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# Effects of carbon nanotube reinforcement and grain size refinement mechanical properties and wear behaviors of carbon nanotube/copper composites

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ABSTRACT

Carbon nanotube reinforced copper alloy (CNT/Cu) composites with high strength and good wear resistance have been developed using acid treatment, sintering processes and consolidation techniques. The effects of CNT reinforcement and grain size refinement on the mechanical properties and surface deformations of CNT/Cu composite coatings are investigated by means of nanoindentation and block-on-ring wear tests, respectively. High-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses reveal that the CNTs are firmly implanted in the Cu alloy due to the formation of Cu-oxides at the CNT-Cu interface. The effect of CNT addition on the CNT/Cu coating strength is significantly greater than that of grain size reinforcement. Finally, the present results indicate that the addition of CNTs to the Cu matrix reduces the surface deformations of the CNT/Cu composite coatings due to the formation of a carbonaceous solid-lubricant film at the contact interface during sliding.

## 1. Introduction

The discovery of carbon nanotubes (CNTs) by Iijima in 1991 revolutionized the materials science field [1]. CNTs have many outstanding properties, including a high mechanical strength [2–5], good chemical stability [6,7], and excellent electrical conductivity [8–10]. As a result, they provide an ideal candidate for the efficient reinforcement of multi-functional composite materials with optimal properties and a superior performance. Copper (Cu) based metallic composites are widely used in electrical applications and for package materials due to their superior electrical and thermal characteristics [11–13]. However, poor strength and stiffness of such materials limit the proliferation of the metal into other fields. Several recent studies have uncovered that the mechanical and tribological properties of matrix materials can be improved through the addition of CNTs [14–20]. Thereby, the mechanical properties of CNT reinforced Cu (CNT/Cu) composites are important because potential applications depend on their stability and stiffness.

Lim et al. [14] investigated the effects of CNT reinforcement on the mechanical and tribological properties of Cu matrix nanocomposites by means of ball-on-disc sliding tests. The results showed that the strengthening effect of the CNTs could be enhanced by coating the nanotubes with nickel (Ni). Moreover, the addition of CNTs or Ni-coated CNTs both improved the tribological performance compared to that of a non-reinforced Cu specimen. Kim et al. [15] characterized the hardness and wear resistance of CNT/Cu nanocomposites using pin-on-disc wear tests and showed that the wear loss of the CNT/Cu nanocomposites was around 35% lower than that of a pure Cu specimen. Sun et al. [16] showed that the tensile strength of CNT/Cu composites improves with a reducing CNT diameter due to a corresponding increase in the total interfacial bonding area between the CNTs and the Cu matrix. Rajkumar et al. [17] showed that the addition of CNT reinforcements reduced the wear rate of pure Cu specimens in pin-on-disc wear tests due to the formation of a carbonaceous film at the contact surface, which reduced the frictional heating effect and lowered the friction coefficient as a result.

Most of researches have suggested that the strength of metal composites can be improved not only through CNT addition, but also through an annealing-induced grain refinement effect [18–20]. Meanwhile, the specific fabrication related to molecular-level mixing process has been applied to achieve the improvement in interfacial bonding strengths between the CNTs and the surrounding metal matrix [21–23]. However, the published literature provides scant information regarding the full range of strengthening mechanisms in CNT/Cu composites. Specifically, no previous studies have identified the detailed relationship between the grain size effect and the CNT reinforcement

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effect on the improved mechanical and tribological response of CNT/Cu composites. Therefore, the present study synthesizes CNT-reinforced Cu matrix composites using a powder metallurgy technique including molecular-level mixing and sintering process and then investigates their mechanical and tribological properties using nanoindentation tests and block-on-ring wear tests, respectively. The morphologies of the CNT/Cu composites and the interfacial structures between the nanotubes and the Cu matrix are also examined using high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. Finally, the possible explanations and identifications for the effects of CNT reinforcement and grain size refinement on determining the properties of such CNT/Cu composites are discussed.

## 2. Experimental

### 2.1. Fabrication of CNT/Cu composites

Well-structured multi-walled CNTs (MWCNTs) with an average diameter of 18 nm and lengths of 1.6–2.2 μm were fabricated using a micro-wave plasma chemical vapor deposition (MPCVD) method [24–26] (see Fig. 1). The CNTs were agitated ultrasonically in isopropylalcohol (IPA) for 20 min and the resulting solution was then evaporated to obtain individually dispersed CNTs. The CNTs were functionalized with carboxyl and hydroxyl groups via immersion in a solution of $H_2SO_4/HNO_3$ (3:1 ratio) in order to produce active sites for subsequent reaction with the Cu ions [27]. Moreover, these functionalized CNTs were treated with 250 ml of oleylamine (Aldrich, Tech-Grade 70%) in a reaction chamber at room temperature for 3 h. 3 g of copper(II) acetate monohydrate [Cu(ac) $H_2O$, Aldrich] were added to the mixture, which was then sealed and purged in an argon-protected environment for 2 h. The mixture was heated to approximately 520 K at a uniform heating rate of 10 K/min and was maintained at this temperature for 20 min. A heterogeneous nucleation of the Cu-oxides was then induced on the CNT surface by means of slow cooling to room temperature. The resultant CNT/Cu-oxide powders were transformed to chemically-stable CNT/$Cu_2O$ via a calcination process at 573 K in air for 2 h followed by a reduction process under a hydrogen atmosphere. Notably, the calcination and reduction processes improve the CNT/Cu bonding strength through the production of interfacial oxygen atoms [15,28–30]. Finally, the CNT/Cu powders with 0.3, 0.5 and 1.0 weight percent (wt%) were isostatically consolidated at 350 MPa for 5 min and then isothermally sintered in a vacuum for 2 h at 1123 K (See my final comments in this paragraph) to produce the CNT/Cu composite [31], in which wt% is defined as the mass of CNTs divided by the total mass of the CNT/Cu composite times 100 (i.e.,$\mathrm{wt\%}_{(\mathrm{CNT})} = \left(\frac{\mathrm{mass}_{(\mathrm{CNT})}}{\mathrm{total\ mass}_{(\mathrm{CNT/Cu\ composite})}}\right) \times 100$).

In practice, the grain size distribution of the CNT/Cu composites can be controlled by adjusting the sintering conditions, i.e., temperature, pressure and annealing time [32–35].

### 2.2. Mechanical characterization of CNT/Cu composites

The mechanical properties of pure Cu samples with various grain sizes and CNT/Cu composite samples with various levels of CNT addition (0.3–1.0 wt%) were investigated by means of nanoindentation tests performed at room temperature (295 K) using a Hysitron nanoindenter (Hysitron Inc.) fitted with a diamond Berkovich pyramid tip and interfaced with a Veeco Dimension 3100 atomic force microscope (AFM, Veeco Metrology Group). For each specimen, the load-displacement data were recorded continuously as the tip was driven into the composite material and then smoothly removed. The resultant load-displacement (*L-D*) curves were then used to estimate the critical strength and hardness of each sample [36]. The nanoindentation hardness of each sample was obtained from the *L-D* curves in accordance with

$$H = \frac{P_{\max}}{A_c} \tag{1}$$

where $P_{\max}$ is the maximum load imposed on the surface of the specimen and $A_c$ is the projected area [32]. For a Berkovich pyramid tip, the projected contact area is a function of the contact depth and can be calculated directly from the displacement measurements obtained during the nanoindentation test [37,38].

The tribological properties of the pure Cu and CNT/Cu samples were investigated using block-on-ring wear tests performed under dry conditions against SKD11 steel workpieces with a hardness ranging from 32 to 35 HRC. In performing the tests, all of samples and workpieces were adhered in turn to blocks. Moreover, the ring hardness ranged from 63 to 65 HRC (nitride treatment), while the average surface roughness (Ra) was equal to 3.68 μm. The tests were performed at loads ranging from 10 to 50 N with a constant sliding speed and total sliding distance of 1.65 m/s and 5940 m, respectively. The sample block was weighed before and after each wear test in order to determine the mass loss. The mass loss was then converted to a corresponding volumetric wear rate value. The morphologies of the contact surfaces following the wear test were observed using SEM.

## 3. Results and discussions

Fig. 2(a) and (b) present an SEM image and corresponding EDS analysis of the Cu-CNT powder. As shown in Fig. 2(a), the CNTs are uniformly coated with Cu and have a diameter of approximately 50–70 nm. The strong oxygen peak in Fig. 2(b) confirms not only the occurrence of CNT oxidation, but also the formation of Cu-oxides during the functionalized

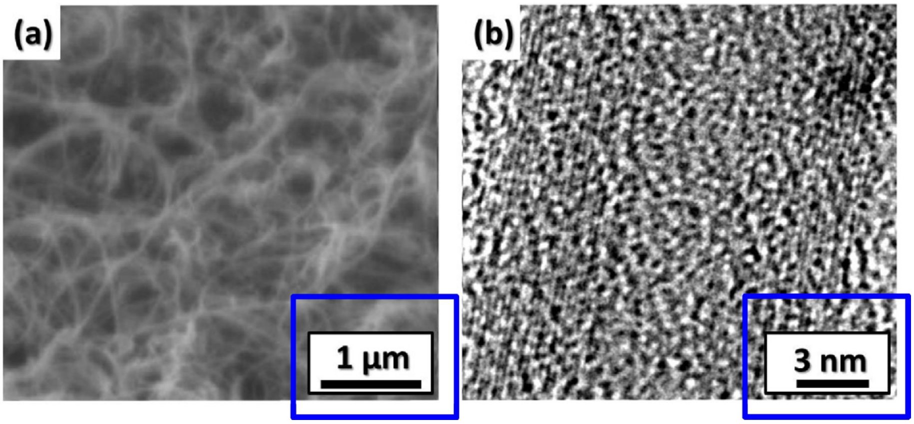

**Fig. 1.** (a) SEM and (b) HRTEM images of MWCNTs.