



Review Metallurgical Challenges in Carbon Nanotube-Reinforced Metal Matrix Nanocomposites

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Received: 14 July 2017; Accepted: 11 September 2017; Published: 22 September 2017

Abstract: The inclusion of carbon nanotubes (CNTs) into metallic systems has been the main focus of recent literature. The aim behind this approach has been the development of a new property or improvement of an inferior one in CNT-dispersed metal matrix nanocomposites. Although it has opened up new possibilities for promising engineering applications, some practical challenges have restricted the full exploitation of CNTs' unique characteristics. Non-uniform dispersion of CNTs in the metallic matrix, poor interfacial adhesion at the CNT/metal interface, the unfavorable chemical reaction of CNTs with the matrix, and low compactability are the most significant challenges, requiring more examination. The present paper provides a broad overview of the mentioned challenges, the way they occur, and their adverse influences on the physicomechanical properties of CNT-reinforced metal matrix nanocomposites. The suggested solutions to these issues are fully addressed.

Keywords: carbon nanotube; nanocomposite; dispersion; interfacial adhesion; phase transformation; physicomechanical properties

1. Introduction

Carbon nanotubes (CNTs) as one of carbon allotropes have been discovered in 1991 by Iijima [1]. There are two main types of CNTs including single-walled (SWNTs) and multi-walled nanotubes (MWNTs). CNTs are the monolithic cylinders of one or more layers of the graphene, so that if only one graphene layer is rolled, it is called SWNTs. MWNTs can be also understood by rolling several parallel graphene layers. Both SWNTs and MWNTs are formed with open or closed ends [2]. The morphology of MWNTs highly depends on their fabrication process, where Russian doll tubes are formed using perfectly concentric cylinders, and scroll tubes can be formed when a single graphene sheet is rolled as scroll [3]. All carbon atoms in the perfect structure of CNTs (except those present on the edges) are bonded in a hexagonal lattice. The presence of impurities drastically degrades the final properties of the tubes. MWNTs have larger diameters than SWNTs, where the diameter of SWNTs ranges from 0.8 to 2 nm and the diameter of MWNTs varies between 5 and 20 nm [2]. Furthermore, the size and surface area of CNTs are of prime significance, so that they can play an important role in the antibacterial applications, where a decrement in CNTs size may significantly improve their antibacterial efficiency

through the increase of the specific surface area [4]. Also, the variation of geometrical dimensions in CNTs can significantly affect their final properties due to a change in the length to diameter ratio. However, the final properties of SWNTs and MWNTs do not change in the same manner with the aspect ratio variation. For instance, the Young's modulus of SWNTs deeply depends on the size and chirality, while the elastic modulus of MWNTs slightly changes with the diameter variation [5]. Although CNTs are among the strongest materials in nature, their mechanical properties vary in different directions. The results confirm the higher Young's modulus and tensile strength in the axial direction compared to the radial one [6].

Owing to their appropriate mechanical, electrical, and thermal properties, CNTs have been extensively used in a wide range of the engineering applications such as high-strength and conductive composites, energy storage devices, and hydrogen storage [7]. Moreover, due to a favorable combination of strength and weight, CNTs are commonly used in the aerospace and automobile industries [8]. In these cases, CNTs are used whether in pure state or as a reinforcement in the metal, ceramic, and polymer matrix nanocomposites [9–11]. As to CNT-reinforced nanocomposites, the aim is the development of a new property or improvement of present properties.

In general, the incorporation of CNTs into metallic matrices improves the mechanical properties of such binary systems (e.g., microhardness and fracture toughness) or electrical properties. However, they may adversely affect the properties [12]. Despite the mentioned advantages, this approach mainly faces four major challenges as follow:

- (i) Favorable dispersion of CNTs throughout the matrix. A composite with improved properties will be obtained when the reinforcements are uniformly distributed through the matrix. Otherwise, the micro-pores as well as agglomerated particles may form all over the microstructure [13,14]. To overcome this challenge, a broad spectrum of dispersion methods is developed. Among these techniques, the mechanical methods [15], surface treatment [16], and chemical methods [17] are the most conventional. Each of these techniques has their own advantages and disadvantages, being discussed in the next sections.
- (ii) Unfavorable chemical reaction of CNTs with matrix at high pressures, elevated temperatures, and induced strains. It is usually accompanied by the formation of defects. On the other words, to thermally decompose CNTs in exposure to a metallic matrix, the presence or formation of defects is required. It is shown that the thermal decomposition of CNTs can bilaterally affect the final properties of the nanocomposites. In other words, the final properties strongly depend on the chemical composition of the formed intermetallics [18,19].
- (iii) Poor interfacial adhesion between CNTs and the matrix due to the hydrophobic nature of the CNTs. This shortcoming deteriorates the load bearing between the matrix and CNTs. Moreover, intensive phonon scattering arisen from the insufficient adhesion can significantly enhance the electrical resistivity [20]. It is noteworthy that the interfacial adhesion can be improved whenever a controlled superficial chemical reaction between CNTs and metallic matrix occurs. On the other words, the poor interfacial adhesion can be considered as a sub-challenge under the title of "chemical reaction of CNTs with metallic matrix". This review paper has adopted such a policy.
- (iv) Low compactability of metallic powders. The incorporation of CNTs into metallic powders can decline the relative density of final CNT-metal compacts, if the agglomeration of CNTs is heavy and their volume fraction is exceedingly high.

As a general conclusion, the aforementioned challenges should be considered simultaneously in order to produce a CNT-reinforced metal matrix composite with superior properties. The present paper provides a broad overview of these challenges and their potential effects on the properties of CNT-dispersed metal matrix nanocomposites in some details. Also, the practical solutions to these challenges are introduced and their positive influences on the physicomechanical properties of the nanocomposites are studied. It is noteworthy that the full review of the potential effects of CNT addition on the physicomechanical properties of metallic systems is not the main purpose of the present review paper. However, one can find such information in [21,22].

2. Metallurgical Challenges in CNT-Metal Matrix Nanocomposites

2.1. Dispersion of CNTs (Carbon Nanotubes)

To date, a wide variety of research works are conducted with the aim to produce CNT-reinforced metal matrix nanocomposites with superior physicomechanical features for a broad range of functional and structural applications. However, the incorporation of CNTs into the metallic matrices is severely restricted due to both outstanding challenges: (i) Non-uniform dispersion of CNTs throughout the metallic matrices, and (ii) weak interfacial adhesion between CNTs and metallic matrix. In comparison to carbon particles and fibers, CNTs are more likely to be non-uniformly distributed inside the metallic systems due to their comparatively high aspect ratio and extraordinary specific surface area [23].

2.1.1. Water Solubilization of CNTs

A majority of electronic, thermal, and optical applications in which CNTs are used for the fabrication of novel devices or development of new emerging platforms need the large-scale production of stable CNT suspensions with a uniform dispersion and no agglomeration [24]. It is while the van der Waals attraction between CNTs results in their agglomeration and the formation of bundles (Figure 1) due to high surface area [25]. To overcome this practical challenge, some solutions are suggested. Better dispersion of CNTs in water as an important medium for biomedical and biochemistry applications is recognized by various methods such as using surfactants, polymers or chemical functionalization [24]. As to the chemical functionalization, a covalent bond is established between the chemical species and carbon atoms located at side walls or end caps of CNTs. However, this method suffers from two main problems [23,26–28]:

- (i) CNTs may shorten, get severe damages during the functionalization process, and lose their superior mechanical properties and distribution of π -electrons. As a general rule, the electron transport strongly depends on the surface structure of CNTs, because the structural damages can serve as phonon scattering sites and interrupt the transport properties of nanotubes.
- (ii) The strong acid solutions normally used for functionalization are hazardous to environment and hard to handle.



Figure 1. SEM (scanning electron microscope) images of (**a**) multi-walled carbon nanotube (MWCNT) bundles and (**b**) agglomerations [29] (Reproduced with permission from [29], Elsevier, 2012).

The aforementioned disadvantages have persuaded the researchers to develop other dispersing methods based on non-covalent modifications to uniformly distribute CNTs in water. These techniques benefit from two advantages over covalent functionalization methods:

- (i) They induce no damages to CNTs, so that the electron transportation along the nanotubes remains intact; and
- (ii) CNTs are capable of forming an ordered network through the supermolecules acting as non-covalent modifiers. Among these modifiers, polymers and surfactants are the most conventional. These agents can thread themselves onto CNTs (Figure 2a) or wrap themselves around them (Figure 2b) [28,30,31]. Surfactants are also employed for dispersing CNTs in metal matrix nanocomposites.



Figure 2. Non-covalent functionalization of carbon nanotubes (CNTs): (**a**) With a surfactant and (**b**) with a polymeric agent [32] (Adapted with permission from [32], Elsevier, 2016).

2.1.2. Dispersion of CNTs into Metallic Systems

The practical results show that the dispersion process of CNTs inside the metallic matrices can be completely different and more difficult than water media. This is because an intrinsically different phase (i.e., metal) is added to the system which makes the process more complex. Among these complexities, the CNT/metal interfaces and the poor wettability of CNTs by metal matrices are of prime significance. As generally accepted, an increment in CNT content can result in further agglomeration due to increased possibility of contacts between CNTs and decreased wettability. Therefore, dispersing individual CNTs in metallic systems with the reasonable spacing is a critical challenge for engineers and researchers [10,25].

The agglomeration of CNTs decreases the superior strengthening effects of nanotubes in CNT-metal matrix nanocomposites and deteriorates their physicomechanical properties. Moreover, the inhomogeneous dispersion of CNTs gives rise to non-homogeneity and anisotropy in these binary systems. On the other hand, it may impede the full sintering and reduces the relative density, wettability of CNTs, and resultant mechanical properties [16,33–35].

The above-mentioned challenges about the agglomeration and poor wettability of CNTs in metallic matrices have persuaded the researchers to discover more-efficient methods to uniformly distribute the nanotubes in these material systems. Their huge explorations have resulted in a wide variety of practical dispersion methods, although they are not classified into generally accepted standard categories. In fact, some literature has suggested different arbitrary classifications of the newly developed dispersion methods. For instance, they can be classified into four main groups: (i) Pre-treatments such as functionalizing, ultrasonication, and surface treatments; (ii) Mixing CNT with a metal precursor such as electrodeposition; (iii) Mixing CNT with a metal powders through milling prior to the consolidation routes; and (iv) Post-treatments such as extrusion and rolling.

There are some different approaches for categorization of CNT dispersion methods. From the phenomenological perspective, they may be classified into three main groups: (i) Colloidal mixing in which physical reactions occur between CNTs and other species present in aqueous and inorganic media; (ii) Chemical mixing through which CNTs react chemically with other components; and (iii) Mechanical mixing which uses a mechanical force to detach CNTs from each other. However, all the categorized groups have no distinct boundaries, so that one dispersing method can belong to two or three groups in the same time. For instance, the ultrasonication method, which usually belongs to colloidal mixing, can be categorized in the chemical mixing group, if a chemical reaction occurs during the sonication of CNTs in the aqueous medium. As another example, the metallization is considered as a chemical mixing method, but it needs a complementary mixing method such as milling. As a result, the researchers have their arbitrary classification principles which are not general rules. Furthermore, CNT-metal dispersion methods are progressively updated and modified, so that the sharp boundaries between them are gradually faded. Table 1 summarizes some of the common dispersion methods among which the milling, ultrasonication, the application of surfactants, and metallization are explained in the next sections. Also, their possible challenges and suggested solutions are extensively discussed.

Ball Milling

In this procedure, a milling container with several hard balls is used for dispersing CNTs inside the metallic systems. During the milling, metal powders become fractured and welded again, so that CNTs are entrapped between them [15,36]. Since the primary powders as well as CNT bundles are entrapped between balls or balls and the container wall, the grinding motion of milling balls separates the nanotubes from each other, destroys the agglomerations, and disperses CNTs among the metallic powders. The milling time is one effective processing factor determining the degree of dispersion. As the mixing proceeds, the agglomeration is alleviated. Moreover, in the initial steps of milling, metallic powders have round shapes, and CNTs are dispersed at their surfaces. However, as the mixing continues, soft metallic powders flatters, and CNTs are embedded in the powders [15,36]. Generally, the mechanical milling is less able to inhibit CNT agglomerations, as seen in Figure 3 [37].



Figure 3. CNTs agglomeration in 5 wt % CNT-Al blends processed by mechanical milling for 30 min [38] (Adapted with permission from [38], Elsevier, 2011).

Dispersion Method	Principles	Advantages	Disadvantages	Studied Metallic Systems	
Ball milling	In this method, CNTs and metallic powders are milled in a container with hard balls.	 Mass production Commercial applications Easy processing Low cost Possibility of in-situ functionalization during the mixing The possibility of in-situ alloying 	Generation of defects in CNTs Cutting or breaking of CNTs Inclusion of contaminants into the system Long-time procedure	Al [39], Ni [40], Mg [12], Cu [41], Fe [42], and their alloys	
Ultrasonication	 Mass production Commercial applications Easy processing The possibility of in-situ functionalization or surfactant by using high frequency sound waves. Mass production Easy processing The possibility of in-situ functionalization or SDS (soduim dodecyl sulfate) treatment during the mixing Low cost 		Al [14], Cu [43], Fe [44] and their alloys		
Surfactants	In this method, non-covalent surfactants are embedded on CNTs surfaces with the aim to decrease the CNTs affinity to stick together.	 Mass production Commercial applications Easy processing The possibility of in-situ functionalization or SDS treatment during the mixing Low cost 	Low CNT content can be uniformly dispersed Need for a mechanical method to disperse CNTs throughout the metallic powders	Al [45], Ti [18], Ni [46], and their alloys such as CuZr and CuZrAl [47]	
Metallization (i.e., decoration with metals)	In this method, CNTs are coated with a metallic layer such as Cu, Ni, Co, Mo, and W before their introduction into the matrix.	- High efficiency (depending on the dispersion method used for metalized CNTs)	Need for an additional mixing method such as mechanical mixing for producing dense parts	Al [16] and Cu [48]	
Hetero-agglomeration principle	In this method, oppositely charged CNTs and metallic powder are co-deposited. CNTs and metallic powders are charged through a chemical step such as ultrasonication in acidic media.	 The possibility of uniformly dispersing CNTs up to 5 vol % Mass production - Production of CNT-containing systems with no damage 	Relatively high cost	Al [17]	
Molecular level dispersion	A chemical or physical reaction occurs between functionalized CNTs and metallic ions in a solution medium.	 The possibility of uniformly dispersing high CNTs content (up to 10–15 vol %) in metallic matrices The possibility of embedding CNTs inside the metallic powders rather than dispersing them at particles surfaces 	Practical complexity Limited production scale	Cu [49,50], Ag [51], Ni [52], AgPd [53], Al [54], and AlCu [55]	
In-situ chemical synthesis	In this method, CNTs are directly synthesized from the vapor phase on the metallic powders.	 Mass production The possibility of automatization The possibility of uniformly dispersing a high CNTs content in metallic systems 	Need for expensive equipment	Mg [56], FeCr [57], Cu [58], AlCu [59], Al [60], and Fe [61]	

Table 1. A short description of CNTs (carbon nanotubes) dispersion methods in metal matrix nanocomposites, their advantages and disadvantages.

Table 1. Cont.

Dispersion Method	Principles	Advantages	Disadvantages	Studied Metallic Systems
Electroless deposition	In this method, CNTs are immersed in an electrolyte solution containing metal ions. During the process, the nanotubes are covered by ions through developing potential. A substrate can be used on which CNTs and metallic ions are simultaneously deposited.	 Commercial applications High efficiency The possibility of combination with other mechanical mixing techniques such as ultrasonication for better CNTs dispersion The possibility of uniformly dispersing other components 	 Only used for some metals High cost Need for a supporting mixing method to obtain a full efficiency 	Cu [62], Ni [63], Al [64], Au, and Pt [65]
Electrodeposition	In this method, CNTs are embedded in an electrochemically formed metallic film. This film is deposited as metallic ions transfer from cathode or electrolyte solution to the anode.	 Commercial applications High efficiency The possibility of combination with other mechanical mixing techniques such as ultrasonication for better CNTs dispersion The possibility of uniformly dispersing other components 	 Only used for certain metals High cost Not easy to handle Need for a supporting mixing method to obtain a full efficiency 	Ni [66], Cu [67], Sn-Bi [68], Cu-Ni [69], and Ni-Co [70]
Using hybrid reinforcements	In this method, CNTs are added to other components such as SiC, A_2O_3 , and graphite for better distribution. The ball milling is the most conventional method for mixing the hybrid reinforcements.	 The possibility of obtaining higher mechanical properties due to strengthening effects of hybrid reinforcements High efficiency Cost-effective 	 Need for an additional mixing process such as ball milling The possibility of formation of unwanted intermetallic compounds 	Al [71], Cu [72], Mg [73]
Preform infiltration	In this method, an initial preform of CNTs and other components is fabricated, and the molten metal is infiltrated into it.	 The possibility of selectively dispersing CNTs at a macro level High efficiency to prevent the agglomeration 	 Metallic component needs to be melted Restrictions imposed by shape geometry Need for a two-step procedure Relatively high cost 	Al [74,75]
FSP/SLM induced dispersion	After the fabrication of bulk CNT/metal nanocomposites, friction stir processing (FSP) or selective laser melting (SLM) is used for re-dispersing CNTs.	 High efficiency (depending on the dispersion method used before the fabrication) 	 Imposition of additional cost Only used for finished CNT/metal bulk nanocomposites 	Al [76], Cu [77]
Induction melting-based dispersion	In this method, a solid metal with a CNT-containing flux is poured into an induction furnace. The presence of such a flux decreases the melting temperature of the solid metal. Finally, CNTs are dispersed by induction-formed fluctuations.	Mass productionEasy to handle	 Additional cost due to melting of the used metal Need for expensive instruments 	Al [78], Ti [79]
Casting-based methods such as stir casting and squeeze casting	In these methods, CNTs are dispersed in a molten metal through stirring or squeezing.	 Mass production Easy to handle Comparatively low cost 	 Additional cost due to the melting of the metals Comparatively low efficiency 	Al [80]

To improve the CNT dispersion in metallic matrices, a process controlling agent (PCA) such as polyacrylic acid (PAA) or methanol is usually used. These chemicals are utilized not only for better dispersion, but also for CNTs functionalization (Figure 4).



Figure 4. TEM (transmission electron microscopy) images of (**a**) as-synthesized CNTs, (**b**) CNTs ball milled with NH₄HCO₃ as a functionalizing agent and process control agent (PCA), and (**c**) CNTs milled with no PCA. The presence of chemicals is shown to result in improved CNTs dispersion [81] (Reproduced with permission from [81], Elsevier, 2008).

Despite the ability to functionalize CNTs, the mechanical milling is capable of in-situ alloying as a subsidiary mechanism for strengthening CNT-metal matrix nanocomposites. Moreover, it can produce the metallic nanostructures whose mechanical strength is higher than that of conventional nanocomposites. Such grain structures arise from the formation of large numbers of dislocations inside the metallic powders due to high plastic deformation.

As another advantage, a close control over the particle size and particle size distribution in ball milled powder systems is possible. These characteristics are controlled by two competing mechanisms during the milling: (i) Cold working, which results in decreased ductility, particle fracturing, and reduced particle size; and (ii) Cold welding, which results in increased particle size [40,82,83].

Besides the aforementioned advantages, the mechanical milling may induce structural damages to CNTs such as breaking or shortening, especially when the dwell time is extended. These defects confine the processing time [84]. They may be also formed when the milling is conducted under inappropriate practical conditions. The non-controlled milling results in formation of carbides through a chemical reaction between the damaged nanotubes and reactive metallic powders such as Al. Such reactions may occur even at comparatively low milling temperatures.

Among the various milling apparatuses, the planetary milling imposes less energy on metallic powders and CNTs, especially in comparison with high-energy mechanical milling. The higher the energy imposed on the powder blend, the higher the volume fraction of defective nanotubes will be [82]. In contrast, high energy milling can evenly embed CNTs in the metallic powders, while the planetary milling is usually incapable of uniformly dispersing CNTs. It may persuade the CNT agglomerations and locate them at the external surface of metallic powders rather the diffusion into them. Furthermore, a useful combination of practical conditions is required to obtain high-quality nanocomposites [85]. Figure 5 shows the way the nanotubes may be mechanically dispersed throughout Al matrix.

It seems that the utilization of a chemical modification or a processing control agent as well as the low energy milling technique can successfully reduce the structural damages of CNTs [82].

Another practical method to prevent the chemical reactions during the milling is the suppression of heat-induced changes in metallic powders through cryogenic techniques. Cryogenic milling is referred to as the milling procedure at very low temperatures (usually below 100 K). Such temperatures give rise to the increase in brittleness of metallic powder, reduction in grain growth, resultant grain refinement, and decrement in grain size. In this case, the hardness of CNT-metal matrix nanocomposites increases by the Hall-Petch mechanism. Therefore, such methods are able to reduce the processing

st possibility of chemical reactions. Interestingly

time and bring forth finer grains with the lowest possibility of chemical reactions. Interestingly, if the cryogenic milling is conducted with the presence of carbon-containing PCA such as stearic acid, their carbons may react with metallic powders and form carbides during the milling or subsequent sintering processes [82].



Figure 5. SEM images of a CNT-Al blend after milling by high energy milling (**a**–**d**) and low energy milling (**e**,**f**) [85]. The CNTs are uniformly dispersed and embedded in Al powders during high energy ball milling, as shown by yellow arrows (Reproduced with permission from [85], Elsevier, 2011).

The CNTs are uniformly dispersed and embedded in Al powders during high energy ball milling. However, their dispersion has not a uniform pattern, so that there are some Al powders with no CNT. Conversely, all Al powders may obtain CNTs during the milling by low energy milling, but CNT agglomerations still remain, and CNTs are located at the surface of Al powders [85].

In summary, if the best equipment as well as better control over processing conditions is utilized to disperse CNTs among the metallic powders, each method has its own intrinsically certain ability, so that if the CNT loading exceeds the optimal value of each technique (4–5 wt % CNT at the best conditions), the nanotubes tend to form agglomeration. In this case, the pores and poor interfacial bonding can degrade the mechanical properties as well as thermal and electrical characteristics of manufactured CNT-containing metal matrix nanocomposites [86,87]. Consequently, many researchers believe that such a dispersion method and arbitrary practical conditions have low potential to uniformly disperse CNTs in metallic matrix. Some pros and cons of mechanical milling are listed in Table 1.

Ultrasonication

In this method, sound waves with high frequency are used for dispersing CNTs in a solution composed of organic solvents or aqueous surfactants. In order to increase the solubilization of CNTs in

water, the hydrophobic CNT surfaces can be modified by a wide range of surfactants and polymer adsorbates. The mechanism by which the ultrasonication debunds CNTs in a solution containing an aqueous surfactant is composed of four step: (i) A high local shear stress at the end of CNT bundles is induced by the collapse of micro-bubbles formed during the ultrasonication; (ii) Surfactants diffuse into and absorb on CNTs as soon as a gas bubble or gap is formed; (iii) The unzipping process takes place along the longitudinal axis of a particular CNT; (iv) The individual surfactant-coated CNT is released inside the solution [88].

It is worth mentioning that unzipping the individual CNTs from the bundles will not be completed if there is no polymer absorbate or surfactant. This is because CNTs have van der waals attraction to each other which may again [88].

However, the formation of hotspots during the ultrasonication which simultaneously increases the local pressure and temperature may induce some defects in CNTs, form carbon-dangling bonds at their sidewalls, and cut or chop the nanotubes. Such drawbacks decrease the effectiveness of the ultrasonication as a useful method for dispersing CNTs in CNT-containing metal matrix nanocomposites. In order to reduce these disadvantages, organic molecules, for example, poly (methyl methacrylate) (PMMA) or monochlorobenzene (MCB) can be added to form reactive species during the sonication. These species which are generated from decomposition of added organic molecules at the hotspots can chemically react with dangling bonds of CNTs and are easily wiped through burning in oxygen gas. This event may leave holes on the sidewalls [89].

As a holistic conclusion, the ultrasonication has a finite ability to disperse CNTs in metal matrix nanocomposites. According to the literature, the acid-treated CNTs can be uniformly dispersed up to 1 wt % in metallic matrices (such as Al) by this technique. Further addition of CNTs to the matrix results in agglomeration and generation of micropores during the subsequent consolidation stage. These defects may significantly decrease the mechanical, electrical and tribological properties of these binary systems [13,14].

The Application of Surfactants

Active surface agents such as surfactants can significantly improve the surface conditions of CNTs and prevent from their agglomeration and re-bonding. In general, these surface agents consist of two parts: (i) A hydrophilic part with a polar head and (ii) A hydrophobic part coupled with a hydrocarbon chain at the tail of the surfactant molecule. These modifiers enhance the metastability of the colloidal suspensions by providing an electrostatic and/or steric repulsive force between CNTs and reducing their surface energy. Depending on their head group charges, the surfactants are usually classified into three different groups: cationic, anionic, and nonionic or zwitterionic [90]. One of the most conventional anionic surfactants for CNT-reinforced metal matrix nanocomposites is SDS (soduim dodecyl sulfate), wherein the sulfates and hydrocarbon chains act as hydrophilic and hydrophobic parts, respectively. In fact, CNTs can interact with the hydrophobic part of SDS, so that an electrostatic repulsion force is formed between the negatively charged CNTs and the hydrophilic sulfate groups of SDS. Thus, it can remarkably affect the stabilization of CNTs in aqueous media [28]. There are quite a few studies evaluating the application of SDS as a surfactant in metallic matrices. The surveys confirm that there is a defined limit for inclusion of CNTs into the matrices. This is because if the critical level is exceeded, the uniform dispersion of CNTs throughout the metallic matrices is not possible and further incorporation leads to the formation of agglomerated particles [45]. The agglomerated particles can impressively degrade the mechanical properties and functionality of the nanocomposites. However, the introduction of SDS into the metallic systems can improve the CNTs dispersion.

Zwitterionic surfactants are a new class of widely used surface agents for dispersing CNTs in metal matrices. Whereas they are polar and soluble in water, their solubility in organic media is limited. They chiefly consist of cationic and anionic parts attached to the same molecule. The self-assembled monolayers (SAMs) of these surfactants can be also formed on CNT bundles (Figure 6). In this case,



the strong dipole/dipole attraction between SAMs and CNTs overcomes the present van der Waals forces between the individual nanotubes and disassembles the ubiquitous bundles [91,92].

Figure 6. A schematic illustration of the mechanism by which zwitterionic surfactants disassemble CNT bundles [47] (Reproduced with permission from [47], Elsevier, 2014).

The experimentations show that if the CNTs content exceeds 1 wt %, the agglomerated particles will form all over the microstructure of the nanocomposites. Moreover, the processing parameters deeply affect the way the nanotubes are dispersed throughout the matrix, where the mechanical properties can be degraded because of employing an unsuitable process. It is ascribed to the formed pores and degraded interfacial adhesion due to evaporation of the surfactant at high temperatures. Post treatments (e.g., heat treatment) is often employed to remove such pores [92].

Another disadvantage is the lack of control on the reactions between CNTs and the metal matrices, where the intermetallics can be generated as a result of unwanted reactions during the sintering process [92].

It seems that there is an urgent need for other surface treatments such as coating to uniformly disperse the high volume fraction of CNTs throughout the metal matrices.

Metallization

The outermost surface of CNTs can be coated by several metallic elements such as Cu, Ni, Co, Mo, and W, if enhanced interfacial adhesion between CNTs and the matrix is greatly required. Such coatings may contribute to the prevention of CNTs agglomeration all over the matrix [93,94]. It is demonstrated that W-coated CNTs by metal-organic chemical vapor deposition (MOCVD) method can significantly inhabit the CNTs agglomeration. This fact is shown in Figure 7. As clearly seen, the pores or air bags at CNT/metal interface is removed as the main reason for improved interfacial adhesion [48]. The enhanced thermal conductivity of the composites is ascribed to the formation of desirable interface which can remarkably reduce the thermal lost.

Similarly, it is shown that there is no intermetallic formation in the microstructure of (Mo-coated CNT)-Al nanocomposites [16]. It is attributed to the presence of Mo layer, acting as an appropriate barrier to the interfacial reaction between CNTs and the matrix. Additionally, the applied coating is able to impressively increase the volume fraction of the uniformly dispersed CNTs. The mechanical properties of these composites are proved to improve due to desirable dispersion of CNTs throughout the matrix. Despite the improved mechanical behavior, the exploitation of such coatings may slow down the electron movement all over the nanocomposites and deteriorate the electrical conductivity.



Figure 7. SEM micrographs of (W-coated CNT)-Al nanocomposites fabricated by ultrasonication method: (**a**) 5 vol % CNTs, (**b**) 10 vol % CNTs, (**c**) TEM micrograph of (W-coated 5 vol % CNT)-Al nanocomposites, and (**d**) higher magnification of the selected area in (**c**) [48] (Reproduced with permission from [48], Springer, 2012).

Effects of Dispersion Methods on Physicomechanical Properties

In addition to the consolidation and sintering techniques, the dispersion methods may greatly influence the properties of CNT-containing metal matrix nanocomposites. A review on the literature confirms that whenever the used dispersion method is inappropriately selected, so that it keeps or forms CNT aggregates, the mechanical and functional properties of produced nanocomposites may be degraded due to the formation of pores and poor interfacial boundaries between nanotubes and metallic matrix. Figure 8 shows the hardness of some spark plasma sintered (SPSed) CNT-Al nanocomposites as a function of CNT content for different dispersion methods. The aim behind the selection of SPS as the sintering method and Al as the metal matrix is to eliminate the potential effects of sintering process and chemical composition of metal matrix on the properties of these systems as much as possible. As clearly seen, the highest hardness values can be achieved by the mechanical milling due to the formation of severe plastic deformation-induced dislocations and defects in Al matrix. However, if the dispersing process is not suitably controlled, its intrinsic potential will be obtained. For instance, some dispersion techniques result in decreased properties when the CNT content exceeds 1–1.5 wt %. As another example, if the metallization is not done in a suitable manner, or the coating layer is not truly selected for the metal matrix, it cannot enhance the mechanical properties. Such a justification is also applicable to ultrasonication. If the ultrasonication is carried out under non-controlled conditions, the CNTs cannot play their positive role and reduce the mechanical properties after adding a low CNT content.

The tensile strength of MMNCs-reinforced metal matrix nanocomposites has similar trends. The incorporation of CNTs increases the tensile strength of metallic matrices, if they are homogeneously dispersed and make a proper interfacial bonding with the matrix. However, by adding CNTs more than the critical content, a heavy agglomeration occurs and the tensile strength is degraded (Figure 9).

Similar trends are also seen in the thermal conductivity of SPSed CNT-Cu or Al matrix nanocomposites (Figure 10). Generally, the addition of CNTs to the metallic matrices decreases the thermal conductivity due to the grain boundary-induced electron scattering. However, the metallization can increase such a property through enhanced interfacial boundaries between nanotubes and metallic matrix. Besides the metallization, the polymer wrapping and acid treatment can decrease

the degradation of thermal conductivity of Cu matrix by adding CNT due to the formation of enhanced interfacial boundaries. Such methods also have a limited potential to disperse CNTs. If the CNT content exceeds an optimum limit, the agglomeration of CNTs will decrease the thermal conductivity of these binary systems.



Figure 8. Hardness of some spark plasma sintered (SPSed) CNT-Al matrix nanocomposites fabricated by various dispersion methods [13,16,36,95].



Figure 9. The tensile strength of some SPSed CNT-metal matrix nanocomposites fabricated by various dispersion methods [14,96,97].



Figure 10. Thermal conductivity of some SPSed CNT-Cu and CNT-Al matrix nanocomposites fabricated by various dispersion methods [48,98–103].

2.2. Consolidation Challenge

The consolidation of pure metallic powders and their alloys is not a critical challenge, and pure metallic parts with the full density can be obtained by various sintering methods such as hot pressing, hot isostatic pressing, and spark plasma sintering. However, the addition of CNTs to the metallic matrix may greatly affect the consolidation rate and relative density of the binary system. In fact, the poor wettability between CNTs and metallic matrices and the formation of CNT agglomeration-induced pores impede the densification and decrease the relative density of the nanocomposites; no matter what the sintering method is. As a result, producing a fully dense CNT-reinforced metal matrix nanocomposite is a critical challenge which highly depends on the dispersion of CNTs in the metallic matrix. Actually, the selection of a proper dispersion method capable of homogeneously dispersing CNTs can approach the relative density of the CNT-metal bulk systems to that of pure metals.

Figure 11 shows the relative density of different CNT-reinforced metal matrix nanocomposites as a function of CNT content and dispersion method. As seen, the CNT ddition usually decreases the relative density and sinterabillity of the metallic matrices. Moreover, an increment in CNT content generally brings about more CNTs agglomeration and pores, decreasing the relative density. However, if a proper dispersion method such as the metallization for Cu and electroless deposition for Ag is utilized, CNTs will be homogeneously dispersed in metallic matrices with no declined density. It is noteworthy that each dispersion method has a certain ability to homogeneously disperse CNTs in a specific metallic matrix. If the CNT content exceeds the maximum ability of a mixing method, the agglomeration will occur. For instance, as seen in Figure 11, CNTs up to 2.5 vol % are homogeneously dispersed in Ag matrix through the electrodeposition method. Further an increase in CNT content may degrade the consolidation by inducing the agglomerates and pores.

As a conclusion, the consolidation of CNT-containing nanocomposites highly depends on the uniformity degree of dispersed CNTs. It implies the importance of the dispersion method to achieve a fully dense part. The employment of a suitable dispersion method and addition of CNTs below the critical content may assure the manufacturing of fully dense CNT-reinforced metal matrix nanocomposites.



Figure 11. The relative density of some SPSed CNT-metal matrix nanocomposites fabricated by different dispersion methods [16,48,49,96,104].

2.3. Chemical Reaction with Metallic Matrix

2.3.1. Thermal Decomposition of Pure CNTs

A review on the literature confirms the effective function of CNTs on the structural and functional characteristics of CNT-containing bulk materials. To exploit the full potential of CNTs in nanocomposites, one should deeply understand the structural phenomena and microstructural interactions likely occurring during the synthesis or post-treatments of these new emerging materials. The first key to this issue is the profound consideration of structural transitions and phase transformations of CNTs in pure state and in exposure to a metallic matrix, because they can adversely affect the intrinsically superior properties of pure CNTs [105–109]. Table 2 summarizes the recently reported structural transitions of pure CNTs in a variety of densification methods and their influences on the properties. As seen, less empirical results are reported in the literature addressing these structural changes. In general, any allotropic transition in CNTs is highly undesirable, because it can limit the intrinsically unique features of nanotubes in electronic aspects and load bearing performances [110–112].

An overwhelming majority of reports about the conversion of CNTs to other allotropes is associated with spark plasma sintering, where high pressure and elevated sintering temperatures persuade any thermally activated phase transformation [105,106,113,114]. However, other consolidation techniques such as hydrogen plasma [115], high-pressure/high-temperature annealing heat treatment [116–118] and chemical vapor deposition (CVD) [107,108,119] can thermally decompose the structural geometry of nanotubes. As a practical conclusion, the engineers often strive to prevent from the thermal degradation of CNTs in both pure state and composite form, since it can vanish the final properties [120]. Hence, one can determine two temperature regimes for CNT allotropic phase transformations depending on whether CNTs are preserved: (i) low-power regime and (ii) high-power regime. In the first case, known as safe regime, the processing pressure and temperature are sufficiently low, so that the thermal power cannot destroy the integrity and tubular morphology of nanotubes and thermally activate the mechanisms by which CNTs can structurally convert to other allotropes. In the second case, the elevated temperature or high applied pressure can persuade the thermal decomposition of nanotubes. There is not any sharp temperature boundary between these regimes, depending on the kind of consolidation procedures, type of matrix exposed to CNTs, and activated sintering mechanisms [121].

Fabrication Process	Processing Temperature (°C)	Applied Pressure (MPa)	Processing Duration (min)	Final Phase Structure	Reported Mechanisms for Structural Changes	Reported Changes in Properties Due to CNTs Structural Changes	Ref.
Spark plasma sintering	1500	80	20	diamond	Not reported	Not reported	[105]
Spark plasma sintering	1500	80	20	diamond + graphite	Not reported	Not reported	[113]
Spark plasma sintering + polishing	1600	60	1	graphene	Shear stress induced by polishing which leads to peeling graphene away from CNTs	A significant reduction in friction coefficient due to the much lower friction between formed graphene layers	[106]
Spark plasma sintering	1000, 1500, 2000	50	5	graphene	Not reported	Enhanced thermal stability due to the formation of graphene at a high sintering temperature	[114]
Annealing heat treatment	 (i) Below 2000 (ii) 2100-2400 (iii) 2500-2800 	-	30	 No structural changes the formation of large-sized double-walled carbon nanotubes (DWCNTs) the graphitization of multi-walled nanotubes (MWNTs) and other kinds of crystalline sp² hybridized carbon structures 	Not reported	Not reported	[116]
Spark plasma sintering	1500	80	20	 Partial conversion of CNTs into diamond The formation of n-diamond 	High localized temperatures arisen from the presence of plasma during the sintering as a prerequisite for the formation of diamond	Not reported	[122]
Spark plasma sintering	1700, 1800, 1900, 2000	100	5	- The presence of graphene in all targeted temperatures	The formation of graphene nanosheets due to the evaporation of carbon atoms during the heating stage of SPS and their agglomeration during the cooling stage	An increment in electrical conductivity due to the formation of graphene nanosheets	[123]
Spark plasma sintering + Fe35Ni catalysts	1200	70	20	diamond + graphite	The formation of diamond through a layer-by-layer mechanism	Not reported	[124]
Chemical vapor deposition	700	-	30	graphite	Not reported	Not reported	[107]

Table 2. Overview over a variety of conventional manufacturing techniques, allowable processing windows and structural changes of pure CNTs and their effects on the physicomechanical properties of nanotubes.

Table 2. Cont.

Fabrication Process	Processing Temperature (°C)	Applied Pressure (MPa)	Processing Duration (min)	Final Phase Structure	Reported Mechanisms for Structural Changes	Reported Changes in Properties Due to CNTs Structural Changes	Ref.
Chemical vapor deposition	700	-	56	amorphous carbon	Not reported	Not reported	[108]
Compaction + laser beam heating	2226	17,000	-	diamond	Direct conversion of CNTs to nano-sized diamonds with no an intermediate step such as melting or dissolution	Not reported	[125]
Annealing at high pressure	1300	4500	12	diamond	The conversion of CNTs to quasi-spherical onion-like structures followed by the formation of diamond crystals	Not reported	[117]
Chemical vapor deposition	500	-	2160	highly ordered graphite	highly ordered graphite $CNT \rightarrow carbon nanofiber \rightarrow highly ordered graphite$		[119]
Electrical breakdown method	-	-	-	graphene nanoribbon	Fast unwrapping of MWNTs with no an intermediate step	Not reported	[126]
Hydrogen plasma	726	-	-	diamond	The formation and growth of diamond particles due to the formation of amorphous carbon clusters with sp ³ bonds	Not reported	[115]
Solution-based oxidative process	55–70	-	60	graphene nanoribbons + graphite oxide	The formation of graphene nanoribbons due to complete unravelling of CNT side walls	Not reported	[109]
High temperature annealing heat treatment	1100–2000	_	240 min heating + 480 min cooling process	graphite nanoribbons	 The thermal activation of three different mechanisms for different heat treatment temperatures: The coalescence of SWNTs at 1400 °C followed by rearrangement of the present bonds at 1600 °C to form MWNT The collapse of MWNTs into graphite nanoribbons at temperatures higher than 1800 °C Complete conversion of MWNTs to graphite nanoribbons at temperatures higher than 2000 °C 	Not reported	[118]
High pressure and high temperature heat treatment	1600–2000	≥15,000	10–10,000 s (Exact dwelling time has not been reported)	diamond	The formation of diamond phase as a result of atomic diffusion with no graphitization or formation of intermediate phases	Not reported	[127]

In summary, CNTs may transform into other thermodynamically stable allotropes during the heat treatment process. Among these allotropes, cubic diamond [105], n-diamond [122], mono/multi-layer graphene [106], and graphite sheets [107] are the most extensively reported. However, the way these allotropes can affect the final properties are highly contradictory. Whereas some literatures refer to the deterioration of physicomechanical properties of CNT-based bulk materials, others put emphasis on the drastic improvement of some properties [106,123]. On the other hand, there is no consensus among researchers regarding what temperature range guarantees the conversion of CNTs to other carbon allotropes and which forms of new phases can be formed. For instance, Zhang et al. [123] evaluated the microstructure, mechanical and electrical properties of spark plasma sintered CNTs in pure state and demonstrated the in-situ formation of graphene nanosheets at 1700–2000 °C. It was shown that the formed graphene nanosheets are responsible for improved electrical conductivity in these conditions. Figure 12 indicates the TEM image of this formed graphene nanosheet at 2000 °C.



Figure 12. TEM image of graphene nanosheet formed during spark plasma sintering at 2000 °C [123] (Adapted with permission from [123], Elsevier, 2013).

2.3.2. Chemical Reactions

The chemical reactions between CNTs and metallic matrices can be categorized into two different aspects: (i) The partial chemical reaction at CNT/metal interface and (ii) the complete chemical reaction of CNTs with metallic matrix. If controlled, the former is favorable for the load bearing applications, but the latter can bilaterally affect the physicomechanical properties of CNT-dispersed metal matrix nanocomposites. In the next sections, the practical and scientific aspects of these chemical reactions will be addressed in some details.

Complete Chemical Reactions

(a) CNT-Reinforced Al Matrix Nanocomposites

A review on the literature confirms that Al_4C_3 is the most common in situ formed intermetallic in CNT-reinforced pure Al matrix nanocomposites. However, other intermetallics such as SiC can be formed during the reaction between the alloy matrix and CNTs. In fact, the chemical composition of the formed intermetallics strongly depends on the fabrication temperature and the chemical composition of the alloy matrix. The kinetics of the carbide formation at temperatures lower than Al melting point is negligible. Moreover, the presence of some alloying elements can significantly control the final properties of the nanocomposites. Two different sources are suggested for the formation of Al_4C_3 : (i) Used process control agents (PCA) during the milling process such as stearic acid and (ii) incorporated CNTs. Also, the processing parameters such as temperature, post treatment variables and the size of initial CNTs play an important role in the formation of carbides and controlling their volume fraction, morphology, and geometrical dimensions. It is found that the morphology of Al_4C_3 can be easily changed by applying the post heat treatment or the presence of initial defects in CNT structures. Four types of morphologies including whisker-like, dumbbell-like, needle-like, and tube-like ones can be observed for Al_4C_3 particles, depending on the post treatment conditions and the purity of initial CNTs. Similarly, the volume fraction of the formed carbides deeply depends on the geometrical size of initial CNTs. Generally speaking, the presence of carbides at CNT/Al interfaces improves the mechanical properties of the nanocomposites. It is attributed to the enhanced load transfer between the matrix and reinforcements as a result of carbide formation at the interface. The strengthening effect of the formed carbides depends on their thickness, so that the formed carbides will dissolve back into the melt if the critical thickness is less than a critical limit.

The in situ formation of Al_4C_3 at the Al/CNT interface has been subjected to the extensive research studies. Some research works have considered the precipitation of Al_4C_3 as one of the predominant strengthening mechanisms in CNT-dispersed Al matrix nanocomposites. This compound forms during a chemical reaction between Al matrix and CNTs as:

$$4AI + 3C = AI_4C_3$$

$$\Delta G = -289,512 + 60T, T < 660 \ ^\circ C$$
(1)

The free energy (ΔG) of this reaction is negative by the melting point (660 °C) of Al. It means that Al₄C₃ is thermodynamically stable at temperatures lower than 660 °C. Coincidently, the formation of this carbide at temperatures lower than 660 °C is also reported [128].

The mentioned reaction can be explored for ball milled CNT-Al powder blend. In this case, Al_4C_3 can be formed when the energy state of the mixed powders reaches to a sufficiently high level. It is believed that the long-term milling process can seriously damage the CNTs structure and lead to the in situ formation of Al_4C_3 [87,129]. For instance, Ostovan et al. [87] evaluated the microstructure of the milled powders for 8 and 12 h. It was found that the needle-like Al_4C_3 is just formed after the milling for 12 h. It was attributed to the long-term milling-induced damage in CNTs. As a basic conclusion, the possible CNT amorphization during the sintering process as well as the formation of crystallographic defects in CNTs can significantly facilitate the formation of Al_4C_3 . It is ascribed to the synergetic effects of instability of milled powders after the long-term milling, and generated driving force as a result of thermal processing such as sintering [87].

The literature have suggested two different sources for Al_4C_3 formation: (i) Used process control agents (PCA) during the milling process, (e.g., stearic acid) and (ii) incorporated CNTs. Since the stearic acid is composed of oxygen, carbon, and hydrogen atoms, it can be decomposed into its constituent elements during the long-term milling. On the other hand, the milling process can significantly damage the CNTs structure and enhance their amporphization [130]. The produced atomic carbon from the mentioned sources can easily react with the matrix Al to form Al_4C_3 . More importantly, the formation of Al_4C_3 may consume the CNT walls or the entire CNT [129].

If the alloy matrix is used, other intermetallics can be formed beside Al_4C_3 . The chemical composition of the formed intermetallics strongly depends on the alloying elements. For instance, Al_4C_3 and SiC can be formed as a result of the reaction between Al-Si alloy matrix and CNTs. Bakshi and coworkers [131] showed that the formation of each intermetallic corresponds to the Si weight percent at the fabrication temperature, as shown in Figure 13. As seen, the more the Si content in the alloy, the more SiC particles will form. It is ascribed to increased amount of Si in the liquid melt due to the reaction between Al and C to form Al_4C_3 . It can increase the activity of Si to form SiC. Both reactions will proceed in the same manner until all of carbon content is completely exhausted.



Figure 13. The chemical composition dependence of formed intermetallics on Si weight percent and fabrication temperature [131] (Reproduced with permission from [131], Elsevier, 2009).

In CNT-(Al-Si) nanocomposites, the poor wettability arises from a major difference between the surface tension values of the alloy matrix (about 800 mN·m⁻¹) and CNTs (about 45 mN·m⁻¹) [33]. However, the literature have reported improved wettability with the generation of some intermetallics. It is attributed to reduce contact angle between the alloy matrix and CNTs through the infiltration of Al-Si melt into CNT clusters [131].

The formation kinetics of Al_4C_3 at temperatures lower than Al melting point is slow. For the binary composites in which CNTs react with Al matrix chemically, the presence of alloying elements can significantly control the final properties, because the chemical composition may affect the thermodynamic aspects of the Al_4C_3 -forming reaction [132].

The processing parameters such as temperature, post treatment variables and the size of initial CNTs play an important role in the formation, volume fraction, morphology, and size of the formed carbides in CNT-Al matrix nanocomposites. These compounds can be precipitated at different locations. For instance, the nano-sized Al_4C_3 particles often form on the external surface of CNTs as a result of a reaction between Al and CNT-derived amorphous carbon. In the case of partially graphitized CNTs, the carbides are evolved at the end of damaged CNTs. It is shown that only a little amount of MWNTs can react with the matrix to generate carbides and contribute to enhanced properties of the composites [133].

There are two main factors affecting the morphology of the formed compounds during the reaction between the matrix and CNTs: (i) Post treatment, and (ii) internal defects of CNTs. The morphology of Al_4C_3 precipitates strongly depends on post heat treatment temperature. It has been reported that the carbides grow in the form of nanosized whiskers at 950 °C, while they are more likely to disappear at comparatively lower temperatures [133]. Additionally, one can suppress the formation of these carbides through the close control over the sintering conditions, i.e., the sintering temperature should be kept below Al melting point [134]. Figure 14 exhibits the elongated Al_4C_3 precipitates formed as a result of a high-temperature heat treatment. As obviously seen, the longer the heat treatment temperature, the more elongated the carbides are.

In addition to the processing parameters, the internal defects of nanotubes can also change the way the precipitates are evolved. Two fascinating types of morphologies are reported for Al_4C_3 particles, i.e., dumbbell-like and tube-like. Whereas the first morphology arises from the CNTs tips, the second case originates from defective CNTs [135]. Figure 15 indicates SEM images of grown nano-whiskers during annealing treatment at 950 °C.



Figure 14. HRTEM (High resolution transmission electron microscope) images of MWNT (multi-walled nanotubes)-reinforced Al matrix nanocomposites heat treated at: (**a**) 873 K for 6 min and (**b**) 883 K for 60 min [132] (Adapted with permission from [132], Elsevier, 2016).



Figure 15. SEM images of (**a**) grown nano-whiskers during annealing treatment at 950 °C, and (**b**) the formation of nano-whiskers on the Al grains, as shown by the white arrows [133] (Adapted with permission from [133], Elsevier, 2006).

The geometrical size of initial CNTs is one of the affecting parameters controlling the volume fraction of the formed carbides. The empirical results show that Al_4C_3 particles can easily arise from MWNTs with 40 nm in diameter, while the amount of Al_4C_3 seems to decrease with an increase in diameter by 140 nm examined from the XRD results [38].

Albeit the development of Al_4C_3 carbides in CNT-Al matrix nanocomposites is of prime significance, the way they can affect the microstructure-related and mechanical properties is more important. As generally believed, the presence of carbides at CNT/Al interfaces improves the mechanical behavior of these nanocomposites. This is because the carbides can enhance the matrix capability to efficiently transfer the external load to nanotubes. This approach is in good agreement with the results reported by Tjong et al. [136], Esawi et al. [137], Kwon et al. [130,135] and Chen et al. [138]. Table 3 gives some information about the presence of Al_4C_3 in some CNT/Al composites with high strengthening effect. The results indicate that the formation of Al_4C_3 maybe doesn't have an adverse effect on the composite strength. The recent study by Chen et al. [138] reveals that nano-sized interfacial Al_4C_3 can noticeably enhance the load transfer efficiency, resulting in improved composite strength.

The way the intermetallics affect the final properties of the nanocomposites strongly depends on their thickness. The critical thickness is estimated as [131]:

$$t_{\rm cri} = -V_{\rm M} \times (\Delta \gamma / \Delta G_{\rm f}) \tag{2}$$

where $V_{\rm M}$ is the molar volume of the formed carbide, $\Delta \gamma$ is the increase in total surface energy due to newly formed interfaces, and $\Delta G_{\rm f}$ is the free energy of formation per mole of carbide. Further growth of the formed carbides can be achieved when the thickness reaches to a critical value. It can remarkably improve the wettability through diminishing the contact angle [131].

Table 3. The variation of tensile strength in CNT-dispersed Al matrix nanocomposites with the volume fraction of Al_4C_3 precipitates (SPS: Spark plasma sintering).

Amount of Added CNTs	Fabrication Method	Increase in Tensile Strength Value (%)	Ref.
2 wt % MWNTs	Sintering \rightarrow hot extrusion	57.5	[139]
5 vol % MWNTs	$SPS \rightarrow hot extrusion$	128	[120]
5 wt % MWNTs	Sintering \rightarrow pressing \rightarrow annealing	184	[128]

The in situ carbides evolved in CNT-(Al-Si) nanocomposites grow through two different pathways: (i) At the Al₄C₃/Al-Si interface and (ii) at the Al₄C₃/CNT interface. In accordance with the suggested model, the diffusion of carbon atoms present in CNTs structures act as the predominant mechanism for vertical growth of Al₄C₃ [131]. Figure 16 gives a schematic illustration of vertical and parallel growth of the carbides on CNTs.



Figure 16. A schematic view of growth mechanisms of Al_4C_3 dispersoids on CNTs. It indicate the vertical migration of Al and C atoms for the formation of Al_4C_3 carbides [131] (Reproduced with permission from [131], Elsevier, 2009).

As a summary, the formation, volume fraction, morphology, and size of the formed carbides in CNT-Al matrix nanocomposites depend on the processing parameters such as temperature, post treatment and purity of the initial CNTs. The in situ formed intermetallics can improve the mechanical properties of CNT-reinforced Al matrix nanocomposites through enhanced load transfer between the matrix and the reinforcements.

(b) CNT-Reinforced Ti Matrix Nanocomposites

A review on the literature confirms that TiC is the most common in situ formed intermetallic in CNT-reinforced Ti matrix nanocomposites. This compound often forms at the boundaries of the sintered powders, if the initial CNTs are wrapped by initial Ti powders. The minimum reaction temperature required for the generation of TiC precipitates is 800 °C. The evaluation of the kinetic aspects of TiC formation in CNT-Ti binary systems has proved the faster formation kinetics of TiC compared to CNTs. The volume fraction of the formed TiC dispersoids differs with the chemical composition of the incorporated carbon allotrope into Ti matrix, e.g., CNT and graphite. TiC particles may form in two different morphologies including spherical and elongated ones. The applied

dispersion method for mixing the initial powders, processing parameters such as sintering temperature and the initial volume fraction of CNT, as well as the application of post heat treatments can remarkably affect the mechanical properties of the composites. Generally, the empirical results have demonstrated the positive effects of the formed intermetallics on the physicomechanical properties of the nanocomposites.

There are several intermetallic compounds which can be formed during the reaction between Ti and carbon allotropes. Among these compounds, TiC is the most common [18,140]. It can be formed during a solid-state reaction between Ti and CNTs [18,140,141]. The standard free energy of the reaction may be obtained using the following equation:

$$\Delta G = -184,571.8 + 41.382T - 5.042T \times \ln T + 2.425 \times 10^{-3}T^2 - 9.79 \times 105/T (T < 1939 \text{ K})$$
(3)

The minimum reaction temperature required for the generation of TiC precipitates in CNT-Ti binary systems is 800 °C. These particles often locate at the boundaries of the sintered powders, provided that the initial CNTs are wrapped by initial Ti powder. It is found that reaction between the nanotubes and Ti matrix is promoted by an increment in the sintering temperature [141]. As to CNTs, the mentioned reaction is fast and produces more TiC particles. Thus, TiC dispersoids are the dominant phase in the microstructure.

The volume fraction of the formed TiC precipitates strongly depends on which carbon allotrope is incorporated into Ti matrix. Figure 17 shows the microstructure of Ti matrix reinforced with 0.4 wt % CNTs or 0.4 wt % graphite. As clearly seen, higher amounts of TiC dispersoids are present throughout Ti matrix in the MWNTs-reinforced composite (as indicated by white arrows) [142].



Figure 17. Optical images of Ti matrix reinforced with: (**a**) CNTs and (**b**) graphite [142] (Adapted with permission from [142], Elsevier, 2013).

TiC particles can form in different morphologies. For instance, Kondoh et al. [140] have shown the formation of two different shapes of TiC particles, namely spherical particles and elongated ones. Spherical particles are evolved as a result of incomplete disassembling of MWNTs, while extrusion-induced severe plastic deformation leads to the generation of elongated ones. Thus, the post treatment can affect the morphology of the formed intermetallics. Figure 18 shows the microstructure of the extruded composites, wherein Figure 18a indicates the uniformly distributed reinforcements throughout Ti matrix and Figure 18b confirms the desirable bonding between Ti matrix and TiC particles.

The experimental measurements confirm the positive influence of TiC precipitation at CNT/Ti interfaces on the physicomechanical properties of these nanocomposites [18,35,50,140]. The higher the volume fraction of incorporated CNTs, the superior the mechanical properties of the composites are [18,140]. However, the exact strengthening mechanism of intact CNTs has not been clarified [18]. As practical variables, the used method for mixing the initial powders, processing parameters such

as sintering temperature, and initial volume fraction of CNTs, as well as the post heat treatment can remarkably affect the mechanical properties of the composites [18]. In the case of the mixing method, Munir et al. [143] have demonstrated that unlike the solution ball milling (SBM) process, TiC can be formed when the initial powders (Ti powder + 0.5 wt % MWNTs) are mixed by high energy ball milling. However, the in situ TiC particles can be formed by using both methods whenever 1.0 wt % MWNTs are incorporated into Ti matrix. As to the potential effects of the processing parameters on the mechanical behavior of CNT-Ti matrix nanocomposites, Xue et al. [141] have demonstrated that the compressive yield strength of the nanocomposites decreases with an increase in the sintering temperature before a slight rise. This is originated from the combined effect of increased relative density and structural damage of CNTs. Finally, the relative density of in situ formed TiC dispersoids increases with an increment in the volume fraction of initial CNTs. Thus, the higher the initial CNTs volume fraction, the better the mechanical properties will be [142]. In the case of the way a post heat treatment can affect the mechanical behavior, it is shown that the properties can be degraded upon increasing the post annealing temperature. This decrease is "gradual", because the presence of TiC dispersoids throughout Ti matrix may drastically prevent Ti particles from the extreme coarsening through the particle-pinning mechanism [18].



Figure 18. Extruded CNT-dispersed metal matrix nanocomposites: (**a**) Optical image of the binary systems and (**b**) SEM image of TiC/Ti interface [140] (Reproduced with permission from [140], Elsevier, 2009).

As a summary, the incorporation of CNTs into the Ti matrix can drastically enhance the tensile strength, yield strength, and microhardness values of the matrix. It may be ascribed to the dispersion effect of un-bundled CNTs and in situ formed TiC particles, as shown in Figure 19.



Figure 19. SEM image of fracture surface of CNT-Ti nanocomposites in different magnifications [140]: (a) ×5000; (b) ×65,000 (Adapted with permission from [140], Elsevier, 2009).

(c) CNT-Reinforced Mg Matrix Nanocomposites

Mg and its alloys are not able to sufficiently wet CNTs. To solve this practical challenge, two general approaches have been suggested: (i) Coating of CNTs by a metallic thin film and (ii) alloying Mg matrix with appropriate elecments. The first solution can efficiently enhance the interfacial adhesion through the prevention of CNTs from clustering. Clustering of CNTs adversely alter the interfacial bonding, resulting in deteriorated mechanical properties. It is found that an intermetallic compound (Mg₂Ni) can be generated through wrapping CNTs by a Ni-based coating and alleviate decreased properties in Mg matrix composites. It is ascribed to an improved bonding at the interface, enhancing the mechanical properties of the nanocomposites with no significant decrement in ductility [12]. From this perspective, the utilization of Mg-Al alloys (AZ-type) such as AZ31, AZ81, Mg-3Al-1Zn, and Mg-6 wt % Al instead of pure Mg is strongly recommended because of the easy formation of ternary Al₂MgC₂ compounds.

Depending on the chemical composition of used Mg alloy matrix and CNTs coatings, the several intermetallic phases of different stoichiometries may form among which Al_2MgC_2 , Al_3Mg_2 , $Al_{12}Mg_{17}$, Al_4C_3 , and Mg_2Ni are of prime significance [144]. Figure 20 shows the needle-like morphology of Al_2MgC_2 ternary carbides.



Figure 20. TEM image of (Mg-6 wt % Al)/CNT interface, indicating the in situ formation of needle-like ternary carbides (Al₂MgC₂) [144] (Reproduced with permission from [144], Elsevier, 2011).

The precipitation of the interfacial intermetallics has an optimum limit, so that the mechanical properties of the nanocomposites may be weakened whenever it is exceeded. Therefore, a close control over the interfacial reactions between CNTs and Mg is highly required. These reactions proceed by simultaneous diffusion of the matrix atoms and carbon atoms present on the superficial regions of CNTs toward the preferred reaction sites. To confine Mg-CNTs reactions along the interfaces, employing a short-term method such as microwave sintering has been suggested. The long-time contact between the matrix and reinforcements may drastically degrade the mechanical properties of the nanocomposites due to the formation of excessive content of the intermetallics [12].

As previously discussed, if the precipitation rate of the intermetallic compounds are closely controlled, enhanced properties can be obtained. This enhancement can be justified by three different mechanisms: (i) Grain refinement, (ii) improvement in load transfer from the matrix to reinforcements, and (iii) appropriate wettability. For instance, it is shown that the Al₄C₃ phase often acts as a suitable grain refiner and boosts the tensile strength of CNT-AZ81 nanocomposites [19]. As another example, the formation of SiC during the sintering of MWNTs-AZ91 powder blend facilitates the load transfer from the matrix to MWNTs and enhances the mechanical properties of produced composites [145]. In addition, the mechanically improved behavior of (Ni-coated MWNTs)-Mg composites is ascribed to

the presence of an adherent and void-free MWNTs /Mg interface due to Mg_2Ni precipitation. Figure 21 shows Mg_2Ni dispersoids at the MWNTs/Mg interfaces [12].



Figure 21. TEM image of (Ni-coated MWNT)-Mg composites, showing the presence of Mg₂Ni intermetallic at the interface [12] (Adapted with permission from [12], Elsevier, 2014).

Similar to CNT-Al and CNT-Ti binary systems, the precipitation of the mentioned intermetallics may bilaterally affect the mechanical properties of CNT-dispersed Mg matrix nanocomposites. The poor failure strain of the composites is attributed to the ubiquitous presence of coarse intermetallic particles. The initial volume fraction of incorporated CNTs, formation of intermetallics, and quality of the formed interface between the Mg and nanotubes are the important factors in determining the mechanical properties of the nanocomposites. It is shown that an increase in the initial amount of incorporated CNTs may promote the refinement of coarse grains and enhance the failure strain [146,147]. Figure 22 shows the evolved microstructure of CNT-AZ31 nanocomposites produced using the disintegrated melt deposition technique followed by hot extrusion. As seen, the formed Mg₁₇Al₁₂ particles are distributed at or along α phase boundaries and give rise to the grain refinement of Mg matrix [148].



Figure 22. Optical image of (**a**) AZ31 and (**b**) 1 vol % CNT-AZ31 nanocomposites fabricated through the disintegrated melt deposition technique followed by hot extrusion at 350 °C. In these systems, Mg₁₇Al₁₂ intermetallics are abundantly formed. These compounds are manifested by black regions, while white regions exhibit α -Mg [148] (Reproduced with permission from [148], Springer, 2012).

The formation of the mentioned intermetallics enhances the mechanical properties of CNT-Ti matrix nanocomposites through guaranteeing the suitable wetting between the matrix and nanotubes. It can significantly prevent the microscale cavities which form at the Ti/CNT interfaces and contribute to improved mechanical properties [12]. Additionally, the formed intermetallics can improve the mechanical properties of the nanocomposites through the restriction of mechanical deformation [148]. The formation of a clean interface with no impurity or defect is shown to improve the mechanical properties [144]. A recent study by Rashad et al. [146] showed that the formed intermetallics in MWNTs-dispersed Mg-3Al-1Zn alloys are refined with the CNTs inclusion. Figure 23 indicates the schematic demonstration of $Mg_{17}Al_{12}$ generation at the interface of Mg-3Al-1Zn/MWNTs composite, where the coarse particles of $Mg_{17}Al_{12}$ can be refined through the incorporation of MWNTs into the matrix.



Figure 23. A schematic view of $Mg_{17}Al_{12}$ particles formed in Mg-3Al-1Zn/MWNTs nanocomposites prepared by powder metallurgy method. The incorporation of MWNTs can drastically refine the particles (β phase corresponds to $Mg_{17}Al_{12}$) [146] (Reproduced with permission from [146], Elsevier, 2015).

A review on the literature confirms that recent research works have strived to attribute the enhanced properties of CNT-Mg composites to the formation of different intermetallics. Fukuda et al. [144] have resorted to Al₂MgC₂ compound. However, an opposite trend has been observed by Pei et al. [110], where Al₂MgC₂ strengthens the carbon nanofiber/Mg interface, but simultaneously leads to decreased mechanical properties. It is ascribed to the difference in the extent of graphitization. In other words, produced Al₂MgC₂ intermetallic in CNT-reinforced composites insignificantly affects the CNTs strength. Table 4 provides the readers with an overview of the fabrication method, chemical composition of the possible intermetallic compounds, and variations in mechanical properties of the composites.

Fabrication Method	CNTs Volume Fraction	Type of Used CNTs	Chemical Composition of the Formed Intermetallics		Variations of Mechanical Properties		Suggested Reasons for Enhanced/Deteriorated Properties	Ref.
Powder metallurgy based wet processing	0.71–1.56 vol % MWNTs	Functionalized; using a zwitterionic surfactant	Al ₂ MgC ₂	-	An increase in yield strength and elongation at failure by 28.5 MPa and 12.2%, respectively	- - -	Presence of clean interface CNTs-induced strengthening Formation of Al ₂ MgC ₂	[144]
Powder metallurgy technique	0.3 wt % MWNTs	Ni-coated	Mg ₂ Ni	-	An increase in microhardness, yield strength, and ultimate strength by 16 HV, 80 MPa, and 66 MPa, respectively. A decrease in ductility by 1.5%	- -	Grain refinement CNTs-induced strengthening Improved interfacial interactions	[12]
DMD (disintegrated melt deposition) technique followed by hot extrusion	1.5 vol % CNT nanoparticles	Unfunctionalized	$\mathrm{Al}_4\mathrm{C}_3$, $\mathrm{Al}_{12}\mathrm{Mg}_{17}$, $\mathrm{Al}_3\mathrm{Mg}_2$	-	An increase in yield strength, ultimate strength, and failure strain by 107 MPa, 114 MPa, and 7%, respectively	-	Grain refinement due to the presence of Al ₄ C ₃ Crack formation-based tensile toughening mechanism	[19]
Squeeze infiltration method	1–5 wt % MWNTs	Acid treated	SiC	-	An increase in microhardness, yield strength, and ultimate strength by 80 HV, 170 MPa and 90 MPa, respectively	-	Grain refinement Improved load transfer owing to SiC formation at the interface	[145]
DMD method followed by hot extrusion	1.0 vol %	Acid treated	Mg ₁₇ Al ₁₂	-	An increase inmicrohardness, yield strength, ultimate strength, and elongation at failure by 29 HV, 34 MPa, 8 MPa, and 3.6%, respectively	-	Grain refinement Strengthening by stable intermetallic phases CNTs-induced strengthening	[148]
Powder metallurgy method	0.25–1.0 wt % MWNTs	Unfunctionalized	Mg ₁₇ Al ₁₂	-	An increase in ultimate strength and failure strain by 10 MPa and 9%, respectively Yield strength remains unchanged	-	CNTs-induced strengthening Refinement of coarse Mg ₁₇ Al ₁₂ particles through the incorporation of CNTs into the matrix, which improves the ductility	[146]
Accumulative roll bonding	3 vol % MWNTs	Unfunctionalized	$Al_3Mg_2, Mg_{17}Al_{12}$		-	-	CNTs-induced strengthening Refinement of coarse Mg ₁₇ Al ₁₂ particles through incorporation of CNTs into the matrix, which improves the ductility	[147]

Table 4. An overview of fabrication method, formed intermetallic compounds, and mechanical properties of CNT-reinforced Mg matrix nanocomposites.

As another interesting result, a slight increment in relative density of CNT-Mg nanocomposites has been observed owing to the formation of in situ intermetallics. For instance, it is found that the incorporation of 0.3 wt % Ni-coated CNTs into Mg matrix increases its density by 0.01 g/cm³ [12].

(d) CNT-Reinforced Cu Matrix Nanocomposites

Similar to Mg and its alloys, Cu is not able to sufficiently wet CNTs. This is because there is a significant difference between the surface tension of Cu and CNTs. Furthermore, it is not expected that Cu reacts with CNTs in conformity with Cu-C phase diagram. Instead, some fissures may form at Cu/CNTs interfaces [149]. Figure 24a shows such an obvious crevice at the interface. The addition of Ti to Cu matrix eliminates these crevices through the formation of a thin TiC layer at the interface, as shown in Figure 24b. Such crevices can significantly degrade the final properties of the nanocomposites, e.g., thermal conductivity, which will be discussed in the next section.



Figure 24. TEM images of CNT/Cu interfaces: (**a**) The formation of a pronounced crevice due to the lack of wettability and (**b**) the precipitation of in situ TiC layer as a result of Ti addition to pure Cu matrix [149] (Reproduced with permission from [149], Springer, 2013).

The improvement of the interfacial bonding between Cu matrix and CNTs has been the focus of many research works. One of the suggested solutions is alloying of Cu matrix using carbide forming elements such as Cr and Ti. It can lead to the precipitation of Cr_3C_2 , TiC, and Cr_7C_3 carbides. The open ends of CNTs and carbon atoms present on the wall defects can serve as the carbon source reacting with Cr [150]. These carbides are generated at the appropriate sites including broken surfaces and reactive edges of the tubes through various bonding mechanisms such as rope anchors, chain-link structures and bridges [151]. The standard free energy (ΔG_T^{θ}) of the reactions may be obtained using the following equations [152]:

$$3Cr + 2C_{(g)} \rightarrow Cr_3C_2 \tag{4}$$

$$\Delta G_{\rm T}^{\theta} = -72.333T \times \ln T + 0.062T^2 + 1,345,000T^{-1} - 0.00001T^3 + 744.180T - 110,762.634$$

$$7Cr + 3C_{(g)} \rightarrow Cr_7C_3 \tag{5}$$

$$\Delta G_{\rm T}^{\theta} = -114.064T \times \ln T + 0.108T^2 + 1,772,000T^{-1} - 0.0000192T^3 + 706.278T - 218,451.845$$

$${\rm Ti} + {\rm C} \to {\rm Ti}{\rm C}$$
(6)

$$\Delta G_{\rm T}^{\theta} = -27.75T \times \ln T + 0.0241T^2 + 665,300T^{-1} - 0.0000003T^3 + 191.888T - 194,857.227$$

In general, Cu-Ti compounds precipitate during SPS, if the Cu-Ti alloy is used as matrix. It is while the Cu-Ti compounds may be decomposed into TiC during the sintering process. The formation of TiC proceeds through the reaction between CNTs and Ti diffused from the primary particle boundaries [20].

An island-shaped Cr_7C_3 can form as a result of a chemical reaction between the open tip of MWNTs and diffused Cr. Other carbides can be evolved due to a reaction between defective sidewalls of MWNTs and Cr atoms [49]. It is shown that the formed carbides at the tip of MWNTs can provide superior load transfer, because they are in contact with more amounts of graphene layers [153].

The studies show that the controlled formation of C-Cu intermetallic compounds at Cu/CNTs interfaces can noticeably improve the physicomechanical properties, thermal conductivity, pitting corrosion resistance, and electrical conductivity of these binary composites. The major strengthening mechanism responsible for this enhancement is the improved load transfer from the matrix to CNTs as a result of carbides precipitation. From mechanical point of view, the Cr_7C_3 particles are reported to effectively transfer the applied tensile loads to MWNTs in CNT-(Cu-Cr) nanocomposites [153]. Also, the yield strength of Cu-Ti alloy increases by 88% through the inclusion of CNTs. It is ascribed to the synergic combination of plastic deformation and stronger interfacial bonding induced by the formation of a thin TiC layer [154].

The literature confirms the degraded thermal conductivity of MWNTs-reinforced pure Cu matrix composites due to the poor interfacial bonding at the CNT/Cu interface. Alloying of Cu matrix may modify superficial regions of MWNTs and drastically enhance the thermal conductivity of the nanocomposites due to increased heat transfer. Improved interfacial bonding is attributed to the carbides formation. Another suggested approach to improving the interfacial bonding is the coating of MWNTs by a metallic layer. Nonetheless, the thermal conductivity of these composites may be considerably degraded due to the formation of excessive impurities during the coating process. In contrast, the generation of metallurgical bonds between Cu-Ti alloy matrix and MWNTs improves the thermal conductivity of the composites due to the formation of TiC dispersoids. This compound can facilitate the electron-phonon coupling and prevent their scattering [149]. As another typical example, the superior thermal conductivity of CNT-(Cu-Cr) nanocomposites can be achieved through the generation of Cr_3C_2 at the interface. These precipitates are perfectly capable of improving the heat transfer efficiency by strengthened interfacial bonding. Figure 25 indicates the precipitation of Cr_3C_2 at the CNT-(Cu-Cr) interface. As a general rule, if the intermetallic compounds form at the interface of these composites, the thermal conductivity will be enhanced. Furthermore, the volume fraction of initial CNTs strongly affects the thermal conductivity of the nanocomposites, wherein the thermal conductivity increases with an increment in the initial volume fraction of CNTs, as shown in Figure 26.



Figure 25. TEM image of Cr_3C_2 precipitates at the CNT-(Cu-Cr) interface [150] (Adapted with permission from [150], Springer, 2013).

As to the electrochemical activity, the presence of the mentioned intermetallics may increase the pitting corrosion resistance of MWNTs-dispersed Cu matrix nanocomposites. This effect is related to enhanced passivation originated from the formation of the carbides. This is the case for the electrical conductivity. The enhancement in electrical properties of Cu-Ti solid solutions reinforced with MWNTs

can be obtained upon the formation of ubiquitous intermetallic compounds. These carbides diminish the concentration of Ti atoms in the matrix solid solution and statistically reduce the scattering sites of charge carriers [20]. For the pure Cu matrix, a similar improvement is observed. It is ascribed to enhanced electron transport as a result of strong interfacial bonding originated from TiC formation at MWNTs-Cu interfaces [154].



Figure 26. Thermal conductivity of CNT-(Cu-Cr) nanocomposites as a function of initial volume fraction of CNTs [150] (Reproduced with permission from [150], Springer, 2013).

In summary, the mechanical, corrosion-related, and electrical properties of the nanocomposites can be enhanced through the in situ formation of some intermetallics as a consequence of improved load transfer, enhanced passivation and suitable electron transport.

(e) Other Composites Systems

Intermetallic compounds can be formed at the interface of pure Ni matrix and CNTs. In most cases, the formation of intermetallic compounds such as a metastable hexagonal Ni₃C at the defect sites of tubes can significantly improve the mechanical properties of CNT-dispersed Ni matrix nanocomposites due to the formation of strong interfacial bonds [52]. Such a scenario is observed in Fe alloys. In these alloys, the iron carbides form as a result of a chemical reaction between the iron matrix and included CNTs. Microstructure-related and mechanical properties of the composites are drastically affected by the carbides formation. Lin et al. [155] proved the deterioration of mechanical properties in these composites with carbides precipitation; albeit the reason has not been discussed.

Partial Chemical Reaction

The strength of CNT/metal interfacial bonding is one of the key factors controlling the physicomechanical features of CNT-reinforced metal matrix nanocomposites as well as the uniform distribution of CNTs and high relative density [49]. As a general rule, the weak wettability and poor interfacial compatibility between CNTs and metal matrix degrades the fracture toughness due to the limited interfacial load transfer [156]. Among the widely used methods for the fabrication of metal matrix nanocomposites (MMNCs), powder metallurgy routes provide a better interfacial bonding as compared to casting processes [157]. A model is developed by Coleman et al. [158] describing the tensile strength of CNT-containing composites (σ_c) based on the shear strength of the interface (σ_{shear}). Equation (7) describes this model:

$$\sigma_{\rm C} = \left(1 + \frac{b}{R}\right) \left[\frac{l_{\rm CNT}}{2R} \sigma_{\rm shear} - \left(1 + \frac{b}{R}\right) \sigma_{\rm M}\right] V_{\rm CNT} + \sigma_{\rm M} \tag{7}$$

where *b* is thickness of the interface layer, σ_M is the strength of the matrix and *R*, l_{CNT} and V_{CNT} are the radius, length and volume fraction of CNTs, respectively.

Zhou et al. [159] used an in-situ pull-out technique to quantitatively evaluate interfacial shear strength (IFSS) in CNT-Al nanocomposites. They bonded the end of the protruding CNTs directly to the tip of an atomic force microscopy (AFM) cantilever and pulled them out from Al matrix. They reported that the estimated tensile strength of the nanocomposite based on the shear lag model using the obtained IFSS values is consistent with the experimental ones. To date, the direct microscopic method for determination of IFSS values have also been employed for CNT-filled ceramic [160] and polymer [161] matrix nanocomposites. It is inferred that the tensile strength of the nanocomposites can be maximized by thickening the interfacial region through the formation of a crystalline coating around CNTs or their functionalization or in situ formation of metal oxide/carbide interlayer at boundary zones. For instance, shear strength of CNT-Al nanocomposites is enhanced by the formation of interfacial Al_4C_3 carbides during a chemical reaction between defective CNTs and molten Al in the interboundary areas [120,162]. Figure 27 shows the interfacial regions in CNT-Al matrix nanocomposites. As seen, several in situ phases are embedded in the grain boundary layer of Al-CNT sintered compacts including Al_2O_3 , amorphous carbon black, graphite and Al_4C_3 phases [120]. The formation of carbides on the surface of CNTs at Al/CNT interfaces diminishes the contact area between CNTs and Al matrix with poor wettability and substitutes the Al/Al carbide interfaces with a lower wetting angle than that of CNT/Al boundaries (~55° vs. 130–140°) [162,163]. The stronger the physicochemical interactions between these two phases, the more adhesive the interface will be. To simply describe metal/ceramic physical interaction, the work of adhesion (W_{ad}) is defined as: (i) The amount of energy released whenever two free surfaces are brought into contact or (ii) the work per unit area of interface which is reversibly performed to separate the two phases. W_{ad} can be given by the following equation [128,164]:

$$W_{\rm ad} = \sigma_{\rm LV} (1 + \cos\theta) \tag{8}$$

where σ_{LV} is the surface tension and θ is the contact angle between two phases. Therefore, W_{ad} as a measure of the interfacial adhesion could be enhanced by improving the wettability through extensive interfacial chemical reactions. From this point of view, Al₄C₃ formation at the CNT/Al interface increases the interfacial adhesion from 200 mJ/m² for Al-C system to1156 mJ/m² for Al-Al₄C₃ (calculated at 1100 °C) and consequently counteracts delamination and improves the load transfer efficiency [128].



Figure 27. TEM images of the grain boundary regions in CNT-dispersed Al matrix nanocomposites: (a) Micrograph of the whole grain boundary including (1) Al, (2) alumina, (3) CNT, (4) amorphous carbon black, (5) graphite, and (6) Al_4C_3 phases; (b) interfacial region between CNT and Al matrix; and (c) HRTEM image and SAD (Selected area diffraction) pattern of Al_4C_3 phase. The region with the broken alumina phase is indicated with the white arrow [120] (Reproduced with permission from [120], Elsevier, 2009).

On the contrary, some research works have reported the adverse effects of the carbide formation on the CNT/Al interfacial bonding and degradation of mechanical properties in CNT-Al nanocomposites due to a weak interfacial adhesion [165–167]. However, some researchers have demonstrated directly or indirectly the desired influences of CNT/metal matrix interfacial reactions on the mechanical features of the nanocomposites regarding the fact that the CNT/metal interfacial load transfer is a direct function of the interfacial bonding. Zhou et al. [168] produced the Al₄C₃ nanostructure at the end of CNTs incorporated into Al matrix through an appropriate heat treatment and investigated the thermal expansion behavior of the nanocomposite as a criterion of CNT/Al matrix interfacial bonding. They observed stress contrast around carbides as an evidence of a friction trace, leading to the enhancement in their anchor effect from Al matrix. This carbide-induced anchor effect minimizes the local interfacial slippage and constrains the matrix deformation. Consequently, the thermal expansion exhibits a linear and reversible behavior under cyclic thermal load, indicating a reduced interfacial slippage between CNTs and Al matrix at the presence of Al₄C₃ precipitates.

It is proven that CNT/metal interfacial adhesion strongly depends on the applied method for dispersion of CNTs inside the matrix. Among the various discussed methods, molecular-level process and metallization of CNTs are the most effective. Kim et al. [49] used molecular-level process prior to spark plasma sintering to fabricate CNT-filled Cu nanocomposites. They reported enhanced hardness and wear resistance in spark plasma sintered CNT-Cu nanocomposites than pure Cu with good CNT/Cu interfacial bonding as well as uniform CNTs distribution in the matrix and high relative density. Metallization of CNTs using chemical vapor deposition (CVD) [16] and electroless coating [95] is one of the effective approaches to achieve a strong metal/CNT interfacial bonding as well as a homogeneous dispersion of CNTs inside the matrix. It can improve the load transfer from matrix to CNTs through the metallic coating. In another study, He et al. [128] fabricated CNT-reinforced Al nanocomposites with enhanced mechanical properties via the in situ chemical vapor deposition process and ascribed the strong interfacial bonding to the formation of transition thin layer of Al_4C_3 between CNTs and Al matrix.

Clean oxide-free surfaces of metallic powders are a prerequisite for obtaining a good CNT/metal interfacial adhesion. To meet this challenge, some additives in CNT-metal systems are utilized to reduce the oxide content. Owing to its negligible solid solubility, good adhesion with Cu, and high thermodynamic stability, 0.5 wt % ruthenium (Ru) as an air-stable transition metal was exploited in a recent survey to reduce non-protective oxide films on Cu surfaces. Furthermore, Ru contributes to increased thermal conductivity of CNT-Cu binary systems as a result of enhanced CNT/Cu interfacial adhesion and inhibition of the heat carrying phonons scattering at the CNT/Cu interfaces and weak interfacial bonding-induced pores. However, if Ru content exceeds 2.5 wt %, a reduction in hardness is observed due to the restricted densification of the powder system. It arises from high melting point of Ru, serving as a diffusion barrier during the consolidation process. Also, using 1 wt % Ru decreases the electrical conductivity of pristine copper, because the interfacial resistance occurs due to high electrical resistivity of Ru than Cu (7.1×10^{-6} vs. $1.68 \times 10^{-6} \Omega \cdot cm$) [169].

Interestingly, metal oxide formation on the surface of the particles may strengthen the interfacial adhesion in some CNT-reinforced metallic systems. For instance, Kondoh et al. [97] fabricated CNT-Mg nanocomposites by spark plasma sintering of CNT-coated Mg particles and reported in-situ formation of MgO dispersoids during the consolidation process as well as a thin MgO film on the surface of Mg particles due to the atmospheric corrosion. They confirmed that the diffusion of carbon atoms into the MgO structure provides an enhanced interfacial adhesion with CNTs. This phenomenon is mechanistically similar to the epitaxial growth of chromium carbide nanostructures mostly Cr₇C₃ at the CNT/Cu-Cr interface as a result of the substitutional diffusion of Cr atoms into radially unzipped defects of CNTs. It is schematically shown in Figure 28. The results show that the formation of Cr carbide nanostructures may potentially increase the efficiency of interfacial load transfer while preserving CNTs structure [170]. It is further surveyed by Kathrein et al. [171].



Figure 28. A schematic view of epitaxial growth of Cr carbide at the CNT/Cu-Cr interface via the substitutional diffusion of Cr atoms into the nanotubes during sintering [170] (Reproduced with permission from [170], Elsevier, 2013).

The nanocomposite processing parameters such as applied temperature/pressure and post thermal/mechanical treatments are among factors affecting CNT/matrix interfacial adhesion. Guo et al. [172] fabricated CNT-Al nanocomposites through spark plasma sintering followed by hot rolling process and reported that higher sintering temperature (630 °C vs. 590 °C) provides a stronger cohesion force for Al-CNTs and Al-Al particles due to higher degree of densification.

3. CNT Pinning-Induced Grain Refinement

In addition to the load bearing capacity, CNTs can affect the grain size of the metal matrix nanocomposites. In fact, the incorporation of CNTs into a metallic matrix results in lower grain size due to the CNT-induced pinning effect. Such an effect arises from the low dimensions of CNTs which can pin the grains of the metal matrix similar to nanosized round particles. The more the CNT content, the higher the effectiveness of boundary pinning and the lower the grain size are [42,101,173,174]. Figure 29 shows the STEM (Scanning transmission electron microscope) micrographs of Cu and CNT-Cu nanocomposites after the consolidation by high pressure torsion (HPT). As obviously seen, an increase in CNT content may feasibly reduce the grain size and narrow its distribution thank to the grain pinning effect [42].

The mean grain size (*D*) of reinforcement-containing metal matrices can be estimated by the Zener pinning relation [174]:

$$D = \frac{k \times r}{f^n} \tag{9}$$

where k is a proportional dimensionless constant, f is the volume fraction of the secondary phase, and r is the mean reinforcement radius, respectively. The secondary phase particle (i.e., CNTs) acts as a frictional force against the grain boundary migration and hinders the grain growth. As seen in Equation (7), the strengthening effect of particles depends on their radius (diameter). The smaller the diameter of CNTs, the smaller the mean grain size of the metallic matrix will be. Moreover, the average distance between CNTs is another factor which greatly affects the pinning effect. An increase in CNT content gives rise to lower distance between CNTs, increased interfacial energy absorption and decreased grain size. Additionally, for a constant CNT content, the average distance between short CNTs are lower than that between long ones. As a result, short CNTs have stronger pinning effect and result in lower grain size [174].

Such a grain refinement affects the mechanical properties of CNT-dispersed metal matrix nanocomposites. In general, CNTs can increase the mechanical strength of metal matrices through a variety of mechanisms: (i) Load transfer from the metallic matrix to CNTs, (ii) reduction in the matrix grain size through the pinning effect (Hall-Petch relation), (iii) CNT-induced Orowan looping mechanism, (iv) solid solution strengthening due to the diffusion of carbon atoms from CNTs to

the matrix, (v) secondary phase (particle) strengthening due to the in-situ formation of carbide particles by a chemical reaction between CNTs and the metal matrix, (vi) work hardening of the matrix due to the formation and accumulation of dislocations at CNT/metal interfaces caused by thermal mismatch between CNTs and metal matrix, and (vii) the strengthening effect induced by impurities originating from the mixing methods [175]. Depending on the type of matrix and the fabrication method, one or some of these mechanisms may be stimulated. Another factor affecting the strengthening mechanisms is the physical and size-dependent properties of CNTs. For instance, if the thermal expansion coefficient of CNTs is considerably different with that of the matrix, the dislocations will build up at CNT/metal interfaces and enhance the mechanical strength of the nanocomposite. Moreover, the diameter and length (i.e., aspect ratio) of CNTs may influence the strengthening mechanisms in metal matrices. Among the aforementioned strengthening mechanisms, the load transfer mechanism is the most influential. Typically, the higher length or lower diameter of CNTs (i.e., higher aspect ratio) results in better load transfer and higher mechanical properties such as improved yield strength and elastic modulus. However, when the aspect ratio of CNTs is lower than a critical value, the Orowan mechanism is dominant [175,176].

Beside the positive effect of long CNTs on enhanced mechanical properties than short ones, long nanotubes are usually more sensitive to agglomeration. As a consequence, the dispersion of shorter CNTs is an easier task than that of longer ones [34]. Using a high content of long CNTs may induce the agglomeration and degrade the mechanical properties of final nanocomposite.



Figure 29. STEM (scanning transmission electron microscope) images of Cu and CNT-Cu nanocomposites fabricated by high pressure torsion (HPT): (**a**) Pure Cu, (**b**) 5 vol % CNT-Cu, and (**c**) 10 vol % CNT-Cu nanocomposites. The left images are provided by bright-field mode, and the right ones by high-angle annular dark-field mode [41] (Reproduced with permission from [41], Springer, 2013).

4. Conclusions and Outlook

The present review paper has provided a broad overview of practical challenges in the fabrication of CNT-dispersed metal matrix nanocomposites. These challenges have been categorized into four main groups: (i) Non-uniform dispersion of CNTs throughout the metallic matrix, (ii) thermal decomposition of CNTs and chemical reaction with the metallic matrix, (iii) poor interfacial adhesion, and (iv) low compactability. One can obtain a CNT-metal matrix nanocomposite with superior properties if all of four challenges are appropriately overcome. A large number of research works have focused on these issues and strived to suggest feasible solutions to them. Their strategy is often based on the better dispersion of CNTs through the effective prevention of their agglomeration and close control over the processing parameters for suppressing the unwanted phase transformations and preventing from unfavorable microstructural features. Although these solutions remarkably enhance the physicomechanical properties, each of them has its own limitations. It seems that the future research works should find their way toward development of new solutions for uniform dispersion of CNTs in metallic matrices, so that the electrical and thermal properties are improved as well as mechanical ones. It seems that the future research works should focus on the development of more efficient ways to uniformly disperse CNTs in the metallic systems or introduction of new methods for efficient consolidation of metallic powders mixed with CNTs.

Acknowledgments: The present work has been conducted by some active members of the "Advanced Materials Research Group (AMRG)" founded by Abolfazl Azarniya in 2016. The authors would like to acknowledge all team members including Anne Jung (from Saarland University, Saarbrücken, Germany), Mohammad Mirzaali (from Delft University of Technology, Delft, The Netherlands), Dariusz Garbiec (from Metal Forming Institute, Poznań, Poland), Ridvan Yamanoglou (from Kocaeli University, Kocaeli, Turkey), Temel Varol (from Karadeniz Technical University, Trabzon, Turkey), Mohammad Abedi and Dmitry Moskovskikh (from National University of Science and Technology MISIS, Moscow, Russia), Flávio Bartolomeu and Georgina Miranda (from University of Minho, Braga, Portugal), Xabier Garmendia (from University of Liverpool, Liverpool, UK), Joseph Ahn (from Imperial College London, London, UK), Yaser Shanjani (from Stanford University, Stanford, CA, USA), Chor Yen Yap, Sing Swee Leong, and Wai Yee Yeong (from Nanyang Technological University, Singapore), Marek Weglowski (from Institute of Welding, Gliwice, Poland), Wessel Wits (from University of Twente, Enschede, The Netherlands) and some others for their best efforts. These scientific partners are a part of AMRG's forthcoming research publications.

Author Contributions: Abolfazl Azarniya, Mir Saman Safavi, Saeed Sovizi, Amir Azarniya, and Biao Chen outlined the review, performed the literature search and wrote the manuscript. Hamid Reza Madaah Hosseini and Seeram Ramakrishna helped in compiling the wide information related to the topic and data presentation and performed technical editing for all corrections. Hamid Reza Madaah Hosseini and Seeram Ramakrishna also helped in finalizing the manuscript and developed the idea of the topic and were responsible for the correspondence.

Conflicts of Interest: The authors declare no conflict of interest.

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