Achieving Mechanical and Conductive Anisotropy in Carbon Nanotubes/Cu Composites

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Abstract. Cu matrix composites reinforced by Multi-walled Carbon Nanotubes (MWCNTs) were prepared aiming to enhance the mechanical performance of Cu through MWCNTs while preserving its excellent axial conductivity. The microscopic structure, mechanical performance and electroconductivity of the composites were characterized, and the related mechanism was discussed. MWCNTs dispersed uniformly in Cu matrix and arranged in the direction of drawing. The composites showed obvious orthogonal anisotropy. The mechanical properties of the composites increased with the content of MWCNTs. The composite with 10vol.% MWCNTs has the best strength and hardness, which was better than most of data in the literature. However, the highest enhancement efficiency of 3vol.%-MWCNTs/Cu composite was the highest. The main enhancement mechanism was load transmission effects and dislocation. The electroconductivity and thermal conductivity of 5vol.%-MWCNTs/Cu composite parallel to the drawing direction reached the maximum value. The main strengthening mechanism was that Ni-Cu coating on MWCNTs leads to strong interface combination between MWCNTs and Cu, which promotes the electron-phonon coupling and reduces electron or phonon scattering at the interface.

Keywords. Carbon Nanotubes, conductivity, mechanical property.

1. Introduction

Pure Cu and Cu alloys have excellent conductivity, toughness, formability, corrosion resistance, reasonable fatigue resistance, low cost and easy to manufacture. Therefore, it is widely used in resistance spot welding electrodes, fuel cell electrodes, cable, motor brush, relay electric contact and other parts that need to pass current[1] electronic packaging, radiator, heat exchanger, heating system, solar absorption panel and other metal sections that need rapid heat conduction [2]. However, low strength and hardness limit the application of Cu in some frontiers, such as high-performance thermoelectric devices, military weapons and aerospace, etc. [3].

The most effective way is to prepare Cu composites by adding appropriate reinforcements. The second strengthening phase added includes Al2O3 [4], B4C [5], TiB [2], SiC [6], Si3N4, graphite [7], Zr2Al3C4, etc. However, the electrical and thermal conductivity of these reinforcements are worse than that of the Cu matrix. For example, the resistivity and thermal conductivity of Al2O3 are $1 \times 10^{12} \Omega \cdot \text{m}$ and 27 W/mK, respectively, lead to the conductivity of composites greatly reduced.

Carbon Nanotubes (CNTs) were discovered firstly in 1991 [8] by Suimio Lijima, and their excellent mechanical, thermal, electrical properties and chemical stability [9] make them ideal reinforcements that can improved obviously the mechanical performance of the matrix without damaging its thermal and electrical conductivity. S R Dong et al. [10] first applied CNTs as reinforcement in copper matrix. Since then, CNTs reinforced copper matrix composites have been extensively studied [11]. L Zhang et al.
prepared CNTs/W composite powder reinforcements by spray pyrolysis. CNTs-W/Cu composites were prepared by low energy ball mill and spark plasma sintering. The mechanical properties, conductivity, microstructure and interfacial structure of CNTs-W/Cu composites were evaluated. The results showed that W particles had a pinning effect on CNTs, but the performance improvement of the composite was limited. The ultimate tensile strength of the 0.6% wt% CNT-W sample was 226 MPa and its elongation was 33%. The conductivity of the 0.8 wt% CNT-W sample was 92.3%IACS.

Although the ball milling method can uniformly disperse CNTs in the metal matrix composite, it is easy to cause damage to CNTs [12]. And it can also contaminate the composites powder. The strength of composites is determined by the aspect ratio of the reinforcements according to shear-lag theory [13]. Ball milling interrupts CNTs and reduce their strengthening effect. For this reason, some studies have tried various methods to disperse CNTs in metal powder. For example, electroless copper-plated CNTs were dispersed and mixed with Cu powder through a uniaxial ice crystal growth assisted freeze-drying method, and the composites were prepared by spark plasma sintering. It was found that the agglomeration of CNTs still existed in the composites [14]. By mixing CNTs/Cu powder in copper salt aqueous solution at the molecular level, the CNTs were uniformly dispersed in the prepared composites. However, a reducing atmosphere was needed to reduce copper oxides [15]. Another method is plasma cavitation bubble, which can obtain short-term uniform dispersion effect by introducing functional groups on CNTs, but it is not suitable for CNTs with metal coating [16]. We used mechanical stirring-assisted ultrasonic method [14] and nitrogen-assisted ultrasonic method [15] to achieve dispersed CNTs uniformly in Cu composites.

In addition, the poor wettability of CNTs to Cu, resulting in weak interface bonding. This is not conducive for CNTs to undertake the task of stress transfer and heat dissipation in copper matrix composites. For this reason, some studies have improved the interface bonding between CNTs and copper matrix by modifying functional groups on CNTs, including atomic oxygen (O), hydroxyl (OH) and carboxyl (COOH) [1-6]. Studies have shown that CNTs were uniformly dispersed in Cu matrix, and a strong interface bond between CNTs and Cu was produced. However, due to electron and phonon losses, oxygen atoms at the interface degraded the thermal and electrical conductivity of CNT/Cu nano-composites. In fact, acid treatment such as functionalization of carboxyl groups on CNTs also caused damage to CNTs [17]. Another way to improve the interface bonding between CNTs and copper matrix is to deposit nickel, Cu or Ag coating transition layers on CNTs by electroless plating. Ni-Cu bilayers was electroless on Single-Walled Carbon Nanotubes (SWCNTs) by us [18]. In the prepared copper matrix composites, SWCNTs were uniformly dispersed, and the SWCNTs/Cu matrix interface was well bonded [19].

S Fu et al. successfully prepared Cu/CNTs composites by using two different precursor preparation techniques, namely alloy method (AM) combined with co-deposition method (CM), and chemical vapor deposition (CVD) combined with spark plasma sintering (SPS). The results showed that the Cu/CNTs composite had limited performance improvement, with a hardness of 102.5HV, tensile strength of 275MPa and electrical conductivity of 92.9%IACS. The process is complicated and costly [20].

In this work, we prepared MWCNTs/Cu composites by hot extrusion and cold drawing processes after electroless nickel-copper double coating on SWCNTs, and investigated the effects of the preparation process on the microstructure, mechanical, electrical and thermal properties of MWCNTs/Cu composites. By analyzing the relation between microstructure and properties of composites, the relevant mechanisms were discussed.

2. Experimental

2.1. Preparation of Composites

The MWCNTs (purity 90%, density 0.22g/cm3, diameter 10-20nm, length 10-30μm) prepared by vapor deposition method were obtained by Chengdu Organic Chemistry Co, Ltd, Chinese Academy of Sciences. The purity of electrolytic Cu powder is 99.8% and the size is between 50-75μm.

A probe ultrasonic generator (frequency 20 kHz, power 60W) was used to ultrasonically treat
MWCNTs in deionized water for 8 minutes to obtain a uniformly dispersed MWCNTs suspension. Next, Ni-Cu bilayers were electroless on MWCNTs. Our previous research has described the process in detail [15]. Then coated SWCNTs were washed, and vacuum dried at 80°C for 4 hours to obtain a dry coated MWCNTs powder samples. The coated MWCNTs, 0.3wt% zinc stearate and Cu powder were mixed together in absolute ethanol and ultrasonic treated for 20 minutes. During the period, a hollow glass rod is used to bubble nitrogen from the bottom of the beaker. Finally, the slurry was vacuum dried. Then the powder was unidirectionally pressed in a die at 500 MPa and room temperature into a cylindrical billet (Φ50×H31mm). Sintering was conducted in argon at 1000°C. The sintered samples were wrapped in a pure Cu sheath (ID (Inner Diameter) × OD (Outer Diameter) = 50mm × 52mm), and then both ends are sealed. After 910°C heat 4h, they were hot-extruded at 850°C into Φ20mm round bars with an extrusion ratio of 7:1. The extrusion barrel was preheated at 850°C, and extrusion speed was 300mm/min. Then the extruded rods were cold drawn into Φ18mm rods. Finally, they were turning to remove 1 mm thickness of the skin, and their diameters become Φ16. The composite samples containing 0vol.%, 1vol.%, 3vol.%, 5vol.%, 7vol.%, and 10vol.% MWCNTs fabricated by the same method are referred to as V0, V1, V3, V5, V7, V10.

2.2. Characterization and Testing
The microstructure of samples was characterized by a field emission transmission electronic microscopy (TEM, JEM-2100F), a scanning electronic microscopy (SEM, Gemini SEM 300) equipped with an energy dispersive spectrometer (EDS), and a metallurgical microscope (Nikon).

The actual sample density was determined by Archimedes method was the average of five measurements. The theoretical density was calculated using the mixing rules of composites. According to the following formula, the density of the samples, namely the relative density ω was calculated:

$$\omega = \left( \frac{\rho}{\rho_t} \right) \times 100\%$$

where ω is the densities of samples, ρ is the actual densities and ρt is the theoretical densities.

The polished samples were microhardness measured at room temperature using an Automatic MicroVickers Hardness Tester (HMM-FA2). A load of 0.49 N was applied to the sample surface and stayed for 15 s. The tensile test uses a dog-bone-shaped specimen (6 mm×2 mm×16.5 mm) processed by EDM. Electronic universal material test machine controlled by microcomputer (CTM-9200) was used for tensile test at the cross head speed of 2mm/min. The tensile data were the average of 5 measurements.

The conductivity of composites was measured with Keithley-2400 current source meter and Keithley-2182 nanovoltmeter. The size of the test sample was Φ18mm×5mm. The thermal conductivity is measured with a laser thermal conductivity analyzer (LFA427/457) under a vacuum of 10⁻¹⁵mbar, and the size of the test sample is Φ10mm×3mm.

3. Results and Discussion

3.1. Microstructure
Figure 1 shows SEM micrographs of MWCNTs. Figure 1 (a-b) shows that raw MWCNTs were tightly bound into ropes due to strong Van der Waals force and electrostatic attraction. The rope bundles up to 1 μm contained hundreds of highly entangled MWCNTs. Figure 1(c) shows the dispersion treated MWCNTs. The MWNTs in the figure are well dispersed with no obvious damage and were still long. Figure 1(d) shows the Ni-Cu bilayers layer plated on MWCNT, which were 60-85 nm in diameter and coated with metallic coating. Our preliminary results suggest that the Ni-Cu electroless coating on MWCNTs has high purity and almost no oxides [16].
Figure 1. (a) & (b) SEM micrographs of original MWCNTs; (c) dispersed MWCNTs; (d) Ni-Cu coated MWCNTs.

Figure 2 shows TEM microscopic images of V10 samples and EDS element analysis results. The vertical direction of alternating light and dark bands in figure 2 (a) is consistent with the direction of extrusion. The bright band was identified as Cu matrix by EDS analysis in figure 2 (b). In figure 2 (d), bright yellow lines indicate the alignment of MWCNTs along the direction of extrusion because of shear strain produced during extrusion.

Figure 2. Images of V10 sample: (a) TEM image, (b) EDS analysis, (c) carbon element distribution, (d) TEM image.

Figure 3 shows TEM images of V10 sample, and the corresponding fast Fourier transform (FFT) and inverse Fast Fourier transform (IFFT). The region to the left of the yellow dashed line in the enlarged image of box b in figure 3 (a) (figure 3 (b)), the plane spacing of lattice fringes ~0.34nm corresponds to the (002) plane of MWNTs. The crystal structures of the outer and inner walls of MWNTs were regular without distortion, entanglement or damage. This further confirmed that the preparation process used in
this work could make the microstructure of MWCNTs remain intact in the composite. The lattice distance on the right side of the yellow line is ~ 0.249 nm and 0.246 nm, respectively, corresponding to the (110) plane of Ni and the (111) plane of Cu2O, respectively. The Ni lattice plane is only partially present. Cu and Ni are face-centered cubic structures and can form different proportions of solid solutions, which will enhance metallurgical bonding. They have similar thermophysical properties.

In figure 3 (a), there are more fringes in darker areas on both sides of MWCNT (figure 3 (c)), originated from high density dislocations. ("T" symbol in IFFT image of figure 3 (c)). These dislocations may result from the formation of Cu2O. They could alleviate the lattice distortion between Cu and Cu2O and realize the smooth transition of Cu lattice plane to Cu2O lattice plane, which is conducive to enhance the interface bonding and load transfer efficiency.

In box d in figure 3 (a) (figure 3 (d)), the lattice distance on is ~0.181nm, corresponding to the Cu (200) plane. Referring to the crystal orientation in figure 3(d), it could be found that the (200) plane of Cu was parallel to the (200) plane of Cu2O. Therefore, the orientation relationship between Cu and Cu2O is Cu(200)//Cu2O(200), which indicates that Cu2O formed in situ, and strong interfacial bonding can be obtained [17] The Cu oxide here might originate from oxygen remaining in voids of the cold pressed block, which partially oxidized Cu coating and Cu powder during sintering.

Figure 3. (a) TEM images of V10 sample; (b) box b in (a) and its FFT image; (c) enlarged FFT image and IFFT image of box c in (a) and its FFT image, the dislocation are marked with "T"; (d) box d in (a) and its FFT image.

3.2. Density and Mechanical Properties
Figure 4 shows the theoretical and measured density of samples after sintering, extrusion and drawing. The most approximate density of sintered samples is ~ 74.5 %. The low density of sintered samples was due to the fact that during uniaxial compaction (UA), the pressure decayed inward along the longitudinal axis and cannot be transmitted to the whole sample. This results in the retention of irregular pores with different sizes in the sintered samples at normal atmospheric pressure, which leads to low density. Hot-extrusion achieved a significant increase in sample densification, with a maximum densification of 97.8%. Because MWCNTs have high Young's modulus and resilience [21], MWCNTs absorb part of the stress caused by powder compaction and hot extrusion. This results in the sample not being compacted effectively. At the same time, the density of extruded samples decreases slowly with the content increasing of MWCNTs. The cold drawing process further increases the densification to 99.7%.
Figure 4. Histogram of actual densities of sintered, hot-extruded and cold-drawn samples with different MWCNTs content.

Figure 5 shows the Vickers microhardness of samples on the planes perpendicular to and those parallel to DD (DD refers to drawing direction). The microhardness of MWCNTs/Cu composites increases with the increase of MWCNTs content, and were all higher than that of pure Cu. The hardness test results of V10 sample obtained on the planes perpendicular to DD was 149HV, which was 51% higher than that of the Cu sample on the same plane (perpendicular to DD). While the maximum hardness of V10 sample on the plane parallel to DD was 110HV, which was only 14.58% higher than that of Cu sample on the same plane (parallel to DD).

According to the Orowan enhancement mechanism reported by X. Long [22] and Z. Zhang [23], MWCNTs can hinder dislocation movement and increase dislocation density around MWCNTs. The dislocation motion stored and inhibited by the composite interfacial amorphous transition regions. All of these contribute to work hardening and make the composite resistant to deformation due to indentation force, resulting in the increase of hardness of composites. In addition, because of the tight bonding interface between matrix and MWCNTs (figure 3), the hardness test load could be transferred from copper matrix to stronger MWCNTs more effectively, the high strength of MWCNTs increased the hardness of composites [24].

Figure 5. Vickers microhardness of samples after drawing on the planes.
Figure 6 shows the stress-strain curves of samples. The tensile test direction was parallel to DD. Figure 7(a) shows that the tensile strength of composite samples after cold drawing increased significantly with the increase of MWCNTs. The UTS of 10vol.%-MWCNTs/Cu composites was 402.5 MPa (an increase of 52.15% compared with pure Cu) and its YS was 357.6MPa (an increase of 56.67% compared with pure Cu), which was superior to the mechanical properties of most MWCNTs/Cu composites reported at present.

The reinforced efficiency (R) of MWCNTs can be obtained by the following formula [25]:

$$ R = \frac{\sigma - \sigma_m}{\sigma_m V_{CNT}} $$

where $\sigma$ is the yielding strengths of composites, $\sigma_m$ is the yielding strengths of Cu, and $V_{CNT}$ is the volume percentage of MWCNTs. Figure 7 (b) compared the enhancement efficiency (R) of CNTs in various processing strategies in this study and in the references. As can be seen, when the content of MWCNTs was 3vol.%, the strength contribution of MWCNTs was the most. Here MWCNTs had higher enhancement efficiency than most reported data.

![Figure 6. Stress-strain curves of samples. The tensile test direction was parallel to DD.](image)

![Figure 7. (a) UTS and YS of samples; (b) CNTs enhancement efficiency(R) here and references [17, 22, 24-27].](image)
The fracture surface morphology of sample V10 is shown in Figure 8. MWCNTs were uniformly dispersed and embedded into Cu matrix. The uniform dispersion of MWCNTs contributes to the uniform load bearing of MWCNTs under tensile load. The dimples with tiny quasi-cleavage surfaces and obvious tearing ridges are uniformly distributed in Figure 8 (b), indicating that plenty of plastic deformation occurred before failure of Cu matrix. Lots of isolated MWCNTs can be seen on the fracture surface, which were short tips rather than long outcroppings, indicating that the interfacial bond between MWCNTs and matrix was strong.

There are three main considerations for the enhancement mechanism of CNTs in metal matrix composites: grain refinement, Orowan ring strengthening and shear lag theory [22]. Chen et al. [26] proposed that the high strength of composites was mainly attributed to the load transfer mechanism of CNTs. A modified shear lag model was used to analyze and estimate the load transfer effect [27].

\[
\sigma_c = \frac{\sigma_m}{V_{CNT}} + \sigma_{CNT} V_{CNT} \left( \frac{L}{2L_c} \right) \quad L < L_c
\]

(3)

\[
\sigma_c = \frac{\sigma_m}{V_{CNT}} + \sigma_{CNT} V_{CNT} \left( 1 - \frac{L}{2L_c} \right) \quad L > L_c
\]

(4)

where \(\sigma_c, \sigma_m, \sigma_{CNT}\) are the yield strength of composite, matrix and MWCNT (~39GPa); \(V_{CNT}\) is the volume percentages of MWCNTs; \(L\) is the length of MWCNT (~6μm); minimal length \(L_c = \frac{\sigma_{CNT}d}{2\tau_m}\) (~3.085μm), \(d\) is the diameter of MWCNTs (~20nm), \(\tau_m = \frac{1}{2} \sigma_m\) is shear bond strength of matrix.

According to the above theoretical model calculation, the theoretical tensile strength of V10 sample is 290 MPa, 77% of actual measured value. After tensile test, the ductile fracture surface of V10 sample showed a large number of pits, indicating that the addition of MWCNTs had little impact on the ductility of matrix. MWCNTs uniformly implanted into matrix. Moreover, some broken MWCNTs exposed to the fractured surface were observed, indicating that the load was effectively transferred through MWCNTs.

3.3. Electrical Conductivity

Figure 9 shows the electrical conductivity of samples. The electrical conductivity of pure Cu bulk along the testing direction parallel to DD reaches 56.1 MS/m, and that along the direction perpendicular to DD.
drops slightly to 53.9 MS/m. This may be because the Cu matrix grains were elongated along extrusion direction after extrusion and cold drawing, which means that scattering of electrons conducting at the same distance in that direction involves less grain boundary (GB), thus reducing the resistivity caused by GB.

After adding MWCNTs, the conductivity of the composites reduced. This may be because the large size of MWCNTs caused interference of copper lattice period and local elastic strain region, which scattered electrons and thus reduced conductivity. As shown in figure 3(c), many dislocations occurred in Cu matrix near MWCNTs after hot extrusion, which resulted in reduced electrical conductivity. In addition, Cu2O and Ni coatings at the interface of MWCNTs and Cu also increased the resistance to electron transport, and such schottky barrier was not conducive to electron transport [28]. Figure 11(a) shows the electrical conductivity of composites prepared here is better than those reported in most reports.

As can be seen from the electrical conductivity along direction parallel to DD in figure 9 (a), the electrical conductivity began to increase with the increase of MWCNTs contents, and the sample V5 reached the maximum value 54.5 MS/m and then began to decrease. The electrical conductivity of sample V10 was the lowest, which was 46.8 MS/m. This may be due to the following reasons: MWCNTs/Cu composites have higher densification due to extrusion and drawing processes (figure 4). MWCNTs surface chemical plated Ni-Cu resulted in a compact interface binding between MWCNTs and Cu matrix (figure 3), which could realize electron transfer between MWCNTs and matrix. Whereas, as MWCNTs continued to increase, however, as MWCNTs continued to increase, well-dispersed MWCNTs increased the interface acting as the scattering center and thus the interface scattering of free electrons. The electrical conductivity closely related to the interfacial scattering resistivity. According to Fuchs size effect theory [29], interfacial scattering resistivity \( \rho_{int} \) can be calculated by the following formula:

\[
\rho_{int} = \frac{3}{4} \left( \frac{3n^2}{e} \right)^{1/3} \frac{h}{(1-p)} \frac{V_{CNTs}}{d} \left( \frac{n}{d} \right)^{2/3}
\]

where \( h \) is reduced Planck constant; \( e \) is the electron charge; \( p \) is the elastic scattering probability at interface; \( n \) is concentration of electron in matrix and \( d \) is CNTs diameter.

Generally, the electrons elastic scattering can be reduced by improving wettability of the interface. And the electrical resistivity of the interface scattering increases with the decrease of \( p \). In this work, the interfacial bonding was improved by applying Ni-Cu coating, and elastic scattering probability of electrons through the interface \( p \) was increased, thus reducing the resistivity of interfacial scattering and improving the overall conductivity of composite.

The electrical conductivity of composite samples showed orthogonal anisotropy in different electrical conductivity testing directions. The electrical conductivity parallel to DD was higher than that perpendicular to DD. The electrical conductivity of V1, V3, V5, V7 and V10 samples in the direction parallel to DD were increased by about 9%, 26%, 14%, 16% and 19% compared with those perpendicular to DD, respectively. The contact mode between MWCNTs and matrix includes end and side contact [30]. The contact resistance of the former is lower than that of the latter [31]. Because of directional arrangement of MWCNTs in matrix, the transmission of electrons at the interface perpendicular to DD was mainly affected by side contact mode, resulting in low conductivity [32]. Meanwhile, because of high length-diameter ratio of CNTs, and the average free path is longer than [33]. And electrons can pass through the CNTs when there is a good interfacial contact. Compared with conducting current along the direction perpendicular to DD, the electrons travel a longer distance in CNTs arranged along DD, which reduces the electrons scattering at matrix grain boundary and thus improves the electrical conductivity of composites [34]. The electrical conductivity of sample V3 showed the greatest anisotropy. This may be because, all the influencing factors acted together to reach a certain balance in 3 vol.% MWCNTs/Cu composite.
3.4. Thermal Conductivity

Figure 10 shows the thermal conductivity of samples. It can be seen that the trend is similar to the electrical conductivity. The thermal conductivity of Cu bulk along the direction parallel to DD reaches 392.8 W/mK, and that along the direction perpendicular to DD is 383.3 W/mK. The thermal conductivity of the MWCNTs composites decreased. Figure 11(b) shows that the thermal conductivity of MWCNTs/Cu composites prepared here is better than those reported in most reports.

The thermal conductivity along the direction parallel to DD began to increase with the increase of MWCNTs, and the sample V5 reached a maximum value of 385 W/mK. Then began to decrease, and the sample V10 reached a minimum value of 332 W/mK. This may be due to the following reasons: (1) In CNTs/metal composites, electrons dominate the heat conduction in the metal, while phonons dominate the heat conduction in CNTs. Therefore, for heat transfer at the interface of MWCNTs/Cu, energy transfer between electrons and phonons must occur. In this work, the presence of electroless Ni-Cu plating between MWCNTs and copper matrix promoted the necessary electron-phonon coupling and reduced electron and phonon scattering at the interface, thus improving the heat conduction in the overall composites [35] (2) The hot extrusion and drawing processes made MWCNTs/Cu composites had higher compactness (figure 4) and reduced the porosity in Cu matrix, which hindered the phonon scattering and free electron transfer, resulting in the decrease of the thermal conductivity of composites.

The thermal conductivity of composite samples showed orthogonal anisotropy in different thermal conductivity testing directions. The thermal conductivity parallel to DD was higher than that perpendicular to DD. The thermal conductivity of V1, V3, V5, V7 and V10 samples in the direction parallel to DD were increased by about 6%, 9%, 8%, 5% and 6% compared with those perpendicular to DD, respectively. MWCNTs were orientated in matrix by extrusion and drawing. As mentioned above, MWCNTs and Cu matrix have end and side contact, and the thermal resistance of end contact is lower than that of side contact. The transmission of electrons along the interface perpendicular to DD was mainly affected by the side contact mode, leading to lower thermal conductivity of composites. The main heat transfer mechanism of CNTs is phonon-phonon Umklapp scattering. Since the scattering state cannot be entered, the Umklapp scattering was inhibited along the longitudinal axis of CNTs. Therefore, the longitudinal heat transfer increases the total conductivity of the composites along DD.

**Figure 9.** Electrical conductivity of samples along different directions (E_∥ for parallel to DD and E_⊥ for perpendicular to DD).
Figure 10. Thermal conductivity of pure Cu and MWCNTs/Cu composites samples along different directions (K\text{∥} for parallel to DD and K\text{⊥} for perpendicular to DD).

Figure 11. Electrical and thermal conductivity of CNTs/Cu composites in this study and related references [20, 36-44].

4. Conclusion
Cu composites reinforced by 1 vol.%, 3 vol.%, 5 vol.%, 7 vol.% and 10 vol.% MWCNTs were fabricated by nitrogen-assisted mixing powder, electroless plating, hot extrusion, and cold drawing. The composites had orthogonal anisotropy, showing good mechanical properties, while the loss of electrical and thermal conductivity is little.

- The strength and hardness of composites improved with the increase of MWCNTs. The best mechanical property of 10 vol.% MWCNTs. The reinforcement efficiency of 3 vol.% MWCNTs to Cu matrix was the highest.
- The 3 vol.% MWCNTs has the highest enhancement efficiency to matrix, better than most reported data. The load transfer effect and dislocation is enhancement mechanism.
- After adding MWCNTs, the electrical and thermal conductivity of the composites reduced. The electrical and thermal conductivity of the composites along the direction parallel to DD began to increase with the increase of MWCNTs, and the sample V5 reached a maximum value. Then began to decrease. The main strengthening mechanism was that the electroless Ni-Cu plating leads to strong interfacial binding between MWCNTs and matrix, which promotes the necessary electron-phonon
coupling and reduces electron and phonon scattering at the interface.

- MWCNTs/Cu composites showed orthotropic because of MWCNTs directional arrangement. The electrical and thermal conductivity of V10 sample along the direction perpendicular to DD were the worst, which were significantly worse than those along the direction parallel to DD. This is due to the difference in electrical and thermal resistance between end and side contact of MWCNTs and Cu matrix, and the excellent axial conductivity of MWCNT.

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