

Carbon nanotubes reinforced copper composite with uniform CNT distribution and high yield of fabrication

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Dispersion of carbon nanotubes (CNTs) in metal matrix composites has been an unsolved issue since the discovery of CNTs. This paper presents a newly developed fabrication process of bulk Cu/CNT composite with uniformly distributed CNTs. That is, copper encapsulated CNTs powders were firstly fabricated by an electrochemical deposition where CNTs can be completely dispersed in the copper electrolyte assisted by sonication, and then the fabricated composite powders were used to make bulk Cu/CNT composite by a powder metallurgy process. The increment in microhardness of Cu/CNT composite after compaction and sintering was observed to be ~47.6% per 1% CNTs. The developed fabrication process of Cu/CNT composite powders by electrochemical co-deposition can be scaled up to meet specific application needs, and a similar process is expected to be applicable for other metals.

1. Introduction: Nanotechnology pioneer Prof. Richard Smalley has pointed out that carbon nanotubes (CNTs) can significantly increase the properties of metals such as the mechanical and physical properties if the lighter CNTs can be added into metals with desired uniform distribution, since CNTs' excellent mechanical and physical properties, such as exceptional stiffness and strength, high electrical and thermal conductivities [1–6].

Since then the research and development on metallic composites by adding CNTs into metals with different methods have been carried out, under the motivation to make metallic composite with high strength, high thermal conduction together with low coefficient of thermal expansion, high electrical current carrying density, and potential of high electrical conductivity [1–5, 7–14]. If this is successful, there will be many broad promising applications in automobile, aerospace, and electronic packaging [3]. So far various composite processing techniques have been tried for incorporating CNTs into metal matrices, for example ball milling and powder metallurgy, molecular mixing in which CNTs are mixed with metallic salts plus drying and reduction, and electroless- and electro-deposition for film fabrications [3–5, 7–15]. Ball milling process, although it can make bulk composites, has been proven to be ineffective to disperse CNTs uniformly mainly due to the strong inter tube forces in nanoscale. Moreover, extensive milling would damage CNTs [3, 7]. To improve CNTs' separation and dispersion, Cha *et al.* [8] have developed a technique named molecular-level mixing process. Samples after drying/sintering plus reduction of metal from the metal oxide have shown to be effective in increasing the mechanical strength, mainly due to the good CNTs dispersion and the good interfacial bonding strength between the CNTs and metal matrix. However, the process may have difficulties for fabricating bulk materials with high yield due to its intrinsic complexity (i.e., it includes four steps to fabricate Cu/CNT composite powders) as well as space- and time-consuming characteristics.

Electro-deposition has been used widely to fabricate CNTs reinforced metal matrix composite films with a good dispersion of CNTs as well as a good interfacial bonding between metal matrix and CNTs [3, 9, 11–14]. However, pure electro-deposition has difficulties in forming bulk materials, since the yield of deposition is dependent on the current density and time, while large current density plus lengthy time of deposition promotes the tendency of forming voids/cavities in the composites. On the other hand, it is well known that, by varying electro-deposition parameters such

as current density, electrolyte concentrations, and bath temperature, metallic materials in the form of powders can be fabricated via a similar electro-deposition process [16, 17]. However, publications on utilising electro-deposition to fabricate large quantity of metal/CNT powders and then forming the bulk material with increased material properties are still lacking. Therefore, this work seeks to develop an efficient electrochemical co-deposition process to fabricate metal/CNT composite powders followed by a powder metallurgy process to fabricate bulk metal/CNT composite. Since we have demonstrated that uniformly dispersed CNTs can be obtained in the electrolyte prior to electrochemical co-deposition and then CNTs can be co-deposited together with metals to form uniform metal/CNT composite films, this work will make a further step to explore the electrochemical co-deposition process to co-deposit metal/CNT powders as well as to investigate suitability of the powder metallurgy process to fabricate bulk metal/CNT composite.

2. Experimental

2.1. Fabrication of Cu/CNT nanocomposite powders: An electrochemical co-deposition setup as denoted in Fig. 1, similar to previous work for fabrication of Ni/CNT and Cu/CNT nanocomposite films [9, 11–14], was used as the starting point of this work to fabricate Cu/CNT nanocomposite powders. To deposit metallic powders, when compared with deposit films, necessary changes have to be made. Firstly, the electrolyte concentration should be much thinner. Secondly, the deposition current density has to be much larger. For electro-deposition of metal/CNT composite powders, many parameters may affect the final product such as electrolyte concentrations, temperature, power supply (direct or pulse current), surfactant additives, CNT content, and current density. Thus, an appropriate range of the deposition current density varies with the other parameters such as these listed above. For this work, a sulphate bath containing 90 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 20 ml/l 98% H_2SO_4 for electrochemical deposition of copper powders was used together with a power supply. Direct current, with a density of 300 mA/cm², was used in this work. pH of the electrolyte was 0.5–1 and the bath temperature was around 12°C. Approximately 100 mg/L of MWCNTs with functionalisation groups of –COOH (OD < 8 nm, length 0.5–2 µm, and purity of >95%, purchased from Cheaptubes), pretreated by 15 vol.% HNO_3 , was added into the deposition bath assisted by sonication for the dispersion purpose. Pure Cu foil (>99.9 wt.%) with dimensions of 20 × 20 × 0.254 mm

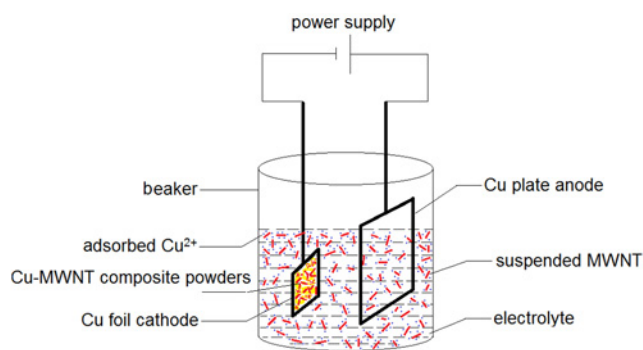


Fig. 1 Schematic of co-electrodeposition of Cu/CNT nanocomposite powders

was used as the cathode. An oxygen-free high conductivity pure Cu plate with dimensions of $60 \times 50 \times 3.18$ mm was used as the anode. To obtain a desired dispersion of CNTs in the electrolyte, the electrolytic bath was ultrasonically agitated for 2 h prior to the electrochemical co-deposition. Due to tendency of agglomeration of CNTs over time, a 10 min of deposition, followed by another time of sonication, was applied. For comparison purpose, pure copper powders were also fabricated with the same electrolyte and the same deposition process but without adding CNTs. The as-deposited powders were collected and washed with DI water and then acetone, respectively, for five times. The fabricated powders were dried at 40°C under a purge gas of regular purity Ar ($>99.9\%$). To minimise oxidation effect from previous fabrication processes, the fabricated powders were reduced by a mixture gas of 15 vol.% H_2 and 85 vol.% Ar (ultrahigh purity, $>99.999\%$) at 300°C . Subsequently, the powders of Cu/CNT and pure copper were used for fabrication of bulk materials with a powder metallurgy process.

2.2. Fabrication of bulk Cu and Cu/CNT nanocomposite: Fabrication of bulk Cu and Cu/CNT composite was carried out by compaction of metallic powders and a subsequent sintering process. Powders for fabrication of each sample were ~ 5 g. The compaction was conducted on a 12 ton manual hydraulic press. A die with the cross-sectional area of 71×8 mm was used, while the thickness was controlled by the amount of powders and the pressure used for the compaction. Although various pressures were tried but a typical pressure used for compaction was 140 MPa with a holding time of 3 min. After compaction, samples were separated from the die and sintered in a horizontal quartz tube furnace. The furnace was pumped down first, and then filled with the ultrahigh purity Ar to purge. The pumping down and filling and the purging processes repeated three times before the heating process was performed. The furnace was heated up to 850°C with a ramping rate of $5^\circ\text{C}/\text{min}$. The furnace was held at this temperature for 4 h for sintering. The samples were cooled down together with the furnace to room temperature. A fluxing of a mixture gas of ultrahigh purity Ar (85 vol.%) and H_2 (15 vol.%) was used during the whole sintering process.

2.3. Characterisation on powders and bulk material: Morphologies and chemical composition of the composite in the form of powders and the bulk materials were investigated. The morphologies of powders and bulk materials were characterised by ZEISS ULTRA 22 SEM (SEM/EDAX). Regarding the composition, EDAX associated with the SEM machine was used to determine quantitatively. However, considering an inaccuracy on detecting light elements like carbon in using EDAX, the CNTs content in the nanocomposite was also determined by a direct weighing method. In doing so, certain weighed Cu/CNT composite powders were dissolved in nitric acid solution. The CNTs in the

nitric acid solution was then centrifuged, washed, dried, and weighed. The content of CNTs in the composite was confirmed to be 0.42 wt.%.

Microhardness test was also performed on bulk material with a Qualitest QV-1000 Series Microhardness Tester. A loading of 50 gf together with a holding time of 10 s were used during the testing. At least ten different positions on each sample were carried out, and the average of these values was reported here.

3. Results and discussion: Fig. 2 shows the morphologies under SEM of as-deposited pure Cu and Cu/CNT powders. The particle size of pure Cu powders was $\sim 1 \mu\text{m}$ (Fig. 2a). With the addition of CNTs, the particle size decreased slightly to $0.6 \mu\text{m}$ (Fig. 2b). This is attributed to the addition of CNTs which acted as the nucleation sites to promote the nucleation, and at the same time to prevent the crystal growth of copper [18].

As more Cu deposited on CNTs, the continuous growth of Cu joined them together to form a cluster (i.e. the composite powders). The powder particle of Cu with embedded CNTs can be observed from SEM characterisation with a higher magnification (Fig. 2c). It shows that the embedded CNTs are uniformly distributed. The rate of deposition is found to be current dependent, i.e. the higher the current density, the greater the deposition rate. For current densities of 300 and $90 \text{ mA}/\text{cm}^2$, the deposition rates are 5.3 and $1.5 \text{ mg}/\text{cm}^2/\text{min}$, respectively, according to our

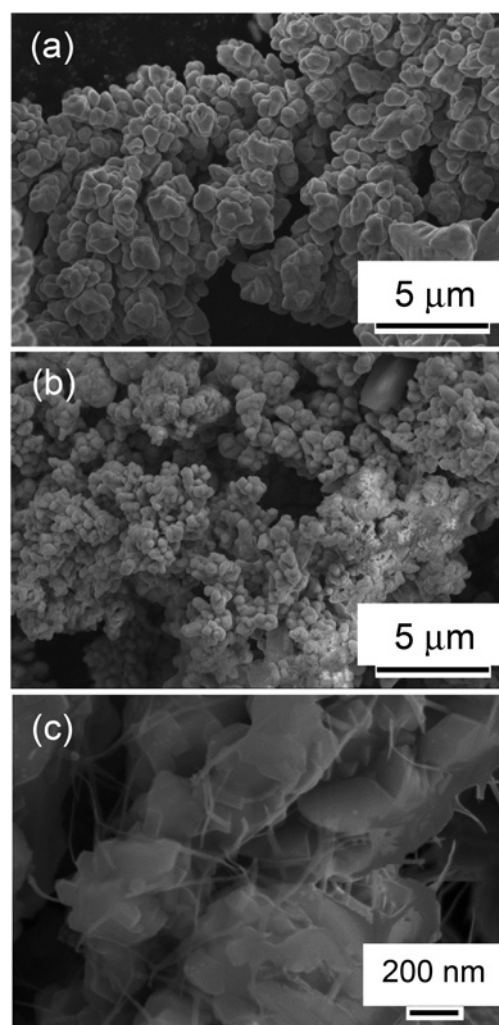


Fig. 2 SEM micrographs of electrodeposited Cu powders
a Without CNTs
b With CNTs
c A higher magnification image of b

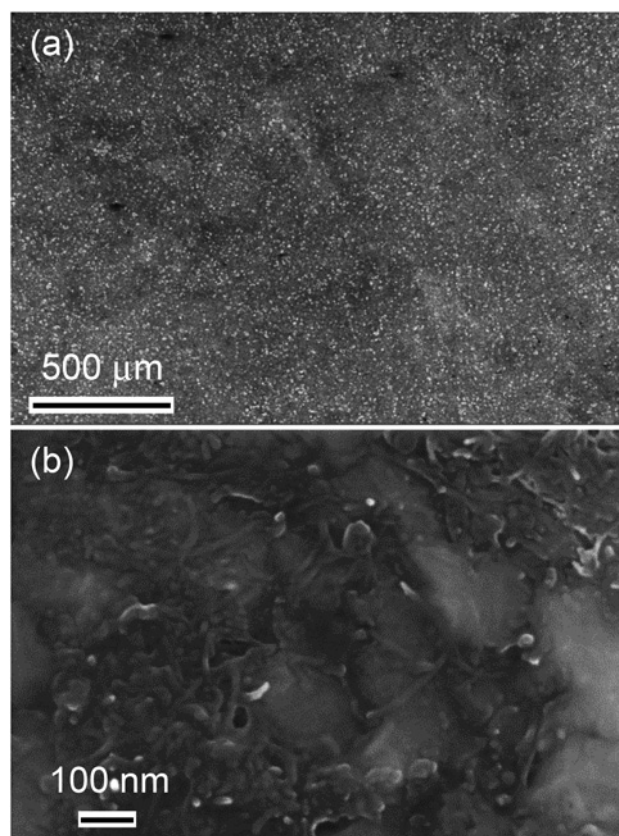


Fig. 3 Example of SEM micrographs with
 a low
 b high magnifications of as-fabricated Cu/CNT nanocomposite

experimental results. Also, the current efficiencies are calculated to be ~90 and 85% for the current densities of 300 and 90 mA/cm², respectively. Therefore, a large yield of deposition of Cu/CNT composite powders can be scaled up with the size of electrode and the number of deposition cells.

The CNTs distribution and morphology in bulk Cu/CNT composite after compaction and sintering are shown in Fig. 3. It shows that the CNTs distribution in the Cu/CNT bulk composite is similar to that in the powders, with CNTs dispersed homogeneously (Fig. 3b). This suggested that after compaction and sintering CNTs retained the distribution from Cu/CNT powders. Thus, Cu/CNT bulk composite with well-dispersed CNTs in copper has been fabricated by this novel two-step process from premade Cu/CNT powders with electrochemical co-deposition.

Microhardness measurements were carried out on both bulk copper and bulk Cu/CNT composite, respectively. The microhardness of Cu without CNTs was 500.6 ± 37.2 MPa. For Cu/CNT composite, the microhardness was 600.8 ± 63.8 MPa. These results suggest that by adding 0.42% CNT into copper (~100 mg/L CNTs loaded in the electrolyte), the hardness has been increased by ~20% for the Cu/CNT composite. This implies that the efficiency of adding CNTs into copper is ~47.6% increment in hardness for 1% addition of CNTs as per a linear relationship observed from our previous work (up to 300 mg/L CNTs loaded in the electrolyte) [11, 12, 14]. The high efficiency is attributed to the well-dispersed CNTs in the fabricated Cu/CNT powders obtained from ultrasonic assisted dispersion of CNTs in the electrolyte used for electrochemical co-deposition. The good dispersion plus good intimate bonding between CNTs and the matrix copper (Fig. 3b) are important for the resultant properties, as observed previously by SEM and FBI/TEM as well as other mechanical tests [8, 11, 12, 14].

It is well known that, during electro-deposition, the concentration of Cu²⁺ nearby the substrate surface will be consumed and relatively lower than that in the bulk solution. When increasing deposition time, the concentration difference between the substrate surface and bulk solution may be enlarged, which promotes the tendency of forming voids/cavities as well as slightly decrease the grain/particle size. However, the effect on the final product of Cu/CNT composite will be minimised after a balance being achieved due to ion transportation under electrical field in the deposition system as well as by the later powder metallurgy process.

The relatively simple two steps of fabrication of Cu/CNT composite by electrochemical co-deposition of Cu/CNT powders followed by a powder metallurgy process can be developed further for fabrication of other types of metals in the form of metal/CNT composites. Other metals included but not limited to are nickel, silver, gold, chromium, zinc, tin etc. When compared with other fabrication methods, the two-step method reported here has advantages to obtain uniformly distributed CNTs in metal matrix together with good intimate interfacial bonding between CNTs and the metallic matrix due to the electrostatic force formed during electrochemical deposition under electrical field. The content of CNTs can be controlled by adjusting electro-deposition parameters such as electrolyte concentrations, temperature, power supply (direct or pulse current), surfactant additives, CNTs content, CNTs pretreatment/functionalisation, and current density. If controlling the content of CNTs in the Cu/CNTs composite powders by increasing the amount of MWCNTs, there is a critical amount and above which the uniformity of the CNTs in the powders deteriorates. One of our future research targets is to find the critical amount since it is a very important parameter for fabrication of Cu/CNT composite.

4. Conclusions: Cu/CNT composite has been successfully fabricated via a two-step process in which uniformly distributed CNTs in copper was firstly obtained by electrochemical co-deposition and a powder metallurgy process was then used to complete the fabrication. Results on microhardness show that an increment of 20% was observed in Cu/CNT composite with the addition of 0.42 wt.% CNTs over pure copper made with the same process. This implies that a 47.6% increase in hardness of Cu/CNT composite with 1% CNTs can be achieved over pure copper. The fabrication of Cu/CNT powders by electrochemical co-deposition ensures uniformly distributed CNTs plus strong interfacial bonding between CNTs and Cu due to electrostatic force applied during the electrochemical deposition process. The yield of Cu/CNT powders is high (e.g. 5.3 mg/cm²/min with a current density of 300 mA/cm²), which means the fabrication of Cu/CNT composite powders can be customer designed to meet the needs of powder output. This two-step process of fabrication of Cu/CNT composite can be developed further for other metallic composites with CNTs where metals can be fabricated similarly to copper by electrochemical deposition.

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6 References

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