Improvisation of mechanical and electrical properties of Cu by reinforcing MWCNT using modified electro-co-deposition process

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Abstract: Multi-walled Carbon nanotubes–copper (MWCNT/Cu) composite powders with variable MWCNT content were synthesized by modified electro-co-deposition method. The electro-co-deposited MWCNT/Cu powders were consolidated by conventional compaction and sintering process. The consolidated products were then hot rolled and cold drawn to fine wires. The MWCNT/Cu composite wire samples were characterized for electrical and mechanical properties. We have been able to achieve an increase of around 8% in electrical conductivity of the form wires repeatedly. It has been observed that there was gradual improvement in the properties with reinforcement of MWCNT in the copper matrix. The betterment of electrical property has been achieved with simultaneous improvement in mechanical properties of the wire. The yield strength of MWCNT/Cu composite wire was found to be four times and the tensile strength two times greater than that of pure copper. The improved properties are attributed to the proper distribution of MWCNTs in the copper matrix and excellent interfacial bonding between MWCNT and composite copper fabricated by the modified method.

1. Introduction:
For betterment of electrical and mechanical properties of polymer and ceramics, Carbon nanotubes (CNTs) have been accepted as an ideal reinforcing element.[1,2]. Several research groups have worked on CNT/polymer and CNT/ceramics composites [3–5] and shown that the reinforcement of CNT can considerably improve the strength, toughness and conductivities of polymers and ceramics. Few research groups are working on reinforcement of CNT in metal matrix [6–17] and synthesized composites which have shown improvement in mechanical properties in comparison to the parent metals. However, there are two main issues 1) the improvement in CNT/metal is not substantial compare to the CNT/polymer and CNT/ceramics composites. This is attributed to the severe agglomeration and non-uniform dispersion of CNTs in the metal matrix. 2) Most of the methods are at laboratory level, costlier and may cause damage to MWCNT during processing. In our previous work [18], we have attempted to answer these two issues and developed a modified electro-co-deposition method, which shows remarkable potential for scaled up production of homogeneously dispersed MWCNT/Cu composite powder.

Using the modified method, we formed MWCNT/Cu composite powder, pelletized the form powder and further fabricated cold drawn wires of the composite. We observed an increase of around 8-10% in electrical conductivity, four times increase in yield strength and two times increase in tensile strength of the formed composite wire in comparison to wires drawn from pure copper. Paper present results on the
microstructure, morphology of the MWCNT/Cu composite powder and electrical and mechanical properties of the form wire fabricated from the powder.

2. Experiment:

2.1 Preparation of Carbon nanotube-copper composite powder:
A detailed experimental process for production of MWCNT/Cu composite powder by modified electro-co-deposition has been described elsewhere [19].
Six ampere DC current was supplied to the electrodes and co-deposition of copper particles and the MWCNTs took place at the tip of the cathode. The cathode was tapped several times during the electro-co-deposition process in order to remove the reduced MWCNTs reinforced copper powder from the tip of the cathode. The process continued until the dark blue solution became colorless which means all the copper and MWCNT were co-deposited. The powder was then removed, rinsed, dried in a vacuum and stored in nitrogen filled airtight vials to avoid the oxidation of the powder.

2.2 Compaction of Carbon nanotube-copper composite powder:
Conventional compaction and the sintering were adapted in this study to fabricate carbon nanotube reinforced copper composites. The compaction of composite powder was performed in a die by uniaxial pressurization of 825 MPa. Disc-shaped specimens with a diameter of 12.7 mm and the thickness of 2 mm were fabricated. The disc shape samples were sintered in an inert atmosphere furnace. The furnace temperature was ramped to 950 °C with a ramp rate of 20 °C/min in 50 min and kept constant for 55 min. Subsequently, the samples were cooled down to room temperature in around 180 min in the furnace itself. Sintered samples were then ground using 1000 and 2400 grade SiC papers by Struers labopol-5 grinding, and polishing machines. In addition to grinding the samples were polished for hardness testing using diamond paste of 3 μm particle sizes.
A home built setup was used to hot roll these samples to the diameter of 2mm. The rod of 2mm diameter was then cold drawn through a series of tungsten carbide dies to 0.724mm wire (AWG #21). Microstructural characterization of composite powder was carried out using scanning electron microscopy (SEM, JEOL JSM - 6390 LV with EDAX), scanning electron microscopy (HITACHI S 4800 SEM), high-resolution transmission electron microscopy (Model JEOL JEM 2000 fx-II) and transmission electron microscopy (Philips CM200) operation voltage of 200 kV.
Dog bone shape tensile test samples of form copper wire with a gage length of 10 mm were tested using BISS UNO 100 universal testing machine at room temperature with a crosshead speed of 0.5 mm/min. An optical microscope (Gippon INC METAPLAN-IN) was used to observe the fracture surfaces of the composite wire and the morphology of the MWCNT/Cu composites.

3. Results and discussion:

3.1 Raw materials and microstructure:
Adsorption of copper on the cathode starts with reduction of the copper ion and which, behaves as a adatom on the cathode surface [20]. It further grows by reduction of more copper ions on the cathode and forms a cluster, which, at the end, leads to dendritic structure[21]. The powder formed by the electro-deposition route, shown in Fig. 1(a), depicts the similar dendritic morphology [22].

HRTEM micrograph of as received MWCNTs is shown in Fig. 1(b), which are highly entangled and also forms small clusters at some sites. Purified MWCNTs are used for the fabrication of MWCNT/Cu composite, which helps in improved property of the composite. The most important feature of the modified electro-co-deposition process is mixing MWCNTs with Cu ions. Not only co-deposition but nucleation and growth of Cu particles on MWCNT surface is observed during the process[19]. The defect sites on MWCNTs are potential nucleation sites and better uniformity in distribution of such defect sites is
responsible for more uniform dispersion of copper. We attribute an optimal ultra-sonication for uniform
distribution of defects on MWCNTs.

Figure 1. (a) FESEM micrograph for the electro-co-deposited copper powder having dendritic
morphology, (b) HRTEM micrograph for the as received MWNTs, (c) HRTEM micrograph for electro-co-
deposited CNT/Cu composite powder showing bridging and properly reinforced MWCNT, (d) HRTEM
micrograph of MWCNTs and the coated copper particles on the surface of MWCNT. (e) FESEM
micrograph of electro-co-deposited Cu/CNT composite powder showing pulled out MWCNT, (f) FESEM
micrograph of Cu/CNT composite powder showing uniform dispersion of MWNT.
Fig. 1 (c) shows the FESEM image of the MWCNT coated with Cu particles. The diameters of copper particles were in range of 100-120 nm. During co-deposition of the Cu and MWCNT, Cu ions were electrodeposited at the tip of the cathode and on the surface of the MWCNT. According to the crystal growth mechanism [20] of metal deposited by the electrochemical process, the spherical or hemispherical structure of the copper crystal on the surface is the stage before formation of dendrite. It implies that the copper ions reduced at some active sites on the surface of the MWCNT during co-deposition of MWCNT and Cu. As the deposition continues, Cu particle forms dendritic structure and grows on MWCNT surface resulting in reinforcement of MWCNT in the copper matrix as shown in Fig. 1 (d). It is observed from Fig. 1 (c) that the copper did not deposit absolutely over whole of the surface of MWCNT, but the nucleation and deposition took place selectively at some sites like, end of the MWCNT and on the outer surface. From Fig. 1(b), it is clear that the ends of the MWCNT are open which itself is a defect and hence the site becomes more active. Therefore, Cu\(^{2+}\) ions reduce easily by accepting electrons form the dangling bond at the end of the MWCNT and deposits there. Similarly, defects on the surface created by ultra-sonication are other potential sites for copper reduction. It is also well known that defects such as pentagons, heptagons, vacancies, dopant or catalyst particles trapped during chemical vapor deposition process, are found to modify the electronic properties of the nano-systems [23–25]. These defect sites on the outer surface are having more broken bonds and hence these sites becomes more active than other sites on the outer surface of MWNTs[26]. From Fig. 1 it is observed that the Cu particles and MWNTs were intact, after rigorous ultra-sonication treatment and this shows that there is very good bonding between Cu particles and MWCNT. Some MWNTs, which are pulled out of the Cu matrix as shown by arrow in Fig. 1 (e) have some unique protrusion shape like triangular pyramid. This triangular pyramid shape is all due to coating of copper on the surface of MWCNT, which shows good bonding between MWCNT and Cu matrix. Hence, it confirms the proper bonding between Cu and MWNTs. FESEM micrograph shown in Fig. 1(f) of MWNT/Cu composite powder shows uniform dispersion of MWNTs. Firm bonding between MWNTs and Cu matrix and uniform dispersion of MWNTs in the copper matrix assure better electrical and mechanical properties.

3.2 Effect of MWNT concentration on Electrical resistivity
The electrical resistance measurement of the MWNT/Cu wire (diameter 0.724 (AWG # 21) and length as 120 mm) was performed using Agilent 4284A precision LCR meter and Agilent 16047A test fixture. An auto balancing bridge method was used for the measurement of resistance. Three specimens for each composite sample were tested, and the final electrical resistance value was obtained by averaging the three values. Resistivity was calculated by using diameter and the length of the specimen. Fig. 2 shows that at the room temperature, electrical resistivity of the MWNT/Cu composites decreases with increase in concentration of MWNT in the electrolyte.
Nevertheless, the performance of carbon nanotube reinforced composites depends on the interface between carbon nanotube and the copper matrix. The carbon nanotube wets poorly with metal matrix, and therefore the interface between the carbon nanotubes and the copper powders is weak. However, an adequate surface treatment of carbon nanotube minimizes the contact resistance. A rough surface on the MWCNT surface helps in better mechanical bonding between the MWCNT and copper matrix. In the present method, appropriate ultra-sonication time aids in detangling the MWCNT as well as create suitable active sites for reduction of copper ions on the surface of MWCNT. This helps in good bonding between MWCNT and copper, foster reduction in interfacial electrical resistance. This approach offers an advantage of metallization of MWCNT. Metallization of MWCNT decreases the interface resistance and hence plummet the contact resistance between MWCNT and copper matrix. Secondly, the MWCNT are all metallic in nature as the band gap decreases with the diameter of the CNT [27]. Hence, the metallic nature of the MWCNT helps in decreasing the electrical resistivity of MWCNT/Cu composite. The majority of the metallized MWCNTs occupies the grain boundaries and forms a network for electrical pathway across the grain boundary thereby decreases the resistivity of MWCNT/Cu composite. From Fig. 2, it is clear that the decrease in resistivity with 125 mg/l MWCNT concentration in the electrolyte is almost same as that of 100 mg/l concentration. For 125 mg/l MWCNT concentration, similar results have been observed for yield strength and tensile strength and hence, that is the saturation point for reinforcement of MWCNT in the copper matrix of this method.

3.3 Effect of MWCNT concentration on the tensile properties of the composite Wire

All the samples were subjected to the tensile testing. It was observed that the failure of all the samples was ductile. The Fig.3 shows the neck formation of the sample (100 mg/L, concentration of MWCNT in electrolyte) during tensile testing, which was a sign of ductile failure. The samples failed with the cup-cone geometry as seen in optical microscope image in Fig.4, in which the outer region failed due to shear whereas the inner region failed due to a tensile force. Fig. 4 (a) and (b) shows the cone and cup formed after the failure of pure copper wire. Both, the cup and cone are almost smooth and no corrugation was observed. Nevertheless, corrugation was observed on the cone and cup formed after failure of
MWCNT/Cu composite as seen in Fig. 4 (c) and (d). The cone end looks corrugated (shown by a black line), which is due to the presence of MWCNTs in the composite.

**Figure 3.** Neck formation of MWCNT/ Cu composite wire during tensile testing. The concentration of MWCNT in the electrolyte is 100mg/L of electrolyte.

**Figure 4.** Optical image of Cone and Cup after tensile failure of the sample. (a)(b) cone and cup after failure of pure copper sample respectively (both ends are almost smooth) (c) cone after failure of sample having 100mg/L concentration of MWCNT in electrolyte (d) Cup after failure of sample having 100mg/L concentration of MWCNT in electrolyte (Highlighted corrugated structure at the cup side all due to presence of MWCNT)
The stress–strain curves as shown in Fig. 5 were obtained from the tensile test of the MWCNT/Cu composites wire as well as the pure copper wire synthesized using modified electro-co-deposition method. The yield strength and ultimate tensile strength were calculated from the stress–strain curves. Fig. 6 reveals that the yield strength increases as the MWCNT concentration in the electrolyte increases. The pure copper wire shows yield strength (0.2% offset strain) of 54 MPa and an ultimate tensile strength of 131 MPa. From Fig. 6, the MWCNT/Cu composite produces yield strength of 228 MPa (for 100mg of MWCNT/L of electrolyte), which is about four times greater than that of pure copper. Moreover, as seen from Fig. 8, the ultimate tensile strength of the MWCNT/Cu composite is about 306 MPa (for 100mg/L of electrolyte), which is more than two times greater than that of pure copper.

The improvement in the yield strength and ultimate tensile strength is attributed to the homogeneous dispersion of MWCNT in the copper matrix at micro-level and strong interfacial bonding, which improves the interfacial load-transfer ability. The increased strength is a sign of successful fabrication of MWCNT/Cu composite by electro-co-deposition process. However, the ultimate tensile strength of 125 mg/L concentration sample is less than the 100 mg/L concentration sample. This is due to the agglomeration of MWCNT on the grain boundaries.

4. Conclusion:
MWCNT/Cu composites wires have been fabricated by modified electro-co-deposition method. The formed wire has better electrical and mechanical properties in comparison to pure copper wire formed by the modified method and also in comparison to commercially available standard copper wire. The results of betterment of properties of form copper wire is attributed to homogeneous dispersion of MWCNTs in the Cu matrix. The electrical resistivity of the MWCNT/Cu composite decreased with addition of MWCNTs by almost 8-10%. The increase in electrical property of form wire has been achieved with a very low vol% MWCNTs (100mg/Lt.).

Moreover, the improvement in electrical properties is seen with a concurrent improvement in mechanical properties of the form wire. The wire produced from MWCNT/Cu composite powder shows four times
yield strength (0.2% offset strain) than the pure copper fabricated by the same method. Moreover, the ultimate tensile strength of the MWCNT/Cu composite is about 306 MPa (for 100mg/L concentration), which is more than two times greater than that of pure copper. The hardness of MWCNT/Cu composite also shows improvement in comparison to that of the pure copper.

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