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Enhanced mechanical properties and wear resistance of cold-rolled carbon nanotubes reinforced copper matrix composites

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Abstract

Multi-walled carbon nanotube (MWCNT)/Cu composite containing 0.5 vol% MWCNTs were prepared by a high energy ball milling followed by conventional sintering and finally cold rolling. Microstructure studies showed that MWCNTs were uniformly dispersed and implanted inside the Cu matrix. The MWCNT/Cu composites showed an improvement in hardness and tensile strength up to 37% and 44% respectively compared to those of pure Cu. The enhancement is attributed to the uniform dispersion and strengthening due to the addition of MWCNTs. The yield strength of the composite has been quantified by several strengthening mechanisms including grain boundary strengthening, dislocation strengthening, Orowan strengthening and load transfer. The calculated results indicated that the load transfer strengthening has the largest contribution to the yield strength of the composite which implied the key role of the interfacial bond strength between MWCNTs and Cu matrix on the strengthening behaviors. The friction coefficient and specific wear rate of the composites were reduced with the addition of MWCNT content due to the self-lubrication effect of CNTs and high mechanical properties.

1. Introduction

Because of the outstanding properties, metal matrix composites (MMCs) have been widely used in many industrial fields such as aerospace, automobile, electrical, electronics, etc. Since discovered in 1991, carbon nanotubes (CNTs) have been considered as an ideal reinforcement material for polymer, ceramic and metal matrix composites due to its unique properties such as high mechanical properties, good thermal and electrical conductivity [1–5]. Recently, many studies on using CNTs for MMCs (i.e. Al, Cu, Mg and Ni) have been published which demonstrated that CNTs could enhance the mechanical, thermal and electrical properties of the composites [6–18]. Among them, CNT/Cu composite is one of the most important composites due to their high potential applications in the electronics and electrical industries [19–22]. Up to now, the most critical issues in the fabrication of the CNT-reinforced MMCs including (i) uniform dispersion of CNTs and (ii) improve the interfacial bond strength between CNT and the matrix. Where the interfacial bond strength has been considered as the key point that contributes to the load transfer between CNTs and the matrix for enhancing the mechanical properties of the composites [9, 10]. The interfacial reactions between CNTs and matrix to form the carbide phase at the interface could be effectively enhanced load transfer in CNT/Al composites [9, 10]. For CNT/Cu composites, there are no reactions between CNTs and Cu matrix at the interface. Therefore, some additional elements such as oxygen, chromium, cobalt have been included in the CNT/Cu composites to improve the interfacial bond strength [12, 15]. Besides, the consolidation processes have been also received great attention due to the inferior mechanical properties of CNT/metal composites caused by low relative densities. Many
techniques have been using to consolidate the MWCNT/Cu composites such as hot pressing, hot isostatic pressing and spark plasma sintering. In which, the conventional sintering shows as a good candidate to prepare the big samples. However, the conventional sintering caused the low relative density ranged 85%–95% [23–27]. Therefore, further processing including plastic deformation (i.e. high-pressure torsion, cold rolling, equal-channel angular pressing) could be applied for the sintered samples to obtain the full density composites. In this study, MWCNT/Cu composites are fabricated by powder metallurgy method. The composite powders are prepared with a combination of wet and dry mixing, followed by conventional sintering and finally, the cold-rolling process was applied to obtain full density composites. The microstructure, mechanical properties and wear resistance of the composites are analyzed.

2. Experimental procedure

2.1. Materials

Commercial copper powder with a purity of 99.9% having an average diameter of 27 μm supplied by PEAXNM Co. Ltd, Russia is used as a matrix material. MWCNTs (96% purity) synthesized by chemical vapor deposition technique with an average diameter and length of about 20 nm and 10 μm in length, respectively, were used as reinforcement material.

2.2. Fabrication of MWCNT/Cu composites

The fabrication process of MWCNT/Cu composites is shown in figure 1 that includes the three main step: (i) preparation of MWCNT/Cu powder by using high energy ball milling technique, (ii) the consolidation of MWCNT/Cu composite by sintering in argon and finally (ii) the deformation process of the composites by cold rolling technique to improve the relative density.

MWCNTs functionalized with carboxylic (COOH) functional group were dispersed into ethanol by an ultrasonic to prepare the CNT suspension with a concentration of 1 g l⁻¹. As received Cu powder was firstly milled and deformed by the planetary mill system to form an angular shape and small-sized Cu particles in order to improve the mechanical linkage with MWCNT. The milling was set up with a rotation speed of 250 rpm for 2 h with the ratio of ball to powder of 10:1 in absolute alcohol environment. The milled Cu powders were then mixed by rotary mixing (200 rpm) under continuous heating (60 °C) to remove a major part of ethanol and then obtain a MWCNT/Cu slurry. The obtained MWCNT/Cu slurry was further milled and mixed by high energy ball milling process with a speed of 300 rpm for 3 h. The milled powder was then dried in vacuum (200 mbar, 3 h) and followed by the reduction in H₂ at 400 °C for 2 h to obtain the MWCNT/Cu composite powder. The concentration of MWCNTs in the composite powder was calculated to be 0.5 vol%. The obtained powders were compacted as a compact size of 22 × 10 × 7 mm which was carried out on a hydraulic press, with a pressure of 200 MPa hold for 20 s. The pressed sample was sintered in argon at a temperature of 900 °C for 2 h to obtain the MWCNT/Cu composite. The sintered MWCNT/Cu composites were cold rolled up to 20% reduction and then
annealed at 650 °C for 3 h to prepare the cold-rolled MWCNT/Cu composites. Pure Cu samples were also prepared with the same conditions to compare and evaluate results.

2.3. Characterizations

The microstructures and morphology of powders and sintered composites were characterized by using optical microscopy (OM, Axiovert 40MAT, Carl Zeiss, Germany) and scanning electron microscopy (SEM, Hitachi S-4800, Japan). The density was measured by the Archimedes method and the microhardness was measured by using an AKV-CO/Mitutoyo, Japan. The tensile tests were measured on dog bone-shaped specimens with a gauge length of 6 mm and width of 1.7 mm using an INSTRON 5583 with a crosshead speed of 0.2 mm min\(^{-1}\) in accordance with ASTM E8. The wear tests were performed by using the pin-on-disk type under dry sliding condition against a polished SKD 61 tool steel at a sliding speed of 200 rpm, an applied load of 50 N, and a rotating distance of 1000 m.

3. Results and discussion

3.1. Microstructure

Figure 2(a) shows the SEM image of the MWCNT/Cu composite powder. As can be seen, CNTs were uniformly dispersed on the surface of Cu powders. The individual CNTs were observed instead of CNT clusters which implied that the uniform dispersion was obtained by the milling and mixing with HEB. In order to observe the distribution of CNTs inside the composites after sintering and cold-rolling, the composite was firstly polished down and then etched in the HNO\(_3\) solution (1 M). As can be seen in figure 2(b), some individual CNTs were implanted inside the Cu matrix. The obtained results demonstrated that the mixing process with the combination of wet and dry mixing shows as a promising method to prepare the MWCNT/Cu composites with the homogeneous distribution of CNTs inside the Cu matrix.

Structural defects of MWCNTs were investigated using Raman spectroscopy. Figure 3 shows the Raman spectra of MWCNT/Cu powder, sintered MWCNT/Cu composite and cold-rolled MWCNT/Cu composite. The intensity ratio \((I_d/I_G)\) between defect band (D-band) and graphite band (G-band) is used to estimate the quality of MWCNTs. The \(I_d/I_G\) ratio was determined to be 0.97, 1.03 and 1.24 corresponding to MWCNT/Cu powder, sintered MWCNT/Cu composite and cold-rolled MWCNT/Cu composite. The obtained result demonstrated that just a few defects induced on the structure of MWCNTs after sintering. However, the \(I_d/I_G\) ratio significantly increases after cold-rolling which implies that the presence of few defects on the surface of MWCNTs. Besides, the G peak is slightly shifted to larger wavenumbers. The shift of the G peak was attributed to the increase of the amorphous carbon content as a result of a convolution between the original G band (approx. 1580 cm\(^{-1}\)) and the D' band (approx. 1620 cm\(^{-1}\)). The obtained results demonstrated that the cold-rolling process caused further defects in the MWCNT structure during the plastic deformation.

3.2. Mechanical properties

The MWCNT/Cu composites consolidated by the conventional sintering techniques show low densification. The relative densities were measured to be 93% and 89% corresponding to the pure Cu sample and MWCNT/Cu containing 0.5 vol% MWCNTs. After cold-rolled, the relative densities of the composites are improved above 99% as shown in table 1. The obtained results are a good agreement with the previous reports [28]. High relative density is a key factor to improve the properties of the composites such as mechanical properties and
wear resistance. The mechanical properties of the composites are shown in figure 4 and table 1. As can be seen in figure 4(c), the hardness of the MWCNT/Cu composite was measured to be 89.5 HV which is 37% higher than that of pure Cu (65.1 HV). It is well-known that the strength of composites not only depends on the relative density of the composites but also depends on the properties of reinforcement materials. The increase in the hardness of the composites with the addition of MWCNTs could result from the nanometer-sized MWCNTs acted as the keys hindered the movements of dislocations [29]. Furthermore, mismatch strains properly develop at the MWCNT/matrix interfaces due to the difference of the coefficients of thermal expansion between MWCNTs and the Cu matrix will block the movement of the dislocations to enhance the hardness of the composites [30].

Figure 4(a) shows the typical tensile strength-strain curves of the MWCNT/Cu composites. As can be seen, the tensile strength of the composites increases with the addition of MWCNT. The UTS of MWCNT/Cu
composite was measured to be 251.6 MPa that is 44% higher compared to the pure Cu (174.7 MPa). Similarly, the yield strength of the MWCNT/Cu composite is two times higher than that of the pure Cu. The enhancement of the yield strength of the composites resulted from the addition and uniform dispersion of MWCNTs inside the Cu matrix. In which, the uniform dispersion of MWCNTs is well-known considering as the key factors that help to improve the mechanical properties of the composite [28]. Figure 5 shows the fracture surface morphology of the MWCNT/Cu composite. As can be seen, some individual CNTs were also observed on the dimples. This implied that the good interfacial bonding between CNTs and Cu matrix during tensile loading resulting in enhancing the load transfer from matrix to CNTs and thus improving the mechanical properties of the composites.

In order to understand the strengthening mechanisms of the composite, several mechanisms including grain boundary strengthening ($\Delta \sigma_{gb}$), dislocation strengthening ($\Delta \sigma_{dis}$), Orowan Strengthening ($\Delta \sigma_{Orowan}$) and load transfer ($\Delta \sigma_{LT}$), were considered for the calculation of MWCNT/Cu composites. Total yield strength of the composite can be estimated using the following equation:

$$\sigma_{YS} = \sigma_m + \Delta \sigma_{gb} + \Delta \sigma_{dis} + \Delta \sigma_{Orowan} + \Delta \sigma_{LT}$$  \hfill (1)

Grain boundary strengthening mechanism is described by the Hall–Petch equation (5) as the following [31]:

$$\sigma_f = \sigma_0 + k_f d^{-1/2}$$  \hfill (2)

$$\Delta \sigma_{gb} = k_f (d_1^{-1/2} - d_2^{-1/2})$$  \hfill (3)

here $k_f = 0.15$ MPa/m$^{1/2}$ is Hall–Petch coefficient for pure Cu [32] and $d$ is a grain size of Cu matrix. As can be seen in figure 6, the grain size of Cu matrix was determined to be 15.7 $\mu$m and 8.8 $\mu$m corresponding to the pure Cu and the MWCNT/Cu composite, respectively. Using these values for equation (3), the $\Delta \sigma_{gb}$ was calculated to be 15.1 MPa.

The thermal mismatch strengthening ($\Delta \sigma_{dis}$) in the $\sigma_{YS}$ of the MWCNT/Cu composite results from the thermal mismatch between MWCNTs and Cu matrix at the Cu/MWCNT interface. It can be described using the equation given by [33]:

Figure 5. The fracture surface of MWCNT/Cu composite (a) low magnification and (b) high magnification.

Figure 6. The microstructure of (a) pure Cu and (b) MWCNT/Cu composite.
Where $\sigma$ ($\approx 1.25$) is the dislocation strengthening efficiency value for copper [32], $G_m$ ($\approx 42.1$ GPa) is the shear modulus of the matrix, $b$ ($\approx 0.256$) is Burgers vector of the matrix, $\Delta T$ ($\approx 875$ K) is the difference between the fabrication and testing temperatures he range of temperature from tensile test to fabrication process, $\Delta CTE$ is the difference in CTE between the Cu matrix ($17 \times 10^{-6}$ K) and MWCNTs ($1-2 \times 10^{-6}$ K) [34], $V_{CNT}$ and $l_{CNT}$ are the volume concentration and an average length of MWCNTs. The $\Delta \sigma_{\text{DIS}}$ contribution was calculated as 21.3 MPa. Furthermore, the dislocation strengthening mechanism could be evaluated via the dislocation density generated during processing. Figure 7(a) shows XRD patterns of the pure Cu samples and MWCNT/Cu composites to calculate dislocation density by using Williamson–Hall method as followings [35, 36]. The dislocation density ($\rho$) could be calculated by the following equation (5) [35]:

$$\rho = \frac{2 \sqrt{3} \varepsilon}{d_b}$$  \hspace{1cm} (5)

Where the microstrain ($\varepsilon$) and crystalline-size ($d_c$) of the composites can be calculated from the XRD peak broadening ($\beta_{hkl}$) by using the Williamson–Hall method given by [36]:

$$\beta_{hkl} \cos \theta = \frac{0.94 \lambda}{d_c} + 4 \varepsilon \sin \theta$$  \hspace{1cm} (6)

where $\lambda$ is the wavelength of Cu Kα radiation. The values of $\varepsilon$ and $d$ were estimated from the slope and intercept by plotting and linear fitting the relationship between $B \cos \theta$ and $\sin \theta$, (figure 7(b)). The value of dislocation density ($\rho$) was calculated using equation (5) to be $1.63 \times 10^{14}$ and $3.84 \times 10^{14}$ m$^{-2}$ for the pure Cu and the MWCNT/Cu composites. As a result, the dislocation density of the MWCNT/Cu composite was higher compared to the pure Cu. In other words, the dislocation strengthening is contributed to the strength of the composite.

MWCNTs considered as nano-sized reinforcements could strengthen the Cu matrix by inhibiting the dislocation motions. Because of the interaction with MWCNTs, the dislocations in the Cu matrix tend to form Orowan loops during plastic deformation. The contribution of the $\Delta \sigma_{\text{Orowan}}$ can be calculated using the following equation [37]

$$\Delta \sigma_{\text{Orowan}} = \frac{0.8 M G_{\text{m}} b}{2 \pi \sqrt{1 - \gamma}} \left( \ln \frac{d_p}{d} + 2 \gamma \right)$$  \hspace{1cm} (7)

Where $M$ ($\approx 3.06$) is the Taylor factor of Cu, $d_p$ is an average diameter of CNTs, $\gamma$ ($\approx 0.34$) is the Poisson’s ratio of matrix and $\lambda$ is the interparticle spacing of dispersed reinforcement in the Cu matrix. For the MWCNT/Cu composite containing 0.5 vol% CNT, the $\Delta \sigma_{\text{Orowan}}$ was calculated to be 12.4 MPa.

The load transfer strengthening mechanism results from the interfacial bonding between reinforcement and matrix. Modified Shear-Lag model is usually used to estimate the load transfer strengthening that is described as the following equation [38].

\[
\Delta \sigma_{\text{LT}} = \frac{8 V_{\text{CNT}} \Delta T \Delta CTE}{b (1 - V_{\text{CNT}}) l_{\text{CNT}}} \]

Where $M$ ($\approx 3.06$) is the Taylor factor of Cu, $d_p$ is an average diameter of CNTs, $\gamma$ ($\approx 0.34$) is the Poisson’s ratio of matrix and $\lambda$ is the interparticle spacing of dispersed reinforcement in the Cu matrix. For the MWCNT/Cu composite containing 0.5 vol% CNT, the $\Delta \sigma_{\text{Orowan}}$ was calculated to be 12.4 MPa.
Where $\sigma_\text{my}$ is the yield strength of matrix ($\sigma_\text{my} = \sigma_\text{my} + \Delta\sigma_{gb} + \Delta\sigma_{dis}$), $l$ and $t$ are the sizes of CNTs parallel and perpendicular to loading direction and $S$ is the aspect ratio of CNTs. In fact, the $S$ of MWCNT can be calculated to be the length divided by diameter. However, the direction of MWCNTs in the composite system is random that is difficult to determine the loading direction. In such a case, the load transfer strengthening can be estimated by using the equation (9). The $\Delta\sigma_{LT}$ was calculated to be 59.2 MPa.

$$\sigma_\tau \approx \sigma_\text{my}V_{\text{CNT}} \left[ 1 + \frac{(l + t)S}{4l} \right] + \sigma_\text{my}(1 - V_{\text{CNT}})$$

Where $\sigma_\text{my}$ is the yield strength of matrix ($\sigma_\text{my} = \sigma_\text{my} + \Delta\sigma_{gb} + \Delta\sigma_{dis}$), $l$ and $t$ are the sizes of CNTs parallel and perpendicular to loading direction and $S$ is the aspect ratio of CNTs. In fact, the $S$ of MWCNT can be calculated to be the length divided by diameter. However, the direction of MWCNTs in the composite system is random that is difficult to determine the loading direction. In such a case, the load transfer strengthening can be estimated by using the equation (9). The $\Delta\sigma_{LT}$ was calculated to be 59.2 MPa.

$$\Delta\sigma_{LT} = \sigma_\tau - \Delta\sigma_{gb} - \Delta\sigma_{TM} - \Delta\sigma_{\text{Orowan}} - \sigma_\text{my}$$

The estimated yield strength was presented in table 2. The contribution of the strengthening mechanisms is plotted as shown in figure 8(b). As can be seen, the load transfer mechanism is the highest contribution to the yield strength of the composites. This again confirmed that the key role of the interfacial bond strength on the strengthening of the mechanical properties of MWCNT/Cu composite systems. The improvement of the interfacial bond strength between MWCNTs and Cu matrix is a key point to increase the mechanical properties of the composites.

The wear properties of the composites are showed in figure 9. The friction coefficient of the MWCNT/Cu composite was measured to be 0.55 which is lower than 30% than that of the pure Cu (0.79) (figure 9(a)). Similarly, the specific wear rate was decreased with the addition of MWCNTs as shown in figure 9(b). The specific wear rate was determined to be $5.62 \times 10^{-8}$ and $3.91 \times 10^{-8}$ cm$^3$ N$^{-1}$m for the pure Cu and the MWCNT/Cu composite respectively. The decrease of the friction coefficient and specific wear rate implied that the composite has higher wear resistance by the addition of MWCNTs. This could be due to the presence of MWCNTs and the improvement in the mechanical properties of the composite. Figure 10 shows the microstructures of the worn surface of pure Cu and MWCNT/Cu composite. As can be seen, the worn surface of the pure Cu shows continuous grooves, many craters and delamination. This indicated that the large portions of the matrix were removed and pulled out during the wear test. On the contrary, just a few craters and delamination were observed on the worn surface of the MWCNT/Cu composite (figure 10(b)). The obtained results demonstrated that the improve the wear resistance by adding MWCNTs. The improvement in the wear resistance of the MWCNT/Cu composite is attributed to the uniform dispersion of CNTs which acted as a lubricating carbon film to reduce the contact between counter disk and matrix for lowering the friction coefficient [23, 28].

### Table 2. Calculation of strengthening mechanisms of MWCNT/Cu composites.

| Sample       | Measured Y.S. (MPa) | Grain boundary strengthening | Dislocation strengthening by CTE mismatch | Orowan strengthening | Load transfer | Calculated enhancement in Y.S. (MPa) |
|--------------|---------------------|-----------------------------|------------------------------------------|---------------------|--------------|-------------------------------------|
| Cu           | 97.9                | —                           | —                                        | —                   | —            | 15.1                                |
| MWCNT/Cu     | 205.9               | 15.1                        | 21.3                                     | 12.4                | 59.2         |                                     |

Figure 8. (a) Yield strength and (b) the contribution of the strengthening mechanisms on the yield strength of the composites.
4. Conclusions

We have fabricated the MWCNT/Cu composites by powder metallurgy method. The obtained results reveal that MWCNTs were uniformly dispersed inside the Cu matrix. The MWCNT/Cu composites showed an improvement in hardness and tensile strength up to 37% and 44% respectively, compared to those of pure Cu. The enhancement is attributed to the uniform dispersion and strengthening due to the effect of MWCNTs addition. The friction coefficient and specific wear rate of the composites were reduced with the addition of MWCNT content due to the self-lubrication effect of CNTs and high mechanical properties.

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