CARBON NANOTUBES REINFORCED COPPER COMPOSITES – A REVIEW

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Abstract

Research reports of past decade on carbon nanotubes reinforced MMC's have shown remarkable results. Carbon nanotubes helps in reducing the density at the same time enhance the mechanical property of the composites which are in demand currently. Copper-carbon nanotubes composite have been successfully fabricated and they are suitable for electrical, thermal and structural applications. Various methods are used to fabricate Cu-CNT composite like powder metallurgy, molecular-level-mixing, electroless deposition, electrodeposition and melt stirring. This paper focuses on powder metallurgy process and its various parameters. Mechanical electrical and thermal properties from various literatures are discussed in detail. Scope for future research work is also highlighted.

Keywords: Carbon nanotubes (CNTs), Multi-Walled Carbon nanotubes (MWCNT) Metal-Matrix composite (MMC's), Powder Metallurgy, Processing, Dispersion.

Introduction

Research on MMC's are being carried out extensively all over the world since several decades, and these composites are delivering promising results. As metal is the primary need for structural, electrical and for thermal management application, and one of the important material for mankind, more efforts are put in to enhance their properties by using suitable reinforcements like carbides, carbon fiber, graphene and carbon nanotubes etc. After the discovery made by Sumio Iijima of carbon nanotubes in 1991,[2] it has attracted the researchers to very great extent to incorporate CNT's in metal matrix because of its prodigious mechanical, electrical and thermal properties. And it is also best known for its chemical inertness. Table 1 gives the information regarding properties of carbon nanotubes.

Properties	Single walled carbon nanotubes	Multi walled carbon nanotubes
Specific gravity	0.8 g/cm³	1.8 g/cm³
Elastic modulus	≈1 TPa	≈0.3-1 TPa
Strength	50-500 GPa	10-60 GPa
Resistivity	5-50 μΩ cm	5-50 μΩ cm
Thermal conductivity	3000 W m^{-1} K^{-1}	3000 W m^{-1} K^{-1}
Thermal Stability	>700°C (in air);2800°C (in vacuum)	>700°C (in air);2800°C (in vacuum)

Table 1: Properties of Carbon nanotubes

There is lots of work carried out on metal-CNT composite; most of the research is concentrated towards Al-CNT, Cu-CNT and Mg-CNT. This paper focuses on Copper-Carbon nanotubes composites.

Copper is well known for its good ductility, electrical conductivity and thermal conduction also exhibits decent mechanical properties. Table 2 gives information regarding properties of copper metal

Properties	Copper
Density	8.96 g/cm³
Elastic Modulus	117 GPa
Yield Strength	70 MPa
Ultimate Strength	220 MPa
Thermal conductivity	400 W m^{-1} K^{-1}
Electrical Conductivity	58.5 S/m

Table 2: Properties of copper

In the middle of 19thcentury copper composite like, Copper-graphite was developed for electrical brusher and copper based friction materials application.[35] Although CNTs are composed of same element as graphite i.e. carbon, CNTs show superior properties as compared to graphite, this led to the idea of Cu-CNT composites.

Fabrication methods

Processing of metal-CNT composite has been challenge due to distinct phase of CNT and copper, difference in coefficient of thermal expansion, wettability issues. Poor wettability affects the load transfer and phonon scattering. Agglomeration of CNT causes dispersion problems. [4] Therefore choice of synthesis method plays very important role. Some of the methods used for synthesis of Cu-CNT are as follows:

1. Powder metallurgy.
2. Electrochemical deposition.
3. Molecular-Level-Mixing.
4. Electroless deposition.
5. Melt stirring.

But most commonly used method is Powder metallurgy route. In this method there is minimal material wastage, high dimensional accuracy and the need for secondary finishing operations is reduced to a great extent. Therefore an attempt will made to outline the steps involved in processing of Cu-CNT composite by Powder metallurgy route.

Annealing of Powder

Before getting into the core steps of processing it is essential to heat treat the powder i.e. annealing. Annealing the powder helps to softens the particles surface. This process is carried out to get rid of carbon or oxygen content which may be present after the powder production. Another advantage of annealing is it helps to relive stress and also removes any oxide layer if present. But most importantly annealing of the metal powder enhances the compressibility during compaction and green strength of compact due to softened surface layer of metal particles. [35]

Sonication of carbon nanotubes

The major problems associated with CNTs is they tend to form clusters due to Van-Dar-Waal force of attraction, because of this reason the dispersion of CNTs in matrix becomes challenging. If agglomeration problem is not solved before reinforcing, it reflects negatively on the results. To overcome this problem CNTs are sonicated either in ethanol or acetone. When high frequency vibrations strike CNTs they get separated to good extent. According to literature surveyed, sonication process is carried out for duration of 30 mins to 1 h. After sonication CNTs are dried in oven.

M. Barzegar Vishlaghi *et al.*[9] have sonicated the carbon nanotubes in acetone for 20 mins and they report CNT clusters were broken and assisted in decent CNT dispersion in matrix.

P. Bakhshaei *et al.*[3] used ethanol to sonicate CNTs, and ultrasonic agitation was carried out for 15 mins, after sonication process CNTs were oven dried at 50°C for 24 h.

Van Trinh Pham *et al.*[12] have treated CNTs in chemical mixture of H_2SO_4:HNO_3 (3:1) at 60°C. This process was carried out to achieve functionalized CNTs. Once the CNTs were successfully functionalized after 4h, they were dispersed in acetone along with copper powder. After drying it was observed that CNTs were wrapped around copper particles.

Ch. Guiderdoni *et al.*[26] Have sonicated CNTs in deionized water, later Cu powder was added to agitation bath and sonication was carried out for 1 min followed by freeze drying the mixture using N_2 for 2 mins.

From above study it is quite clear that sonication of CNTs is important to overcome the Van-Dar-Waal forces which helps in better dispersion.

Ball milling of composite powder

Ball milling is one of the critical steps in powder metallurgy process. It is carried out to disperse the CNTs uniformly throughout the Cu matrix and also to alter the particle size. The various parameters associated with ball milling are Ball to powder ratio (BPR), Rotations per minute (RPM), Milling time duration and type of ball milling machine (Planetary or Horizontal ball mill).

Hongqi Li *et al.*[10] have ball milled the Cu-CNT powder mixture for 5h in an argon atmosphere with BPR 6:1. By studying the morphology, they have reported about the various stages which particle undergoes during ball milling. Size of particle increased from nanometer to micrometer after 5h of ball milling and particle had smooth flat surface. It is assumed that initially the particles are deformed into flat plate like structure which resulted in work hardening. Then they are fractured due to impact by balls. Lastly particle size is increased due to cold welding. All these stages result in dispersion of CNTs in matrix homogenously.

M. Barzegar Vishlaghi *et al.*[9] Have studied the effect of ball milling on Cu/Fe-CNT powder. Cu and Fe powder of known ratio were reinforced with 10% multi-walled carbon nanotubes (MWCNT) and milled with two different ways for 2 different batches as given,

(i) Only Cu and Fe mixture was ball milled for 10h. After 10 h MWCNTs powder was added to milled Cu-Fe mixture and again the process was continued for 5h. The samples were analyzed for every 1, 3 and 5 h. They named them as C1-1, C1-3 and C1-5. So in total 15h of ball milling was carried out.

(ii) In this case the complete powder mixture of Cu/Fe-CNT was ball milled for 15h named it as C2.

After analyzing both the cases it was observed that, MWCNT reduce milling energy as they are self-lubricating in nature. They found that crystallite size increased after the addition of MWCNT. The above result is illustrated in the table below.

Sample	Mean crystallite size (nm)	Lattice parameter (nm)
C1-1	35	0.36239
C1-3	35	0.36235
C1-5	34	0.36251
C2	46	0.36266
15 h milled $Cu_{80}Fe_{20}$	19	0.36284
10 h milled $Cu_{80}Fe_{20}$	23	0.36283

Table 3: Mean crystallite size and lattice parameter

The details of parameters used in ball milling obtained by studying the literature are summarized in the table below.

Journal No.	Type of Ball Mill	Time	RPM	Ball to Powder ratio
[1]	Ball Mill	30 mins	-	6:1
[3]	Planetary Ball Mill	20 h	300	20:1
[4]	Planetary Ball Mill	1 h	200	10:1

[6]	Ball Mill	15 h	-	-
[7]	Planetary Ball Mill	2 h	1200	10:1
[8]	Planetary Ball Mill	24 h	150	-
[9]	Planetary Ball Mill	15 h	300	20:1
[10]	Planetary Ball Mill	5 h	-	10:1
[11]	Planetary Ball Mill	3 h	200	10:1
[12]	Planetary Ball Mill	6 h	300	-
[13]	Planetary Ball Mill	30 mins	4500	-

Table 4: Ball mill parameter details from various literatures

From the literature surveyed it is quite evident that there are no fixed parameter standards followed by the researchers for the above mentioned parameter.

Powder Compaction

In powder compaction process the composite powder is first transferred to either steel or graphite die and compacted by applying uniaxial force to required dimension. Due to complex morphology and mechanical behavior of particles, the powder compaction modeling has been a challenge to achieve. This modeling requires boundary value problem and set of differential equations which should account for conservation of mass momentum balance and conservation of energy. And law accounting stress-strain relation and friction known as constitutive law. The modern FEM modeling is suitable for handling these problems.[35]

The physical processes, initially when powder is poured into die particles are arranged in random order with point contact to neighboring particle. As the force is applied with punch the plastic flow occurs in vicinity of contact. This increases the contact zone and thus center of particles comes close to each other hence densifying the green compact. After densification the compact obtained are called 'Green compact'.[35]

For compaction of Cu-CNT various methods are available like cold pressing, hot pressing and spark plasma sintering (SPS) etc.[36] In SPS process both compaction sintering carried out together under vacuum. In hot pressing and SPS it is necessary to maintain vacuum to avoid oxidation problems.

Sintering of Green Compact

Sintering is the process in which green compact is heated in an inert atmosphere up to 70-85% of matrix melting point. During this process the surface of the particles are partially melted and gets bonded with surrounding particles resulting in stronger compact. Volatile impurities are also eliminated during this process. Sintering is generally carried out under Nitrogen or Argon atmosphere to avoid oxidation problems. When sintering is carried out at higher temperature i.e. close to melting temperature of composite grain growth occurs. This phenomenon is restricted by CNTs resulting in smaller grains. In other words CNTs act as grain refiners resulting in lower ductility and high strength.

Van Trinh Pham *et al.*[12] have studied the effect of three different sintering temperatures on Cu-CNT composite. The three temperature chosen were 850˚C, 900˚C and 950˚C and sintering was carried for 2h. They concluded that sintering the composite at 900˚C with CNT loading of 3% weight gave best hardness result.

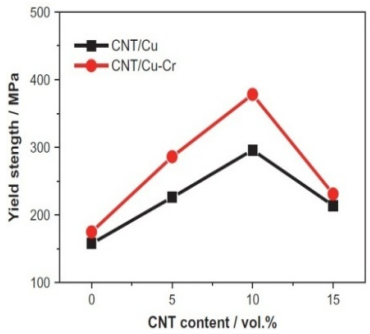
S.R. Dong *et al.*[1] sintered composites at 850˚C for 2h in vacuum followed by secondary rolling process. After rolling process samples were annealed at 600˚C for 3h. It was observed that wear loss reduced due to CNT addition and thin oxide film was formed over the surface which assisted smooth friction. Reports of this literature suggest that reinforcement of 12-15% CNT volume sintered at 850˚C gave best results. Below table gives information of various sintering parameters used by researchers.

Journal No	Sintering Temperature and Time
[1]	850°C (2 h)
[4]	750°C
[5]	SPS 600°C
[6]	1000°C
[7]	750°C
[8]	SPS 700°C
[11]	SPS 500°C
[12]	850°C, 900°C, 950°C (2 h)
[13]	600°C (1 h)
[14]	SPS 550°C
[16]	900°C (8 h)
[17]	SPS 550°C
[18]	800°C (1 h)
[26]	SPS 700°C
[32]	700°C (1 h)

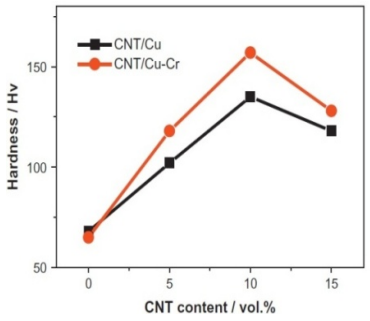
Table 5: Sintering details from various literatures

Various properties

Ke Chu *et al.*[7] have prepared Cu-Cr/CNT and Cu-CNT composites by hot pressing at 750°C. The hardness of Cu-CNT was found to be 135 Hv which was 2 times the hardness of pure Cu. Tensile strength of Cu-CNT composite increased from 168 MPa to 296 MPa which was 128 MPa higher than the pure Cu sample. Both hardness and tensile strength values obtained were for 10% CNT volume addition. The reason given for these remarkable results are homogenous dispersion of CNT in Cu matrix. But at the same time decrease in both hardness and yield strength were observed for 15% CNT volume reinforcement. This is due to agglomeration of CNT at Cu grain boundaries. On the other hand it was observed that Cu-Cr/CNT composite showed remarkable results. Hardness value of 157 Hv and yield strength of 388 MPa i.e. approximately 128% and 135% increase as compared to Cu-CNT composite. Author reports the reason for such high strength is due to good interfacial bonding by formation of Cr_3C_2 layer between Cu-Cr and CNT interface.



(a)



. (b)

Fig. 1 (a).Yield strength of CNT/Cu–Cr and CNT/Cu composites versus CNT content. (b). Hardness of CNT/Cu–Cr and CNT/Cu composites versus CNT content (Ke Chu *et al.*[7])

S.R Dong *et al.*[1] Cu-CNT composite prepare by powder metallurgy route showed the Vickers hardness of 100-115 Hv, but there was significant drop in hardness after 15% CNT volume addition.

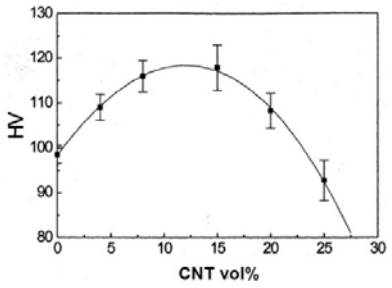


Fig 2. Vicker's hardness (*H*v) of the nanotube/Cu composite on volume fraction of carbon nanotubes (S.R Dong *et al.*[1]).

Kyung Tae Kim et *al.*[8] have successfully processed Cu-CNT composite by SPS process at temperature of 700°C, followed by cold rolling with reduction up to 50% in volume and later the sample were annealed at 650°C for 3 h. Paper reported that cold rolling increases the relative density. The relative density increased from 97-98.5% to 99%. The tensile strength for 10% CNT volume fraction was 281 MPa which is 1.6 times higher as compared to pure Cu sample processed by same method. Young's modulus of 10% CNT volume reinforced composite was doubled (137 GPa) as compared to unreinforced sample which had value of 70 GPa. The yield strength measured was found to be 135 MPa and 197 MPa for unreinforced and10% CNT reinforced composite respectively. At the same time it was observed that Cu-CNT sample showed two steps yielding indicating that dispersion of CNTs in Cu matrix was non-homogenous which is shown in the figure 3.

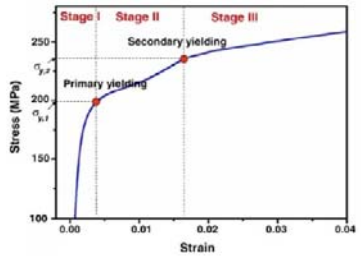


Fig 3. Stress–strain curve showing two-step yielding phenomena, which is dependent on the three different stages (I–III) of deformation, during tensile test of 10 vol% CNT/Cu Nanocomposite (Kyung Tae Kim *et al.*[8]).

Dong. H. Nam *et al.*[11] have treated CNTs with two different aspect ratio. One batch was treated with acid which they called ATCNT and other batch was coated with poly-vinyl-alcohol (PVA) and called it PCNT. Both ATCNT and PCNT were reinforced in Al-Cu matrix. They combined Molecular-Level-Mixing and Mechanical alloying methods to prepare Al-Cu/CNT composites. With 4% volume of ATCNT and PCNT addition the yield strength were 3.8 times higher i.e. 376 MPa and 384 MPa respectively. Whereas Al-Cu sample yield strength was 110 MPa. The ultimate tensile strength values of ATCNT and PCNT were 494 MPa and 470 MPa respectively. Which were 2 times higher as compared to Al-Cu matrix with value of 237 MPa. From above result it is clear that with different aspect ratio i.e. ATCNT and PCNT there was no substantial variation in mechanical properties. However only elastic moduli showed different result i.e. PCNT/Al-Cu showed 30% increase with 93 GPa were as ATCNT/Al-Cu was 73 GPa.

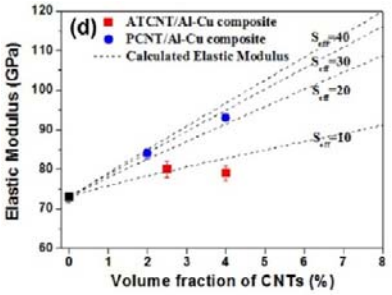


Fig 4. Elastic modulus of PCNT/Al–Cu and ATCNT/Al–Cu composites with volume fraction of CNTs and comparison with the calculated elastic modulus (Dong. H. Nam *et al.*[11]).

Therefore by combining both Molecular-Level-Mixing and Mechanical alloying high strength composites can be produced.

Van Trinh Pham *et al.*[12] have studied the effect of sintering temperature on mechanical behavior of composite. Different weight fraction of CNT ranging from 0.5% to 3.5% was subjected to three different sintering temperatures i.e. 850°C, 900°C and 950°C. The hardness of composite increased with increase in weight fraction of CNT but only up to 3%. After 3% weight the hardness value dropped. For 3% CNT weight reinforcement and sintering at 900°C yielded the best result of 39.4 HB which was 1.4 times higher than pure Cu subjected to same sintering temperature and same CNT weight fraction.

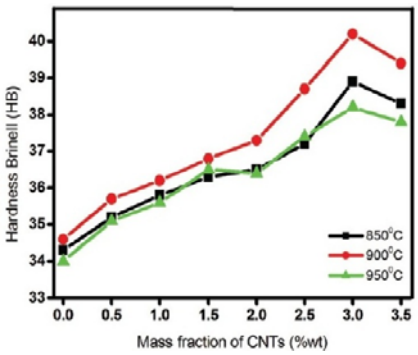


Fig 5. Brinel Hardness (HB) of the Cu/CNT nanocomposite on the mass fraction of the CNTs (Van Trinh Pham *et al.*[12])

They report, reduction in hardness after 900˚C is due to grain growth phenomenon, which also goes well with Hall-Patch theory.

Byung K Lim *et al.*[14] coated CNT with Cu particles by Electroless process followed by consolidating samples at 550°C using SPS process. They observed decreasing in electrical conductivity by increasing the CNT volume fraction in Cu matrix. They concluded that reason for poor electrical conductivity is agglomeration of CNT at matrix grain boundaries which results in scattering of charges.

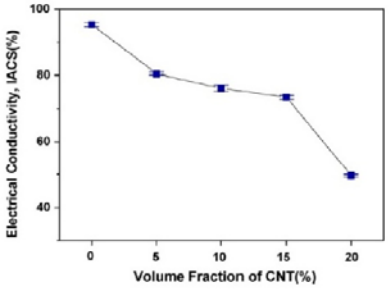


Fig 6. The standard IACS % electrical conductivity for the sintered Cu and the relatedCNT/Cu nanocomposites (Byung K Lim *et al.*[14])

CNT acted like barrier instead of charge carrier which is due to improper alignment of CNT along path of moving charges, porosity and poor wettability. The Vickers hardness showed increasing trend with increasing in CNT volume fraction. At 20% CNT volume the results was 1.4 GPa which is 2.1 times higher than pure Cu. The yield strength of composite increased by increasing CNT volume fraction up to 20%, but after 20% it resulted in catastrophic failure i.e. composite fractured before yielding.

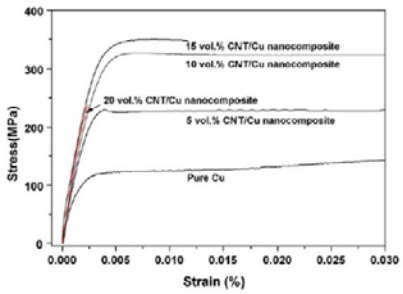


Fig 7. Stress–strain curve of CNT/Cu nanocomposites (Byung K Lim *et al.*[14])

This is due to segregation of CNT. Yield strength values was best at 15% vol measuring 341 MPa which is 2.85 time higher than pure Cu. Elastics property of composite decreased by adding CNT.

Kyung Tae Kim *et al.*[17] prepared Cu-CNT composite by Molecular-Level-Mixing method. They studied the thermal expansion behavior of prepared composite. The results of 5% and 10% CNT volume were 14 ppm K^{-1} and 12.1 ppm K^{-1} respectively which were lower when compared to unreinforced Cu sample with CTE value 17 ppm K^{-1}. This reveals addition of CNT increases the stiffness of composite.

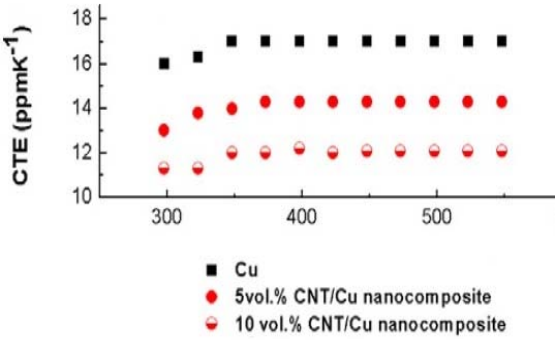


Fig 8. Variation of CTE compared with unreinforced Cu (Kyung Tae Kim *et al.*[17])

Seung. I *et al.*[18] made use of Molecular-Level-Mixing method. By chemically bonding the Cu particles to CNT walls interfacial bonding between Cu and CNT was enhanced. The mechanical results were much higher; yield strength of 360 MPa was measured for 15% CNT volume addition which was 2.3 times higher compared to pure Cu. For 10% CNT volume the results turned out to be 3 times higher with value 455 MPa.

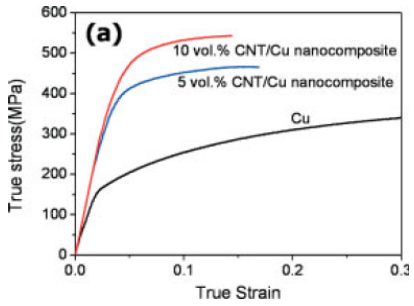


Fig 9. Stress and strain curves of CNT/Cu Nanocomposite obtained by compressive test (Seung. I *et al.*[18])

This signifies that load transfer between Cu matrix and CNT is good due to better interfacial bonding resulted from Molecular-Level-Mixing method.

Chandaramouli Subramaniam *et al.*[21] have deposited Cu on single-walled CNT using electrodeposition method. Prior to this, single walled CNTs were grown by water assisted technique. Here they term CNT as matrix as Cu was deposited on walls of CNT at very small scale. According to our literature survey, this is the only paper which reports similar electrical conductivity as copper with good ampacity, they define ampacity as maximum current density (current carrying capacity of object) were the resistivity remains constant. The measured ampacity of CNT-Cu was 600 MA cm^{-2} were as Cu and Au showed ampacity of 6.1 MA cm^{-2} and 6.3 MA cm^{-2} i.e. CNT-Cu showed 100 times higher ampacity. At the same time electrical conductivity of CNT-Cu composite measured by four-probe method was $4.7 \pm 0.3 \times 10^5$ S cm^{-1} which is close to conductivity of copper (5.8×10^{-5} S cm^{-1}). Very less material exhibit both ampacity and conductivity behavior at the same time. CNT-Cu fabricated by Chandaramouli Subramaniam *et al* showed simultaneous existence of both properties.

Gul. H *et al.*[23] made use of pulse electrodeposition process to obtain copper coating with well-distributed MWCNT. They suggest that pulsed electrodeposition method layer exhibits higher mechanical and tribological properties as compared to layer coated by direct current plating. After successful co-deposition, SEM analysis confirms that by increasing the MWCNT from 0.5 to 4 g/l in electrolyte increases the CNTs in deposit layer. They found homogenous dispersion of CNTs by increasing the MWCNT in the electrolyte up to 4 g/l. They also report that MWCNTs act like nucleation sites hence restricting the crystal growth. Therefore by addition of MWCNT smaller grains are resulted which was confirmed by XRD analysis. Micro-hardness of coated layer increased by increasing the CNTs in electrolyte. The lowest wear rate was observed for 4 g/l MWCNT coated layer. Author suggests that addition of MWCNT up to 4 g/l is optimum.

Gwi-Nam Kim *et al.*[28] prepared Cu-CNT composite by sintering the green compact at 880°C. The prepared sample was hot extruded at 450°C with 20° die angle and 16 mm die diameter. They analyzed particle size behavior for CNT addition of 1%, 5% and 10% weight fraction. They reported that beyond 5% CNT addition crystal growth is restricted resulting in smaller grains there by increasing the strength of composite. The micrograph of composites is shown below.

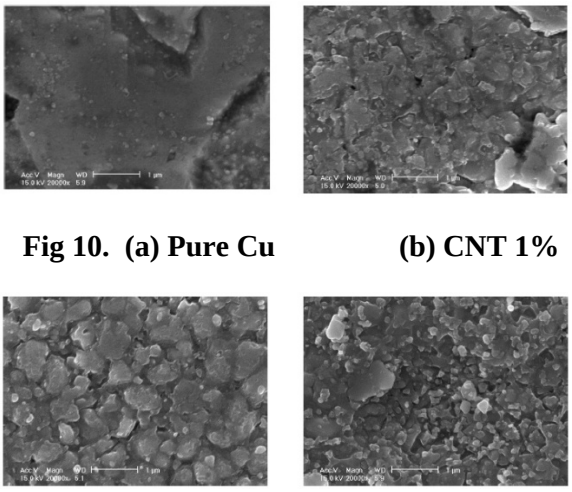


Fig 10. (a) Pure Cu (b) CNT 1%

(c) CNT 5% (d) CNT10%

Fig. 10 SEM micrograph of composites (Gwi-Nam Kim *et al.*[38])

The direct effect of smaller grains was observed on mechanical properties i.e. as the CNT weight fraction increased the hardness value increased from 50 Hv to 239 Hv for pure Cu and 10% reinforced CNT composite respectively. The tensile strength of composite increased from 463.9 MPa to 1463.1 MPa for unreinforced and reinforced CNT sample respectively. The reason for these enhanced results may be due to hot extrusion of composite. By extruding the CNT

composite it is assumed to align the CNT along the extrusion axis which increases the properties. Yield strength of composites increased by increasing the CNT weight fraction as shown in figure below.

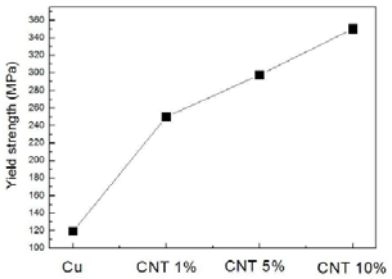


Fig 11. Yield strength versus CNT wt% (Gwi-Nam Kim *et al.*[38])

Conclusion

After extensive literature study, it is quite evident that powder metallurgy is most widely used method to fabricate Cu-CNT composite because of its ease of processing compared to other methods. The major problems and challenges faced in synthesis of Cu-CNT composite were very clear and common in many literature, (i) Non uniform dispersion of carbon nanotubes in Cu matrix, (ii) Wettability issue which resulted in poor load transfer, phonon scattering (iii) Porosity reflecting on density. Although powder metallurgy is most widely used method but Molecular–Level–Mixing yielded some of the best results then followed by Electroless deposition method. This clearly proves CNTs need to be coated chemically with Nano-particles like Copper or nickel for better bonding between matrix and CNT. Therefore more work can be focused on matrix and CNT interfacial bonding and homogenous dispersion on CNT even at higher weight/volume fraction. And there are hardly any paper reporting about fatigue test, corrosion behavior, Impact properties and creep resistance of Cu-CNT composite according to our knowledge, so there is scope for future work in these areas.

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