Synthesis of copper coated carbon nanotubes for aluminium matrix composites

Adnan Maqbool, F Ahmad Khalid, M Asif Hussain and Nabi Bakhsh
Faculty of Materials Science and Engineering, GIK Institute of Engineering Sciences and Technology, Topi 23640, KP, Pakistan
E-mail: adnanmaqbool247@gmail.com

Abstract. In this investigation copper coated carbon nanotubes (CNTs) were prepared to enhance the interfacial bonding between CNTs and aluminum matrix by the molecular-level mixing process. In optimized plating bath of (1:1) by wt. CNT with Cu, thickness of coated CNTs is reduced to 100 nm to promote uniform distribution of Cu nanoparticle on the surface of pretreated CNTs. The mixing of CNTs was accomplished by ultrasonication and ball milling. Scanning electron microscope analysis revealed the homogenous dispersion of Cu-coated CNTs in nanocomposites samples compared to the uncoated CNTs. The samples were pressureless sintered under vacuum. The densification increased with the increase in the CNTs content and is more pronounced in Cu-coated CNT nanocomposites.

1. Introduction
During past few decades, carbon nanotubes (CNTs) have attracted much attention. Especially for composite materials, it is predicted as an ideal reinforcement used in manufacturing of aircraft and sports goods, due to high aspect ratio, strength, elastic modulus and low density [1, 2]. Many researchers have encouraged the use of CNTs as reinforcement in metal matrices. For the fabrication of high strength and elastic modulus, homogeneous dispersion of CNTs is necessary and the interfacial bonding between metal and CNTs should be strong enough to transfer load efficiently. However, no major breakthrough is achieved with CNT/Al composites, because of obstacles related to the interfacial bonding between Al powder and CNTs, and the unavailability of suitable synthesis techniques for homogenous mixing at molecular level between Al and CNTs [3]. In addition, CNTs poor wetting property on Al due to entanglement and difference in density have been great hindrances in its uniform distribution for manufacturing the composites [4]. In case of Co-CNT, Ni-CNT and Cu-CNT composite powders, novel fabrication techniques to obtain outstanding composite powders are possible as the metal oxides (CuO and CoO) are easily reduced to metal Cu and Co [5, 6]. However, the fabrication of CNT/Al composite powder is irreversible once Al gets oxidized.

The researchers who have fabricated CNT/Al composites by conventional powder metallurgy and spray coating processes, have suggested CNT/Al composites as a new advanced structural material having high strength and modulus with low density for possible application in the next generation materials for automobile, sports and aerospace industries [7-9]. This consists of mixing CNTs with Al followed by spark plasma sintering or hot-extrusion. Kwon et al. fabricated CNT/Al composites by dispersion in natural rubber and a combination of processes of SPS and hot extrusion to get highly densified CNT/Al composites [10, 11]. Deng et al. performed isostatic pressing, followed by hot extrusion process. They distributed CNTs on the surface of 2024-Al powder by mechanical mixing
assisted with ultrasonic shaker and fabricated composites which showed increased tensile strength, hardness and young’s modulus [12-14]. Liao et al. fabricated CNT/Al composites by mixing the composite powder in the roller mill followed by SPS sintering and hot extrusion [15-18].

In this study, Cu-coated CNTs were prepared to enhance the interfacial bonding between CNTs and Al matrix by the molecular-level mixing process. To improve interfacial bonding, the enhancement in wettability of CNTs is necessary. For this purpose, CNTs were coated with Cu in the optimized plating bath. Therefore the influence of CNTs dispersion in the Al matrix for both, the Cu-coated and uncoated CNTs was ascertained.

2. Experimental procedures

For the fabrication of Al-matrix composites, Cu-coated and uncoated CNTs were used as the reinforcement in the Al matrix. Two processes: electroless plating and ultrasonic assisted mixing with N2 purging were utilized for the uniform distribution of CNTs. For the enhancement in interfacial bonding of Al matrix and CNTs, a Cu/CNT precursor was prepared by using an electroless plating process and then mixed by planetary ball milling with Al powder.

For the fabrication of the composites, gas atomized Al powder (99.84% pure, with 10 µm average particle size, Angang Group Co. Ltd., China) and multiwalled carbon nanotubes (Sun Nanotech Co. Ltd., China, purity >90%, diameter 10–30 nm) were used in the present study. To get rid of the metallic particles and other impurities, purification and functionalization of CNTs carried out by acid treatment. Purification of CNTs was done in conc. HCl (37%), sonicated at 30 ºC for 5 h and were then soaked for 12 h. Functionalization of purified CNTs was done by mixing conc. HNO3 (65%) in conc. H2SO4 (98%) in the ratio of (1:3). After the functionalization process, CNTs were added in 1M solution of SnCl2·2H2O along with 1 ml of HCl in 100 ml to adjust pH below 1 and sonicated for 30 min. Sensitized CNTs were washed with distilled water followed by filtration. For activation, CNTs were added in .0015 M solution of PdCl2 along with 1.5 ml of HCl to adjust pH below 1 and sonicated for 30 min. Finally, activated CNTs were washed with distilled water followed by centrifugation and filtration. After two-step sensitization and activation, CNTs were exposed to catalytic treatment in CuSO4·5H2O bath for 2 h at room temperature to suspend the CNTs in the solution. Formaldehyde was added in order to reduce the Cu in the bath for 20 min. Initially, 40 vol% CNT/Cu were used in the plating bath i.e. (1:9) wt ratio of CNTs with Cu. To optimize the Cu coating, bath composition was adjusted for the fixed Cu-CNT (1:1) wt. ratio i.e. for 50 mg CNTs bath composition was adjusted according to Cu content in the bath. The plating solution composition was CuSO4·5H2O 196 g, Na3C6H5O7·2H2O 532 g and NaOH was used to adjust the pH equal to 12 and 1 ml of formaldehyde was added drop wise in the solution. The composition (1:1) wt ratio of CNTs with Cu showed satisfactory results and whole solution changed from black to red brown, showing the uniform coating of Cu.

Ultrasonic assisted mechanical mixing of the Al and different compositions of uncoated and Cu-coated CNTs named by CNTs additions (0.25, 0.50, 0.75 and 1.0 wt%) were performed in ethanol. To facilitate uniform distribution and mixing of CNTs; mixture was sonicated at 60 ºC. Nitrogen gas was bubbled from bottom of the beaker by a glass rod that further enhanced the dispersion of Al powder with the CNTs by avoiding powder sedimentation. The process was continued until the thick slurry of the CNT/Al mixture was obtained. 12 g of mixed powder was placed in 250 ml stainless steel mixing jars together with stainless steel balls of 8 mm (Ø). The ball to weight ratio was also adjusted to (10:1). The jars were filled with argon gas and planetary ball mill was used for the mixing of powders, at 200 rpm for 1 h. Ethanol was used as the process control agent (PCA), for the purpose of minimizing cold welding of particles and to avoid sticking of powder with balls and walls of the jar. Uniaxial cold compaction of ball milled powder at 600 MPa was done by hydraulic press in 13 mm high-speed steel die. Pressureless sintering was performed in the tube furnace at 550 ºC for 3 h in the evacuated quartz tube at 10⁻⁴ mbar.

Archimedes principle was used for the calculation of relative density of the sintered compact, with respect to the water as an immersing medium. IR spectrum was obtained by Fourier Transform Infrared Spectroscopy (FTIR) spectrum 2000 (Perkin Elmer). Al was preferentially etched to reveal the CNTs and grain boundaries. Etching was performed at room temperature in a solution of 2 g NaOH, 4 g
Na₂CO₃ and 94 ml of H₂O [19]. Scanning electron microscopy (SEM) was done to examine the distribution of CNTs with in the CNT/Al composites. Microhardness was evaluated with Vickers hardness testing machine. To measure the microhardness, Vickers microindenter was used at load of 100 g. Each hardness value datum was the average of 3 samples.

3. Results and discussion

In this experimental study, Al is in the form of fine spherical powder with average particle size of 10 µm. CNTs are in the form of agglomeration and have the diameter 10–30 nm. Raw CNTs are highly tangled together and in the form of agglomerates. Impurities get attached with the walls and ends of CNTs during the production process. So, impurities are removed after functionalization and it improved the dispersion of CNTs in the matrix. This resulted in the better mechanical properties of composites.

3.1 CNTs functionalization analysis

The infrared spectrum of functionalized CNTs after acid treatment is shown in the Fig. 1. This curve indicates that few organic functional groups formed after the acid treatment on the surface of CNTs. In IR spectrum, there exist three valleys at wave number 3418, 1633 and 1110 cm⁻¹ representing stretching vibration of hydroxyl group (⁻OH), aldehydic group (⁻C=O) and C-O groups respectively. The coexistence of hydroxyl and aldehydic groups may yield the carboxyl group (⁻COOH). This confirms that functionalization of the CNTs is done successfully. These results are very similar to the previous work and in close agreement with the literature [14, 20].

3.2 Electroless CNT/Cu plating

A fabrication approach such as the molecular-level mixing is necessary for CNT/Al composites. Homogeneous dispersion and strong interfacial bonding of CNTs with metal can be achieved by electroless coating [21]. By chemical reaction between functional groups on the surface of CNTs with metal ions, strong interfacial bonding between CNTs and a metal is achieved.

For the evaluation of coating thickness, initially (1:9) by wt CNTs with Cu were treated in the plating solution. Cu particles are decorated and distributed on the surface of CNTs, as shown in the Fig. 2a. It

![Figure 1. FTIR spectrum of CNTs after functionalization](image)
is observed that thickness of Cu-coated CNTs is about 300-500 nm. The size of Cu nanoparticle is less than 100 nm and densely coated on the CNTs, similar results are reported by many research studies [22, 23]. In addition, open end tips of CNTs are found and surface of CNTs is completely embedded in the Cu particles, as shown in the inset of Fig. 2a. In electroless process, some massive crystallite growths are also perceived at isolated spaces on Cu-coated CNTs, which is in accordance to the previous results [24, 25].

Optimizing the plating bath to (1:1) by wt CNT with Cu, thickness of Cu-coated CNTs is reduced to around 100 nm, as shown in Fig. 2b. By comparing the both inset micrographs in fig 2, it can be seen that thickness of Cu coating on the CNTs is successfully reduced. The Cu nanoparticles of few nm are homogenously distributed on the surface of pretreated (Sensitized and activated) CNTs. By the combination of molecular level growth of Cu on the CNTs (Bottom up approach) and controlling the coating thickness to very small and uniform level, excellent quality of Cu-coated CNTs has been achieved [26].

**Figure 2.** SEM micrographs of (a) (1:9) by wt CNT with Cu coating, inset is showing that CNTs are completely embedded in the Cu nanoparticles and (b) (1:1) by wt CNTs with Cu coating, inset is showing Cu nanoparticles are the homogenously distributed on CNTs.
3.3 Densification
By mixing Al powder with Cu-coated and uncoated CNTs, a proper mechanical interaction between Al powder and CNTs can be achieved. As the CNTs content increased, more and more powder is covered with the CNTs, which is also suggested by previous research studies [16, 17]. The Cu-coated CNTs have provided sufficient wettability with the Al and hence a good bonding is achieved.

For the density measurement of Al and CNT/Al composites, Archimedes principle was used and distilled water as an immersion medium. The percentage relative densities of the samples prepared are shown in Fig. 3. The reference density of pure aluminum sample was close to intrinsic Al density (2.70 g/cm³). The composites were fully densified near to their theoretical density. Densification of composite samples increased with increasing wt% of CNTs.

3.4 Microstructure
In sintered composite samples, morphology of Al grains did not change much relative to that of the raw powders, as shown in the Fig. 4a. It is due to the equal pressure being applied around the compacts, which is beneficial for the plastic forming of the powders in order to achieve the full density. The grain boundaries are more visible after repeated etching.

In composite samples, CNTs are homogeneously dispersed at grain boundaries and within the Al particles, as shown in the Fig. 4b. Equiaxed grains are observed in all the composites. This occurs because particles growth is restrained by the pinning effect of the CNTs. Here it is significant to note that because of Cu-coated CNTs, more interfacial bonding with Al matrix is achieved. Hence, small grain size resulted in the Cu-coated CNT/Al composites compared to uncoated CNT/Al composites, where a little grain growth is occurred and relatively bigger grains are observed. Owing to poor wettability in uncoated CNTs, more Al powder are cold welded during ball milling and pinning effect of CNTs in Al particles, is less pronounced compared to Cu-coated CNT/Al composites.

4. Summary
Molecular level mixed Cu-coated CNTs showed uniform dispersion in the Al matrix. Optimizing the plating bath to (1:1) by wt CNT with Cu, thickness of Cu-coated CNTs has been reduced to 100 nm. Wettability of Cu-coated CNTs was increased in Al matrix. The densification increased with the increase in the CNTs content, which is more pronounced in Cu-coated CNT/Al composites due to higher affinity.
and strong interfacial bonding with Al matrix. Scanning electron microscope analysis revealed the homogenous dispersion of Cu-coated CNTs in nanocomposites samples compared to the uncoated CNTs. The densification increased with the increase in the CNTs content and is more pronounced in Cu-coated CNT nanocomposites.

5. Acknowledgments
The authors are thankful to GIK Institute for financial assistance and providing research facilities. They are sincerely thankful to Dr. A. Saeed Hakeem, Dr. Basit Yameen and Dr. Hamid Zaigham of the GIK Institute for their technical support and valuable suggestions.

6. References
[1] P.M. Ajayan, J.M. Tour, Materials science: nanotube composites, Nature 447 (2007) 1066-1068.
[2] P. Harris, Carbon nanotube composites, Int. Mater. Rev. 49 (2004) 31-43.
[3] T. Kuzumaki, K. Miyazawa, H. Ichinose, K. Ito, Processing of carbon nanotube reinforced aluminum composite, J. Mater. Res. 13 (1998) 2445-2449.
[4] R. George, K. Kashyap, R. Rahul, S. Yamdagni, Strengthening in carbon nanotube/aluminium (CNT/Al) composites, Scr. Mater. 53 (2005) 1159-1163.
[5] S.I. Cha, K.T. Kim, S.N. Arshad, C.B. Mo, S.H. Hong, Extraordinary Strengthening Effect of Carbon Nanotubes in Metal Matrix Nanocomposites Processed by Molecular Level Mixing, Adv. Mater. 17 (2005) 1377-1381.
[6] S.I. Cha, K.T. Kim, S.N. Arshad, C.B. Mo, K.H. Lee, S.H. Hong, Field Emission Behavior of a Carbon Nanotube Implanted Co Nanocomposite Fabricated from Pearl Necklace Structured Carbon Nanotube/Co Powders, Adv. Mater. 18 (2006) 553-558.

[7] C. Xu, B. Wei, R. Ma, J. Liang, X. Ma, D. Wu, Fabrication of aluminum-carbon nanotube composites and their electrical properties, Carbon 37 (1999) 855-858.

[8] T. Laha, S. Kuchibhatla, S. Seal, W. Li, A. Agarwal, Interfacial phenomena in thermally sprayed multiwalled carbon nanotube reinforced aluminum nanocomposite, Acta Mater. 55 (2007) 1059-1066.

[9] T. Laha, A. Agarwal, T. Mecknie, S. Seal, Synthesis and characterization of plasma spray formed carbon nanotube reinforced aluminum composite, Mater. Sci. Eng. A 381 (2004) 249-258.

[10] H. Kwon, M. Estili, K. Takagi, T. Miyazaki, A. Kawasaki, Combination of hot extrusion and spark plasma sintering for producing carbon nanotube reinforced aluminum matrix composites, Carbon 47 (2009) 570-577.

[11] H. Kwon, A. Kawasaki, Extrusion of Spark Plasma Sintered Aluminum-Carbon Nanotube Composites at Various Sintering Temperatures, J Nanosci Nanotechnol 9 (2009) 6542-6548.

[12] C. Deng, D. Wang, X. Zhang, A. Li, Processing and properties of carbon nanotubes reinforced aluminum composites, Mater. Sci. Eng. A 444 (2007) 138-145.

[13] C. Deng, X. Zhang, Y. Ma, D. Wang, Fabrication of aluminum matrix composite reinforced with carbon nanotubes, Rare Met 26 (2007) 450-455.

[14] C. Deng, P. Zhang, Y. Ma, X. Zhang, D. Wang, Dispersion of multiwalled carbon nanotubes in aluminum powders, Rare Met 28 (2009) 175-180.

[15] I. Sridhar, K.R. Narayanan, Processing and characterization of MWCNT reinforced aluminum matrix composites, J Mater Sci 44 (2009) 1750-1756.

[16] J.-z. Liao, M.-J. Tan, I. Sridhar, Spark plasma sintered multi-wall carbon nanotube reinforced aluminum matrix composites, Mater Des 31 (2010) S96-S100.

[17] J. Liao, M.-J. Tan, Mixing of carbon nanotubes (CNTs) and aluminum powder for powder metallurgy use, Powder Technol. 208 (2011) 42-48.

[18] J.Z. Liao, M.J. Tan, R.V. Ramanujan, S. Shukla, Carbon Nanotube Evolution in Aluminum Matrix during Composite Fabrication Process, Mater. Sci. Forum 690 (2011) 294-297.

[19] K. Morsi, A.M.K. Esawi, S. Lanka, A. Sayed, M. Taher, Spark plasma extrusion (SPE) of ball-milled aluminum and carbon nanotube reinforced aluminum composite powders, Compos. A 41 (2010) 322-326.

[20] C. Xu, G. Wu, Z. Liu, D. Wu, T.T. Meek, Q. Han, Preparation of copper nanoparticles on carbon nanotubes by electrophoresis plating method, Mater. Res. Bull. 39 (2004) 1499-1505.

[21] S.-H. Joo, S.C. Yoon, C.S. Lee, D.H. Nam, S.H. Hong, H.S. Kim, Microstructure and tensile behavior of Al and Al-matrix carbon nanotube composites prepared by high pressure torsion of the powders, J Mater Sci 45 (2010) 4652-4658.

[22] W.M. Daoush, Processing and characterization of CNT/Cu nanocomposites by powder technology, Powder Metall. Met. Ceram. 47 (2008) 531-537.

[23] J. Silvain, C. Vincent, J. Heintz, N. Chandra, Novel processing and characterization of Cu/CNF nanocomposite for high thermal conductivity applications, Compos. Sci. Technol. 69 (2009) 2474-2484.
[24] L. Ang, T.S.A. Hor, G. Xu, C. Tung, S. Zhao, J. Wang, Decoration of activated carbon nanotubes with copper and nickel, Carbon 38 (2000) 363-372.

[25] W.M. Daoush, B.K. Lim, C.B. Mo, D.H. Nam, S.H. Hong, Electrical and mechanical properties of carbon nanotube reinforced copper nanocomposites fabricated by electroless deposition process, Mater. Sci. Eng. A 513-514 (2009) 247-253.

[26] Y. Peng, Q. Chen, Ultrasonic-assisted fabrication of highly dispersed copper/multi-walled carbon nanotube nanowires, Colloids Surf. Physicochem. Eng. Aspects 342 (2009) 132-135.