties of CNTs encapsulating helical copper nanowire. The helical structures of the copper nanowires were obtained using the "simulated annealing" method. The strain energy curves were shown to predict the interaction between the atoms during the compressive course. They used the model to determine the mechanical properties (critical buckling load and the Young's moduli) of CNTs encapsulating helical copper nanowire with different diameters and lengths. Sun et al.[39] found that not all the maximum strengths of the composites are larger than the corresponding carbon nanotube bases, and they were related with the diameter, length and the CNTs chirality. Some excellent properties of CNTs encapsulating helical copper nanowire were revealed in this study. Trinh et al.[40] reported results on the fabrication and calculation of the friction coefficient of Cu matrix composite material reinforced by CNTs. CNT-Cu composites were fabricated by powder metallurgy method and mechanical properties, such as friction coefficient, were evaluated using the rule of mixtures. Trinh et al[40] determined the coefficient of friction of the CNTs component in the CNT-Cu composites.

Uddin et al.[41] investigated the hardness and electrical properties of CNT reinforced Cu and Cu alloy (bronze) composites. They were fabricated by well-established hot-press sintering method of powder metallurgy. They found that the effect of shape and size of metal particles as well as selection of CNTs influenced significantly the mechanical and electrical properties of the composites. The hardness of CNT-Cu composite improved up to 47% compared to that of pure Cu, while the electrical conductivity of bronze composite increased up to 20% compared to that of the pure alloy. They concluded that CNTs improved the mechanical properties of highly-conductive low-strength Cu metals, whereas in low-conductivity high-strength copper alloys the electrical conductivity was improved. Using high power lasers, Bhat et al.[42] fabricated and studied the mechanical and thermal properties of multi-walled CNT reinforced Cu–10Sn alloy composites. Microstructural observations showed that CNTs were retained in the composite matrix after laser processing. The addition of CNTs showed improvement in strain hardening, mechanical and thermal properties of Cu–10Sn alloy. Composites with 12 vol.% CNTs showed more than 80% increase in the Young's modulus and 40% increase in the thermal conductivity of Cu–10Sn alloy. Bhat et al.[42] found that the yield strength estimates obtained from models based on strengthening mechanisms derived from the Maxwell – Garnett effective medium were shown very accurate.

Xu et al.[43] studied the effect of electrical current on tribological properties of Cu matrix composite reinforced by CNTs. The CNT-Cu composites were reinforced with 10% CNTs and pure Cu bulk were prepared by powder metallurgy techniques under the same consolidation processing condition. They investigated the effect of electrical current on tribological property of the materials using a pin-on-disk friction and wear tester. The results published by Xu et al.[43] showed that the friction coefficient and wear rate of CNT-Cu composite as well as those of pure Cu bulk increased with the electrical current. They identified that the dominant wear mechanisms were arc erosion wear and plastic flow deformation, and CNTs improved tribological properties of Cu composites with electrical current.

Multi-walled CNT-Cu composites, exhibiting chromium (Cr) carbide nanostructures at the CNT-Cu interface, were prepared by Cho et al.[44] using a carbide formation using CuCr alloy powder. The tensile strengths of the CNT-CuCr composites increased with increasing CNTs content, while the tensile strength of CNT-Cu composite decreased from that of monolithic Cu. The enhanced tensile strength of the CNT-CuCr composites was a result of possible load-transfer mechanisms of the interfacial Cr carbide nanostructures. They observed the failure of multi-wall of CNTs in the fracture surface of the CNT-CuCr composites, indicating an improvement in the load-bearing capacity of the CNTs. This result proved that the Cr carbide nanostructures effectively transferred the tensile load to the CNTs during fracture through carbide nanostructure formation in the CNT-Cu composite. Cu matrix composites reinforced with 0.2, 5 and 10 vol% single-walled CNT and 5 and 10 vol% multi-walled CNTs were produced by Shukla et al.[45] using high energy milling of pure copper powder with CNTs and subsequent consolidation by vacuum hot pressing. Significant improvement in hardness of single-walled CNT-Cu composite was observed with increase in CNTs content. In case of multi-walled CNT-Cu composite, hardness reduced for 10 vol% CNT composites. Compression strength of the single-walled CNT-Cu samples was found by Shukla et al.[45] to be higher than the multi-walled CNT reinforced samples.

Tsai and Jeng[46] investigated experimentally and numerically the effect of CNT buckling on the reinforcement of CNT-Cu composites. The CNT-Cu composites with high strength and good damping were developed using acid treatment, sintering processes and consolidation techniques. In this study, strengthening of the composites, with influence of CNT buckling, was demonstrated by experimental nanoindentation tests and molecular dynamics simulations. The experimental results obtained by Tsai and Jeng[46] showed that the buckling behaviour of CNTs in the CNT-Cu composites varies with their slenderness ratio. Their study showed significant buckling behaviour of CNTs in the CNT-Cu composites, where the shorter CNTs (with a smaller slenderness ratio) gave rise to a global buckling and the slender CNTs (with a larger slenderness ratio) induced local buckling. The MD simulation results revealed that the buckling behaviour of the CNTs played a key role in increasing the mechanical strength of CNT-Cu composites.

5. CNT-Iron (Fe) Composites

Iron is a chemical element with the symbol Fe and atomic number 26. It is a metal in the first transition series. It is the most common element (by mass) forming the planet Earth as a whole, forming much of Earth's outer and inner core. It is the fourth most common element in the Earth's crust. Iron metal has been used since ancient times, though copper alloys, which have lower melting temperatures, were used first in history. Pure iron is soft (softer than aluminium), but is unobtainable by smelting. The material is significantly hardened and strengthened by impurities from the smelting process, such as carbon. A certain proportion of carbon (between 0.002% and 2.1%) produces steel, which may be up to 1000 times harder than pure iron. Crude iron metal is produced in blast furnaces, where ore is reduced by coke to pig iron, which has a high carbon content. Further refinement with oxygen reduces the carbon content to the correct proportion to make steel. Steels and low carbon iron alloys with other metals (alloy steels) are by far the most common metals in industrial use, due to their great range of desirable properties and the abundance of iron. A sample of Iron is shown in Figure 6 and its properties are presented in Table 4.

Figure 6. Iron (Fe) sample

Fe matrix has been fairly used for CNT reinforced MMCs. In this section, a total of 8 papers on CNT-Fe composites are reviewed[47-54]. Ding et al.[47] employed mechanical alloying to produce Al_2O_3/Fe, Al_2O_3/Co and Al_2O_3/Ni nanocomposites and found that high-energy mechanical milling leads not only to drastic refinement but also to well dispersion of catalyst precursors in oxide matrixes. After mechanical milling, they observed solid-state alloying and accelerated substitutional reactions between the parent oxides. These nanocomposites possessed the fine-grained and porous structures and thus high reducibility. Large-scale formation of multi-walled and single-walled CNTs were achieved by using these mechanical alloying-derived Al_2O_3/Fe, Al_2O_3/Co and Al_2O_3/Ni nanocomposites.

Table 4. Fe properties

Crystal structure	*body-centered cubic*
Magnetic ordering	*ferromagnetic*
Electrical resistivity	*(20 °C) 96.1 nΩ.m*
Thermal conductivity	*80.4 W.m^{-1}.K^{-1}*
Thermal expansion	*(25 °C) 11.8 µm.m^{-1}.K^{-1}*
Speed of sound	*(r.t.) (electrolytic) 5120 m·s^{-1}*
Young's modulus	*211 GPa*
Shear modulus	*82 GPa*
Bulk modulus	*170 GPa*
Poisson ratio	*0.29*
Mohs hardness	*4*
Vickers hardness	*608 MPa*
Brinell hardness	*490 MPa*
Density (near r.t.)	*7.874 g.cm^{-3}*
Liquid density at m.p.	*6.98 g.cm^{-3}*
Melting point	*1811 K, 1538 °C, 2800 °F*
Boiling point	*3134 K, 2862 °C, 5182 °F*
Heat of fusion	*13.81 kJ.mol^{-1}*
Heat of vaporization	*340 kJ.mol^{-1}*
Molar heat capacity	*25.10 J.mol^{-1}.K^{-1}*

Atomic structures of single-crystalline iron-based nanowires crystallized inside multi-walled CNTs during pyrolysis on silicon substrates with ferrocene as a precursor were analyzed by Goldberg et al.[48] using high-resolution analytical transmission electron microscopy and electron diffraction. Standard crystal lattices (body-centered cubic – bcc, α-Fe; face-centered cubic - fcc: γ-Fe; orthorhombic cementite Fe_3C) were all found to form inside the CNTs. Both bcc and fcc nanowires display a wide variety of lattice planes being parallel to the CNT walls, with none of the orientations being preferable. Both long-period and standard cementite nanowires exhibited well-defined transient zones in the vicinity of nanowire–CNT interfaces, where perfectly ordered carbide lattice fringes disappeared. The results by Goldeberg et al.[48] suggested the non-existence of metastable equilibrium in the nanoscale Fe–C system between carbide and graphite phases during iron crystallization inside graphitic tubular channels.

Shpak et al.[49] used X-ray diffraction, transmission electron microscopy, ferromagnetic and electron paramagnetic resonances to investigate the Fe-filled multi-walled CNTs. The iron within the CNTs was found to be in three phases: the austenite γ-Fe is located at the top of the CNTs, while the ferrite α-Fe and cementite θ-Fe_3C are found close to the substrate. Two ferromagnetic signals were observed by Shpak et al.[49] and identified as those belonging to ferrite and cementite. Ferromagnetic signals revealed a surprising temperature dependence: with decreasing temperature, their integral intensity decreases nearly linearly, and the signals disappear at temperatures below 70 K.

Spark plasma sintering was used by Pang et al.[50] to fabricate dense Fe_3Al/CNT composite with CNT content of 5.0 vol.%, retaining the integrity of CNT in the matrix. They synthesized samples at pressure of 30 MPa and temperature of 1273 K, and studied the composite structure using X-ray diffraction and transmission electron microscope (TEM). Pang et al.[50] concluded that the composites had very promising mechanical properties, such as microhardness of 8.7 GPa, compressive yield strength of 3175 MPa, which is about 95% and 56% higher than monolithic Fe_3Al fabricated under the same process. They indicated that CNTs can be considered for effective nanoscale reinforcement of intermetallics matrix composites.

Pang et al.[51] prepared multi-walled CNTs-Fe_3Al composite using spark plasma sintering and investigated the magnetic properties of the nanocomposite with alternating gradient force magnetometer. They showed that the CNTs-Fe_3Al composite displays good soft magnetic properties and has a similar magnetic hysteresis loops to that of Fe_3Al. The excellent magnetic properties evidenced in their study imply that multi-walled CNTs-Fe_3Al composites might have significant potential for applications in electronic-magnetic nanodevices. Pang et al.[52] performed analyses on the stress in the CNT-Fe_3Al composites. They mentioned that the biphase interface valence electron structure was established on the basis of Pauling's nature of the chemical bond and that the stress occurs by the huge interface electron density difference, thus blocking the Fe_3Al grain agglomeration and growth. They also measured the compressive stress existing in the CNT-Fe_3Al interface with the X-ray diffractions, giving a value of 0.38 GPa. They declare that this experimental result verifies that the stress has a positive effect on the enhancement of mechanical properties of composite.

Using spark plasma sintering, Pang et al.[53] fabricated iron aluminides (Fe_3Al) based composite with different amounts of multi-walled CNTs and studied the influence of CNTs content on the mechanical properties of the composite. They concluded that the compressive yield strength and fracture toughness of the 3 vol% CNT-Fe_3Al composite, compared with the monolithic Fe_3Al, were enhanced 73.6% and 40%, respectively. The defects and alignment direction of CNTs in the matrix affected the mechanical properties of the composite. They also identified that the failure mechanisms include CNTs pulling-out, crack deflection, bridging and CNTs rupture.

Madaleno et al.[54] used catalytic decomposition of ethylene over iron montmorillonite surfaces to synthesize montmorillonite–CNT hybrids. SEM and STEM analyses revealed the presence of CNTs attached to the clay layers and X-ray diffraction results and indicated that sodium montmorillonite layers were intercalated with iron species during the ion-exchange processes and further delaminated due to the growth of CNTs. Due to their pre-exfoliated internal structure and the presence of surface CNTs, Madaleno et al.[54] suggested that montmorillonite–CNT hybrids benefit the enhancement of mechanical properties in polymer nanocomposites.

6. CNT-Magnesium (Mg) Composites

Magnesium is a chemical element with the symbol Mg and atomic number 12. It is an alkaline earth metal and the eighth most abundant element in the Earth's crust and ninth in the known universe as a whole. The free metal burns with a characteristic brilliant white light, making it a useful ingredient in flares. The metal is now mainly obtained by electrolysis of magnesium salts obtained from brine. Commercially, the main use for the metal is as an alloying agent to make aluminium-magnesium alloys, sometimes called magnalium or magnelium. Since magnesium is less dense than aluminium, these alloys are prized for their relative lightness and strength. A sample of Magnesium is shown in Figure 7 and its properties are presented in Table 5.

Figure 7. Magnesium (Mg) sample

Mg matrix is generally used for CNT reinforced MMCs. In recent years, some achievements have been made in the development of CNT-Mg composites. In this section, 13 papers dedicated to this topic are summarized[55-67]. Thakur et al.[55] investigated the synthesis and mechanical behaviour of CNT–magnesium composites hybridized with nanoparticles of alumina. The CNT-Mg composites were prepared by powder metallurgy route coupled with rapid microwave sintering. Nanometer-sized particles of alumina were used to hybridize the CNT reinforcement in the Mg matrix and establish the intrinsic influence of hybridization on mechanical behaviour of the composite. The yield strength, tensile strength and strain-to-failure of the CNT–Mg composites were found to increase with the addition of nanometer-sized alumina particles to the composite matrix. They performed scanning electron microscopy observations of the fracture surfaces of the samples failed in uniaxial tension, which revealed the presence of cleavage-like features on the fracture surface indicative of the occurrence of locally brittle fracture mechanism in the composite microstructure.

Table 5. Mg properties

Crystal structure	*hexagonal close-packed*
Magnetic ordering	*paramagnetic*
Electrical resistivity	*(20°C) 43.9 nΩ.m*
Thermal conductivity	$156\ W.m^{-1}.K^{-1}$
Thermal expansion	$(25°C)\ 24.8\ \mu m.m^{-1}.K^{-1}$
Speed of sound	$(r.t.)\ (annealed)\ 4940\ m.s^{-1}$
Young's modulus	*45 GPa*
Shear modulus	*17 GPa*
Bulk modulus	*45 GPa*
Poisson ratio	*0.290*
Mohs hardness	*2.5*
Brinell hardness	*260 MPa*
Density (near r.t.)	$1.738\ g.cm^{-3}$
Liquid density at m.p.	$1.584\ g.cm^{-3}$
Melting point	*923 K,650°C,1202 °F*
Boiling point	*1363 K,1091°C,1994 °F*
Heat of fusion	$8.48\ kJ.mol^{-1}$
Heat of vaporization	$128\ kJ.mol^{-1}$
Molar heat capacity	$24.869\ J.mol^{-1}.K^{-1}$

Li et al.[56] applied a two-step process to produce CNT-Mg alloy composites. In the first stage, they used a block copolymer as a dispersion agent to pre-disperse multi-walled CNTs on Mg alloy chips. After that, they melted stirred the chips with the dispersed CNTs on their surface. They observed that CNTs were quite successfully dispersed on the surfaces of the Mg alloy chips. The mechanical properties of the CNT-Mg composites were measured by compression testing. They observed that the compression at failure, the compressive yield strength and ultimate compressive strength improved significantly up to 36% by only adding 0.1 wt% CNTs to the Mg alloy. CNT-Mg and CNT-Mg-Ni (Mg–23.5 wt% Ni) composites were processed by Schaller et al.[57] using powder metallurgy, and then charged with hydrogen by annealing at 620 K under a pressure of 0.4 MPa of hydrogen. They performed mechanical spectroscopy and concluded that such a treatment has no effect in the composites with pure Mg matrix. On the other hand, Mg–23.5 wt% Ni alloys, unreinforced as well as reinforced with CNTs, exhibited mechanical loss spectrum, which was deeply modified by hydrogen charging.

Aung et al.[58] mentioned that CNTs may be added to Mg matrix to produce composites of better mechanical properties, but their effect on the corrosion behaviour was not well understood. They studied the corrosion resistance of pure Mg and its composites reinforced with 0.3 and 1.3 wt.% CNTs in 3.5 wt.% NaCl solution using immersion testing and electrochemical measurements. They found that the corrosion rate was increased considerably by the presence of CNTs because of microgalvanic action between the cathodic

CNTs and the anodic Mg matrix.

An advanced powder metallurgy process that disperses un-bundled CNTs was developed by Kondoh et al.[59]. They applied it to fabricate a Mg matrix composite reinforced with CNTs. When approximately 1 vol.% CNTs were added, the extruded pure Mg and AZ31B alloy composites displayed an extremely large increase of the tensile yield stress of 25–40%, compared to Mg materials containing no CNT. They also verified the presence of MgO thin layers of 2–4 nm thickness at the interface between α-Mg and the un-bundled CNTs. This resulted in an effective tensile loading transfer at the interface, which significantly improved the tensile strength and yield stress of the CNT-Mg composites. However, they also observed that the elongation was less than 5% and the composites exhibited a very poor ductility. They attributed this fact to the ductility of the MgO layers at the interface between α-Mg and CNT.

Srivatsan et al.[60] studied the influence of CNTs and processing on cyclic fatigue and fracture behaviour of a magnesium alloy. CNT-Mg alloy (AZ31) was fabricated using the technique of solidification processing followed by hot extrusion. They performed tests on both composite and unreinforced alloy at two different load ratios spanning tension-tension loading and fully-reversed tension - compression loading under total stress amplitude-control. The comparison between the CNT-Mg alloy and the unreinforced counterpart made by Srivatsan et al.[60] revealed more than 200% improvement in cyclic fatigue life. At all values of maximum stress, the high cycle fatigue response of both the reinforced and unreinforced magnesium alloy was found to degrade. They also presented the synergistic and interactive influences of reinforcement and processing on microstructural development, cyclic fatigue life and kinetics governing fracture behaviour. Srivatsan et al.[61] studied the influence of CNTs on the tensile response and fracture behaviour of Mg alloy. They discussed the conjoint influence of reinforcement and processing on microstructural development, microhardness, tensile deformation and final fracture behaviour of the Mg alloy composite and comparisons were made with the unreinforced alloy (AZ31). They highlighted the interactive influences of the CNT reinforcement and processing in governing engineering stress versus engineering strain response and tensile properties. Srivatsan et al.[61] discussed the macroscopic fracture mode and intrinsic microscopic mechanisms governing quasi-static deformation and fracture behaviour of both the CNT reinforced and unreinforced magnesium alloy. Srivatsan et al.[62] developed further studies on the microstructure, hardness, tensile properties, tensile fracture, high cycle fatigue characteristics, and final fracture behaviour of CNTs-Mg alloy composite with 1.0 vol.% CNT. They found that the elastic modulus, yield strength, tensile strength of the reinforced Mg alloy was noticeably higher compared to the unreinforced counterpart. The ductility, quantified both by elongation-to-failure and reduction in cross-section area of the composite was higher than the monolithic counterpart. A comparison of the CNT-Mg alloy with the unreinforced Mg revealed a noticeable improvement in cyclic fatigue life.

Park et al.[63] evaluated the mechanical properties of magnesium matrix composite reinforced with Si coated CNTs. Multi-walled CNTs reinforced Si coatings were prepared using solid reaction method between pure silicon powders and CNTs. MMC with CNTs reinforced AZ91 were fabricated by the squeeze infiltrated method. They found that the Si coated CNTs led to improvement in the wettability, distribution, bonding strength in the CNT-Mg composite. They also concluded that the squeeze infiltration technique was a proper method to fabricate Mg-based composites because it reduces casting defects such as pores and matrix/reinforcement interface separation. Park et al.[63] concluded that the tensile strength increased with the reinforcement of Si coated CNT to magnesium alloys.

Mg composite reinforced with CNTs were produced by Fukuda et al.[64] using both pure Mg and AZ61 Mg alloy matrix. They highlighted the superior mechanical properties of the CNT-Mg composite. The composites were produced via powder metallurgy route containing wet process using isopropyl alcohol based zwitterionic surfactant solution with unbundled CNTs. The produced composites were evaluated with tensile test and Vickers hardness test and analyzed by X-ray diffraction and field-emission scanning electron microscopy. They observed that Al_2MgC_2 compounds formed at the interface between Mg matrix and CNTs effectively reinforced the interfacial bonding and enabled tensile loading transfer from the Mg matrix to CNTs. Furthermore, they also clarified that the microstructures and grain orientations of the composite matrix were not significantly influenced by CNT addition. Mg containing 6 wt.% Al alloy composites reinforced with CNTs were fabricated with powder metallurgy based wet-processing by Fukuda et al.[65]. They observed that both yield stress and tensile strength improved with the addition of CNTs. Field emission-transmission electron microscopy microstructural analysis clarified that needle-like ternary carbides of Al_2MgC_2 were synthesized at some interfaces between magnesium matrix and CNTs, and the other interfaces were clean without any other materials or defects. The tensile loading transfer from Mg matrix to CNTs was effectively strengthened by both the production of Al_2MgC_2 compounds and the clean interface between Mg matrix and CNTs.

Zhou et al.[66] studied the tensile mechanical properties and strengthening mechanism of hybrid CNT and silicon carbide nanoparticle-peinforced Mg alloy composites. AZ91 Mg alloy hybrid composites reinforced with different hybrid ratios of CNTs and silicon carbide (SiC) nanoparticulates were fabricated by semisolid stirring assisted ultrasonic cavitation. Their results showed that grains of the matrix in the AZ91-(CNT + SiC) composites were refined after adding hybrid CNTs and SiC nanoparticles to the AZ91 alloy, and the room-temperature mechanical properties of AZ91-(CNT + SiC) hybrid composites were improved comparing with the unreinforced AZ91 matrix. In addition, the tensile mechanical properties of the AZ91 alloy-based hybrid composites were considerably improved at the mass hybrid ratio of 7:3 for CNTs and SiC nanoparticles. The tensile and yield strength increased about 45-55% after gravity permanent mould casting. They attributed the increase in the room-temperature strength of the hybrid composites to (i) the larger hybrid ratio of CNTs and SiC nanoparticles, (ii) the coefficient of thermal expansion mismatch between matrix and hybrid reinforcements, (iii) the dispersive strengthening effects (Orowan strengthening), and (iv) the grain refining (Hall-Petch effect). CNT-Mg composite powders were produced by Sun et al.[67] and synthesized by in situ chemical vapor deposition of acetylene in Co/Mg catalyst powder at 480 °C. The factors influencing the morphology and yield of CNTs, including the compositions of the Co catalyst and the ratio of carbon source to carrier gas, were investigated by Sun et al.[67]. Their results showed that CNTs had a mean size of 15 nm and were highly graphitizing and homogeneously dispersed on the Mg powder. Ball milling of CNT-Mg composite powders for short times enabled embedding of CNTs into Mg, resulting in grain refinement. They concluded that tensile strength of CNT-Mg composites reached an average of 285 MPa, thus leading to an increase of 45% compared to commercial pure Mg.

7. CNT-Nickel (Ni) Composites

Figure 8. Nickel (Ni) sample

Nickel is a chemical element with the chemical symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals and is hard and ductile. Because of nickel's slow rate of oxidation at room temperature, it is considered corrosion-resistant. Historically this has led to its use for plating metals such as iron and brass, to its use for chemical apparatus, and its use in certain alloys that retain a high silvery polish, such as German silver. About 6% of world nickel production is still used for corrosion-resistant pure-nickel plating. Nickel was once a common component of coins, but has largely been replaced by cheaper iron for this purpose. A sample of Nickel is shown in Figure 8 and its properties are presented in Table 6.

Table 6. Ni properties

Crystal structure	*face-centered cubic*
Magnetic ordering	*ferromagnetic*
Electrical resistivity	*(20 °C) 69.3 nΩ.m*
Thermal conductivity	$90.9\ W.m^{-1}.K^{-1}$
Thermal expansion	(25 °C) $13.4\ \mu m.m^{-1}.K^{-1}$
Speed of sound	(r.t.) $4900\ m.s^{-1}$
Young's modulus	*200 GPa*
Shear modulus	*76 GPa*
Bulk modulus	*180 GPa*
Poisson ratio	*0.31*
Mohs hardness	*4.0*
Vickers hardness	*638 MPa*
Brinell hardness	*700 MPa*
Density (near r.t.)	$8.908\ g.cm^{-3}$
Liquid density at m.p.	$7.81\ g.cm^{-3}$
Melting point	*1728 K, 1455 °C, 2651 °F*
Boiling point	*3186 K, 2913 °C, 5275 °F*
Heat of fusion	$17.48\ kJ.mol^{-1}$
Heat of vaporization	$377.5\ kJ.mol^{-1}$
Molar heat capacity	$26.07\ J.mol^{-1}.K^{-1}$

In comparison with Al and Mg, Ni matrix is not widely used for CNT reinforced MMCs. In this section, 5 papers dedicated to this topic are briefly described[68-72]. Wang et al.[68] studied the friction and wear behaviour of electroless Ni-based CNT composite coatings. Ni-based CNT composite coatings with different volume fraction (from 5 to 12 vol.%) of CNTs were deposited on medium carbon steel substrates by electroless plating. The friction and wear behaviour of the composite coatings were investigated by Wang et al.[68] using a pin-on-disk wear tester under unlubricated condition. Friction and wear tests were conducted by these authors at a sliding speed of 0.0623 m/s and at an applied load of 20 N. Their experimental results indicated that the friction coefficient of the composite coatings decreased with increasing the volume fraction of CNTs due to self-lubrication and unique topological structure of CNTs. Within the range of volume fraction of CNTs from 0 to 11.2%, the wear rate of the composite coatings showed a steadily decreasing trend with increasing volume fraction of CNTs. However, the wear rate of the composite coatings increased with further increasing the volume fraction of CNTs due to the conglomeration of CNTs in the matrix.

Ni matrix reinforced with multi-walled CNTs were processed by Scharf et al.[69] in a monolithic form using the laser-engineered net shape processing technique. They performed Auger electron spectroscopy maps and determined that the CNTs were well dispersed and bonded in the Ni matrix and no interfacial chemical reaction products were determined in the as-synthesized composites. Mechanisms of solid lubrication were investigated by Scharf et al.[69] using micro-Raman spectroscopy spatial mapping of the worn surfaces to determine the formation of tribochemical products. The CNT-Ni composites exhibited a self-lubricating behaviour, forming an in situ, low interfacial shear strength graphitic film during sliding, resulting in a decrease in friction coefficient compared to pure Ni.

CNT-Ni composites were processed by Singh et al.[70] using a laser deposition technique known as the laser engineered net shaping process. Mechanical milling of the powder consisting of nickel powders and CNTs resulted in more homogeneous distribution of the CNTs in the Ni matrix and two distinct scales of reinforcements within the composite. The larger reinforcement scale consisted of submicrometre to micrometre sized bundles of CNTs while the smaller scale consists of individual CNTs within the Ni matrix. High resolution transmission electron microscopy indicated that the CNT-Ni interface was well bonded without the presence of any significant interfacial reaction product. Raman spectroscopy revealed that the degree of disorder and defects in the CNT bundles in the nickel matrix varied as a function of bundle size.

CNTs filled with metals can be used in capacitors, sensors, rechargeable batteries and so on. Atomic arrangement of the metals plays an important role in the function of the composites. Liu et al.[71] showed that Ni and NiO nanoparticles in CNTs are crystalline, resulting in the occurrence of lattice shrinkage. Lattice shrinkage caused a misfit of the lattice constant between the Ni and the internal CNT surface (from theoretical 1.21% to actual 0.86%). They observed that this variation was beneficial to heterogeneous nucleation of Ni crystal nucleus on the surface at a point with the lowest interfacial energy at coherent interface. According to their findings, one-dimensional nanostructures can be changed and controlled during synthesis by use of CNTs as a template.

Hwang et al.[72] performed interface analyses of ultra-high strength CNT-nickel composites processed by molecular level mixing followed by spark plasma sintering. They found that CNT-Ni composites exhibiting a yield strength of 710 MPa, about 3.7 times higher than monolithic Ni. They attributed the enormous strength increase in these composites to the homogeneous distribution of CNTs in the Ni matrix coupled with the formation of well-bonded, high strength, contaminant-free CNT-Ni interfaces, as revealed by high-resolution transmission electron microscopy. Such interfaces effectively transfer load between CNTs and Ni matrix in the CNT-Ni composites.

8. CNT-Titanium (Ti) Composites

Titanium is a chemical element with the symbol Ti and atomic number 22. It is a lustrous transition metal with a silver color, low density and high strength. It is highly resistant to corrosion in sea water, aqua regia and chlorine. The element occurs within a number of mineral deposits, principally rutile and ilmenite, which are widely distributed in the Earth's crust and lithosphere, and it is found in almost all living things, rocks, water bodies, and soils. Titanium can be alloyed with iron, aluminium, vanadium, molybdenum, among other elements, to produce strong lightweight alloys for aerospace (jet engines, missiles, and spacecraft), military, industrial process (chemicals and petro-chemicals, desalination plants, pulp, and paper), automotive, agri-food, medical prostheses, orthopedic implants, dental and endodontic instruments and files, dental implants, sporting goods, jewelry, mobile phones, and other applications. The two most useful properties of the metal are corrosion resistance and the highest strength-to-weight ratio of any metal. In its unalloyed condition, titanium is as strong as some steels, but 45% lighter. A sample of Titanium is shown in Figure 9 and its properties are presented in Table 7.

Figure 9. Titanium (Ti) sample

Table 7. Ti properties

Crystal structure	*hexagonal close-packed*
Magnetic ordering	*paramagnetic*
Electrical resistivity	*(20 °C) 420 nΩ.m*
Thermal conductivity	$21.9\ W.m^{-1}.K^{-1}$
Thermal expansion	$(25\ °C)\ 8.6\ \mu m.m^{-1}.K^{-1}$
Speed of sound	$(r.t.)\ 5{,}090\ m.s^{-1}$
Young's modulus	*116 GPa*
Shear modulus	*44 GPa*
Bulk modulus	*110 GPa*
Poisson ratio	*0.32*
Mohs hardness	*6.0*
Vickers hardness	*970 MPa*
Brinell hardness	*716 MPa*
Density (near r.t.)	$4.506\ g.cm^{-3}$
Liquid density at m.p.	$4.11\ g.cm^{-3}$
Melting point	*1941 K, 1668 °C, 3034 °F*
Boiling point	*3560 K, 3287 °C, 5949 °F*
Heat of fusion	$14.15\ kJ.mol^{-1}$
Heat of vaporization	$425\ kJ.mol^{-1}$
Molar heat capacity	$25.060\ J.mol^{-1}.K^{-1}$

Ti matrix is not widely used as Al and Mg for CNT reinforced MMCs, but very recent works have been published. In this section, 6 papers focused to this theme are reviewed[73-78]. Xue et al.[73] prepared CNT-Ti composites using the heterogeneous coacervation method followed by spark plasma sintering, and studied the morphology, phase structure and elevated temperature compressive properties. They observed that the CNTs were well dispersed onto the Ti particles, and parts of them were converted into TiC along the interface after SPS due to solid-state reaction. They concluded that the compressive yield strength declined before a slight rise with the increase in sintering temperatures, which indicated that the reinforcements and dense structure played the combined action.

CNT-reinforced TiNi matrix composites were produced by Feng et al.[74] and synthesized by employing elemental powders. Two methods have been used to control the interfacial reaction between CNTs and Ti, which heightened the quality of CNTs (graphitized multi-walled CNTs) and shortened the time of over-eutectic temperature sintering (two-stage hot pressed sintering). They found that a major TiNi parent phase with different proportions of intermetallic compound phases was obtained by varying the second stage sintering temperatures. The specimens with second stage sintering temperature at 1050°C exhibited predominant mechanical properties, and the GMWCNTs retained their original size. Feng et al.[75] indentified a slight decrease in average friction coefficient and a great decline in volume loss (reaching to 63.1%) in TiNi matrix composites prepared by sintering 1 vol.% multi-walled CNTs with Ti and Ni elemental powders. They concluded that in situ TiC and the remaining CNTs act as reinforcements and plays the major role in the improvement. Their study explored the possibility of developing novel TiNi matrix tribocomposites.

Cai et al.[76] prepared CNT-reinforced TiNi matrix composites using spark plasma sintering employing elemental powders and studied the phase structure, morphology and transformation behaviours. They found that thermoelastic martensitic transformation behaviours could be observed from the samples sintered above 800°C even with a short sintering time (5 min), and the transformation temperatures gradually increased with increasing sintering temperature because of more Ti-rich TiNi phase formation. They argued that method supplies a basis for preparing CNT-reinforced TiNi composites.

Kondoh et al.[77] investigated the high-temperature properties of extruded titanium composites fabricated from CNTs coated titanium powder. The pure Ti matrix composite reinforced with CNTs was prepared by spark plasma sintering and hot extrusion via powder metallurgy process. Ti powders were coated with CNTs via a wet process using a zwitterionic surfactant solution containing 1.0, 2.0 and 3.0 wt.% of CNTs. They observed that situ TiC formation via reaction of CNTs with titanium occurred during sintering, and TiC particles were uniformly dispersed in the matrix. The tensile properties of the composites were evaluated by Kondoh et al.[77] at room temperature, 473, 573 and 673 K, respectively. They concluded that the mechanical properties of extruded CNT-Ti composites at elevated temperature remarkably improved by adding a small amount of CNTs, compared to extruded Ti matrix. They attributed this evidence to the stabilization effect of TiC dispersoids originated from CNTs on the microstructure of extruded Ti composites. CNT and graphite (Gr) reinforced Ti metal matrix composites were fabricated by Li et al.[78] via powder metallurgy. They prepared 0–0.4 wt% CNT/Gr and Ti mixture powders by rocking mill. Microstructures and mechanical properties of the as-extruded Ti composites were investigated by Li et al.[78] to evaluate strengthening effects of CNT/Gr on Ti matrix. They mentioned that the mechanical strength of CNT/Gr-Ti composites augmented for increasing CNT/Gr content from 0.1 to 0.4 wt%. Compared to pure Ti, the yield strength and ultimate tensile strength of Ti-0.4 wt% CNT composites increased 40.4% and 11.4%, respectively. Compared to pure Ti, the yield strength and ultimate tensile strength of Ti–0.4 wt% Gr increased 30.5% and 2.1%, respectively. They also discussed the strengthening mechanism, which included grain refinement, carbon solid solution strengthening and TiC/carbon dispersion strengthening.

9. Conclusions

Since the discovery of carbon nanotubes (CNTs) and their excellent mechanical properties, they have been used as exceptional nanofibres. The simultaneous (i) improvement of available processes to produce pure carbon nanotubes (CNTs) and (ii) enhancement of existing techniques to fabricate better matrix materials, paved the way to obtain high performance composite materials, with optimized mechanical properties. CNTs have been introduced into polymers, ceramics, cement-based materials and metals, the latter designated as metal matrix composites (MMCs). Today, many applications of CNT reinforced composites exist but CNT reinforced MMCs are still scarce and only found in very specific applications. During the last decade, several works have been dedicated to improve the behaviour of CNT reinforced MMCs. This review described the state-of-the art in this field and highlighted the excellent and promising mechanical, thermal, electrical properties of CNT reinforced MMCs.

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