


Carbon nanotubes–reinforced copper matrix composites produced by melt stirring

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Abstract

Due to their geometry and extraordinary mechanical properties, carbon nanotubes have been envisioned as promising enhancements for metal matrix composites. In this article, we report on our melt stirring approach for incorporation of carbon nanotubes into a copper alloy matrix and on the experimental results obtained by assessing the material properties. The existence of carbon nanotubes in the copper matrix after processing was proven by Raman analysis. We found that the small amounts of carbon nanotubes (0.1 wt%) in the composites influenced mechanical and abrasive wear properties.

Keywords

Metal matrix composites, carbon nanotubes, compression, wear

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Introduction

Copper (Cu) alloys are widely used for friction-type bearings due to their good compression load resistance, excellent wear performance and high thermal conductivity. In the last decades, nanostructured carbon, for example, carbon nanotubes (CNTs) arouse the scientific world's attraction because of its remarkable physical and mechanical properties.^{1–4} The conclusion seems obvious that one would like to combine the properties of the well-known standard material with CNTs to a metal matrix composite (MMC) with improved physical and mechanical properties. The main challenges of developing metal matrix/CNT composites are to realize a homogeneous dispersion of individual CNTs in metal matrix and high interfacial shear strength. To meet these demands, research on Cu matrix/CNT composites containing different volume fractions (5–25 vol%) of multi-walled carbon nanotubes (MWNTs) was carried out using pre-dispersion steps such as ball milling^{5,6} or molecular level mixing^{7–10} followed by powder metallurgy techniques such as sintering^{5,6} and plasma spark sintering.^{7–10} Compressive yield strength could be doubled^{7,9,10} by the addition of only 5 vol% of MWNTs. In contrast, the friction coefficient and the wear loss start to decrease significantly by addition of MWNTs with a minimum at about 15 vol% MWNTs.^{5,6} With densities of 1.8 g cm^{-3} for MWNTs

and 8.9 g cm^{-3} for copper, 5 vol% and 16 vol% correspond to 1 wt% and 3 wt%, respectively. However, in literature, no information can be found on producing Cu matrix/CNT composites via a melt stirring route. In contrast to sintering, a melt stirring process allows cost-efficient production of semi-finished products, for example, through continuous casting. In order to achieve a homogenous CNT dispersion and high interfacial shear strength, the following aspects, which pose the main challenges, have to be considered. The agglomeration behaviour of CNTs due to high van der Waals forces has to be taken into account as well as the non-wetting behaviour of graphite by liquid copper.¹¹ An additional challenge is the high process temperature of about 1150 °C , which could take effect, especially under oxidizing atmosphere, on the structural stability

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of CNTs. In this work, CNT-reinforced copper alloy composites were produced by a two-step melt stirring method, which has been described by Li et al.¹² The two-step process includes, first, a pre-dispersing procedure of MWNTs on the copper alloy chips in order to breakdown big agglomerates and, second, the fabrication of MWNT/Cu alloy composite by a melt stirring technique to further disperse the CNTs in the melt. In previous research,^{12–13} it has already been shown that by adding a small amount of MWNTs (0.1 wt%), the mechanical properties of the MWNT/Mg composites have been improved. In this article, we adapted the developed pre-dispersing procedure to produce Cu alloy/CNT composites with high melting temperatures.

Test set-up and procedure

Copper alloy (CuSn₁₀Ni₈Zn₃) was used as matrix. For the first experiment (CuSn_{0.1MWNTc}), the block copolymer Disperbyk-2150 (BYK Chemie GmbH), which has been confirmed to be sufficient for dispersing CNTs in organic solvent,¹⁴ and furthermore, the matrix¹⁵ was dissolved in ethanol in a small beaker. Then MWNTs (mass ratio to the block copolymer 1:1, Baytubes C 150P) were added to the as-prepared solution. This mixture was sonicated at room temperature for 15 min followed by a stirring step for 30 min at 250 r min⁻¹ to homogenize the solution. After addition of the copper alloy chips, the suspension was further stirred at 30 r min⁻¹ inside a fume hood to evaporate ethanol, and therefore, the separated CNTs were deposited on Cu chips. After the pre-dispersion step, scanning electron microscopy (SEM; e-Line, Raith GmbH) was used to analyse the surface of MWNT-coated Cu alloy chips (see Figure 1(b)). MWNT-coated Cu alloy chips were then placed in a cylindrical ceramic crucible, which was heated up to 1150 °C in a tube furnace under inert gas atmosphere to avoid oxidation. When the copper alloy chips were molten, the melt was mechanically stirred at 350 r min⁻¹ for 5 min to further disperse the MWNTs.

After stirring, the molten MWNT/Cu composite was poured into cylindrical graphite moulds. The cooled samples were machined into cylindrical shaped specimens ($d = 6$ mm, $h = 10$ mm) for subsequent compression tests and ($d = 8$ mm, $h = 25$ mm) for fretting corrosion testing. According to the described procedure, Cu alloy composites of a content of 0.1 wt% MWNT were produced. Reference samples were produced using exactly the same procedure but from pure copper alloy chips (CuSn_{ref}) and from 0.1 wt% MWNT Cu composite (CuSn_{0.1MWNT}) without pre-dispersion step (i.e. the MWNTs were simply added together with the Cu alloy chips in the crucible of the melt stirring furnace). The produced specimens were analysed by compression testing and fretting corrosion testing to determine the ultimate compressive strength, friction coefficient and abrasive loss. Compression tests were conducted at ambient temperature using standard compression testing equipment (Universal testing machine 1484, 210-kN load cell; Zwick GmbH) using DIN 50106. Sliding wear and friction tests were performed under dry condition on pin-on-disc apparatus with the composite specimens serving as the pin. The experiments were operated using a load of 1 N mm⁻² at a sliding velocity of 0.5 m s⁻¹ under dry conditions. The counterparts in the experiments were fabricated from 16MnCr₅ (C: 0.14–0.19 wt%, Mn: 1.00–1.30 wt%, Cr: 0.8–1.1 wt%) with Rockwell hardness of HRC58 and a surface roughness of < 0.8 μm. To assess the incorporation of MWNTs in the tested Cu alloy composites, the compressed samples of CuSn_{ref} and CuSn_{0.1MWNTc} were dissolved in a 2% HCl solution, filtered and analysed with Raman spectroscopy. Raw MWNTs were also checked by Raman as reference.

Results and discussion

SEM analysis was used to study the microstructure of the raw MWNTs and the MWNT pre-coated Cu alloy chips. Figure 1(a) shows a SEM image of the MWNTs

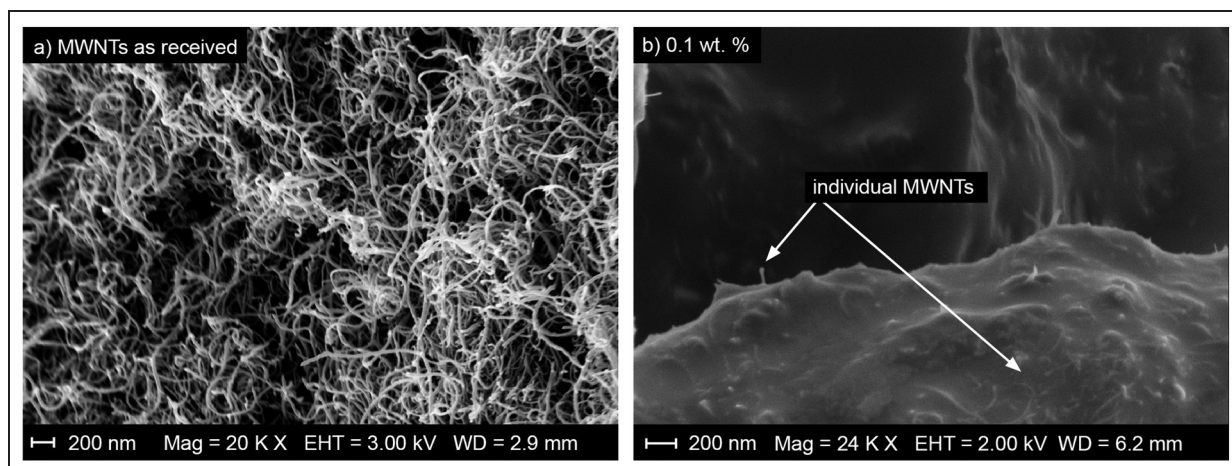


Figure 1. SEM images of (a) raw MWNTs as received and (b) 0.1 wt% MWNTs dispersed on the surface of a copper alloy chip. MWNT: multi-walled carbon nanotube.

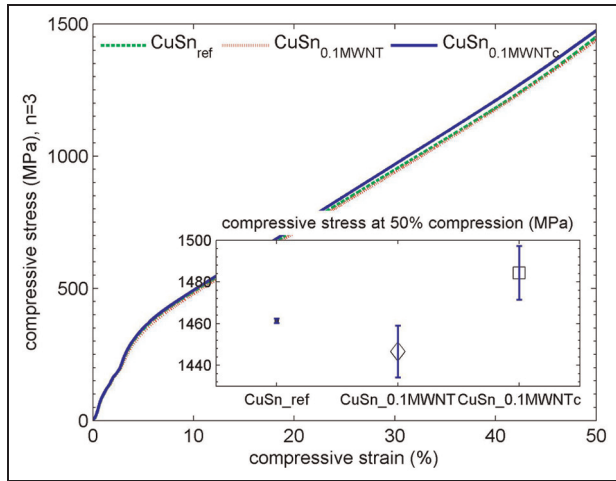


Figure 2. Compressive stress of copper alloy (CuSn_{ref}), copper alloy + 0.1 wt% MWNT non-pre-dispersed (CuSn_{0.1MWNT}) and copper alloy + 0.1 wt% MWNT pre-dispersed (CuSn_{0.1MWNTc}). Ultimate compressive stress at 50% strain. MWNT: multi-walled carbon nanotube.

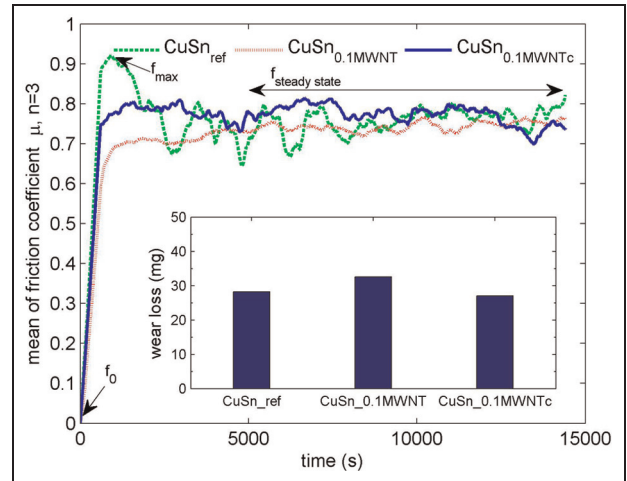


Figure 3. Mean (n = 3) of friction coefficient of copper alloy (CuSn_{ref}), copper alloy + 0.1 wt% MWNT non-pre-dispersed (CuSn_{0.1MWNT}) and copper alloy + 0.1 wt% MWNT with pre-dispersion (CuSn_{0.1MWNTc}) and exemplary wear loss of one sample. The inset shows the wear loss of one tested sample of each batch (reference Cu alloy, pre-dispersed/non-pre-dispersed MWNT/Cu).

Table 1. Pin-on-disc set-up and measured friction coefficients: initial f_0 , maximum f_{max} and final $f_{steady\ state}$.

Cu alloy/MWNT composite on 16MnCr5 $p = 1\text{ N mm}^{-2}$; $v = 0.5\text{ m s}^{-1}$; $T = 23\text{ }^\circ\text{C}$				
	f_0	f_{max}	$f_{steady\ state}$	
	CuSn _{ref}	< 0.1	0.92	0.76 ± 0.029
	CuSn _{0.1MWNT}	< 0.1	0.77	0.74 ± 0.011
	CuSn _{0.1MWNTc}	< 0.1	0.80	0.77 ± 0.024

MWNT: multi-walled carbon nanotube.

as received. The micrograph shows clearly that the raw MWNTs are agglomerated in big bundles. Figure 1(b) illustrates SEM images of dispersed MWNTs on copper alloy chips. Individual MWNTs can be found on the copper alloy surface after the pre-dispersion process. Based on random inspection, we conclude that for an amount of 0.1 wt% MWNTs, during step 1, MWNTs have been homogenously dispersed on the Cu alloy chips. Figure 2 shows the measured compression strength. From a compression of approximately 10%, the samples with pre-dispersed MWNTs (CuSn_{0.1MWNTc}) show an increased load resistance compared to the other samples (CuSn_{ref}, CuSn_{0.1MWNT}). The inset image shows that the ultimate compressive stress at 50% strain was increased by the addition of pre-dispersed MWNTs; whereas, the addition of raw MWNTs to the copper alloy chips results in a decrease of the ultimate compressive stress, which could be explained by the fact that the non-dispersed MWNT agglomerates act as defects in the Cu alloy composites instead of reinforcements. The addition of MWNTs to

the copper alloy melt leads to a significant increase in scatter of the measured values, which could be due to an increase in inhomogeneities of the casted matrix caused by MWNTs. There is no obvious change of compressive yield strength.

Table 1 shows the chosen parameters for the pin-on-disc set-up and the initial, maximum and steady-state friction coefficients for each sample. Initial friction coefficients are taken right after beginning. The steady-state friction coefficient is the mean value for 10^3 s after the running-in time of 5^3 s. The occurring maximum friction coefficients of the samples containing MWNTs (both pre-dispersed and non-dispersed) are lower than of the reference sample. Figure 3 depicts the graphs of the measured dry dynamic friction (n = 3, smoothed by moving average $w = 600$). The pure copper alloy shows distinctive stick-slip behaviour, whereas the samples containing MWNTs show lower fluctuations. This phenomenon according to which no peak at the beginning of a friction curve is observed was explained by Blau¹⁶ by the occurrence of a thin film of lubricious contaminant. Hence, the effect depicted in Figure 3 supposedly is generated by a film of worn out MWNTs during manufacturing of the samples. The inset in Figure 3 shows exemplarily the wear loss of one tested sample of each batch (reference Cu alloy, pre-dispersed/non-pre-dispersed MWNT/Cu). For the small number of samples measured here, no significant difference in the wear behaviour could be observed. Literature^{5,6} shows that improvements to friction behaviour could be reached by adding 15 vol%, respectively, 3 wt% of MWNTs. We conclude that adding 0.1 wt% of MWNTs is too little to significantly lower the friction coefficient using MWNTs' self-lubricating properties. Figure 4 shows

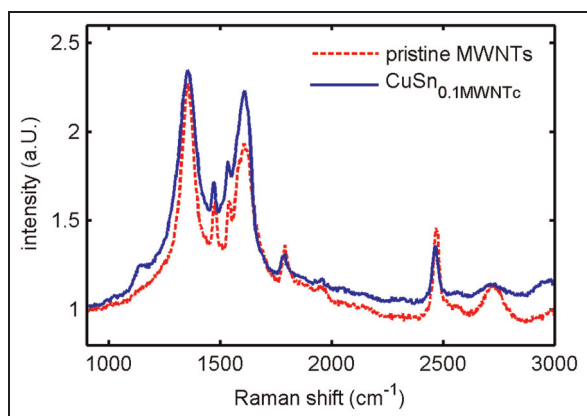


Figure 4. Relative intensities of Raman first and second order peaks of pristine MWNTs and filtered $\text{CuSn}_{0.1}\text{MWNTc}$ compression sample.

the Raman spectroscopy of pristine MWNTs and filtered residues of $\text{CuSn}_{0.1}\text{MWNTc}$ compression sample dissolved in 2% HCl acid. For the sample of CuSn_{ref} , no residues were detected on the filtration paper after the dissolving process. Due to the distinctive Raman peaks, we conclude that MWNTs were enclosed in the matrix of the $\text{CuSn}_{0.1}\text{MWNTc}$ compression sample and the influence of the properties on the composites could be attributed to the addition of CNTs.

Summary and future prospects

In this research, Cu alloy/MWNT composites were successfully produced by melt stirring. The pre-dispersion process helped to disperse MWNTs rather homogeneously on the Cu alloy chips in the first step. The characterization of the composites testing results indicated enhancements with respect to the tribological and mechanical properties for the samples containing pre-dispersed MWNTs even with a very small amount (0.1 wt %). Raman analysis confirmed the incorporation of MWNTs in the Cu alloy composites after the process. In summary, our results show that generally there exists a positive effect of MWNT embedded in a Cu alloy matrix on tribological and mechanical properties of Cu alloy/MWNT composites. In order to realize the full potential of Cu alloy/MWNT composites, more experiments will be carried out.

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