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Tailoring the contact thermal resistance at metal–carbon nanotube interface

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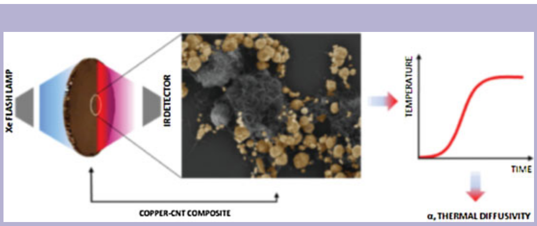
Copper-decorated carbon nanotubes (CNTs) were synthesized and used as conductive filler to improve the heat transport capabilities of copper matrix. Thermal properties, i.e., thermal diffusivity and thermal conductivity, of copper composite were measured and compared with those containing pristine and functionalized CNTs. Experimental results revealed that composites enriched with nanohybrids where Cu nanoparticles were covalently bonded to CNTs had thermal conductivity four times higher than those containing the same content of pristine CNTs.



Evaluation of thermal interface resistance in copper-CNTs composites by means of the flash method.

1 Introduction

The current trend in thermal management and electronic packaging is for smaller, low density materials with improved thermal behavior performance. Carbon nanotubes (CNTs) with their superior thermal properties are ideal candidates for engineering, e.g., metal composites with high thermal conductivity. When it comes to metal composites, the interface thermal resistance between CNTs reinforcement and the matrix is one of the most critical factors which determine the overall thermal conductivity of the composites [1]. The quality of this interface, however, might be improved by introducing strong chemical bonds between the nanotubes and the matrix.

In this work we present various approaches for CNTs sidewalls modification in the fashion that decreases thermal interface resistance between CNTs and copper matrix. The influence of interface modification on the effective thermal conductivity and thermal diffusivity of the composites was evaluated by means of xenon flash method. Furthermore, experimental values were compared with analytical estimation of the thermal conductivity of Cu-CNTs composites based on effective medium approximation (EMA).

2 Experimental

2.1 Sample preparation

The MWCNTs were non-covalently functionalized by polymer wrapping using cationic polymer sodium polystyrene sulfonate (PSS) [2]. CNTs were oxidized with a mixture of sulfuric and nitric acid (1:3, v/v) according to the procedure described elsewhere [3]. The functionalized nanotubes (CNT-PSS or CNT-COOH) were suspended in water and ultrasonically treated until the homogenous suspension was obtained. Next, the copper salt (copper acetate) was added to the suspension and the reaction mixture was stirred overnight at room temperature. After 12 h the suspension was heated up to 70 °C to evaporate the solvent. The obtained powder mixture was then calcinated at 200 and 350 °C for 1 h, respectively, in order to decompose copper acetate to copper oxide nanoparticles. The mixture was then reduced under H_2 at 350 °C for 2 h to transform the CuO to Cu. Different Cu-CNT composites were prepared with 0.2, 1, 3, 10 wt% of CNTs in copper matrix.

The composite powder mixtures were homogenized in planetary ball-mill machine (Fritsch) at 4500 rpm in rotary speed and 30 min in duration. The homogenous powder mixtures were consolidated into bulk Cu nanocomposites using cold pressing and plasma sintering technique. In the cold press approach the composite powder was compacted using a hydraulic lab hand press (PW20, Paul-Otto Weber GmbH) with an applied force of 130 kN. The compressed samples were subsequently sintered in a tube furnace (ROF 7/50, Heraeus) at 600 °C in a vacuum of 10^{-6} Pa for 60 min.

Full densification of the composite powder was performed by spark plasma sintering (SPS) technique (H PD 250, FCT Systeme GmbH). The powder was pre-compacted in a graphite die with 40 mm in diameter under a pressure of 6 kN. Next the samples were sintered at 600 °C for 5 min in a vacuum with an applied pressure of 50 MPa.

2.2 Sample characterization The laser flash method was used to measure thermal diffusivity (α) with the XenonFlash XFA 500 instrument (Linseis Messgeräte GmbH). All measurements were performed on samples with the size of Ø13 mm × 1 mm, placed in a chamber, where one surface of the sample was heated by an intense energy pulse and the temperature extrusion on the opposite surface was recorded by an infrared recorder. The specific heat of the samples was measured by a differential scanning calorimeter (DSC) PT1 (Linseis Messgeräte GmbH) using single-crystal sapphire as a reference material. Thermal conductivity was calculated from the equation Eq. (1), where λ, C_p, and ρ represent thermal conductivity, specific heat and bulk density of the sample, respectively.

The microstructure characterization was carried out on a scanning electron microscopy (SEM) Hitachi S-4800 with a cold FEG and transmission electron microscopy (TEM) Tecnai G^2 20 S-TWIN (accelerating voltage 200 kV).

3 Results and discussion The Cu-MWCNT composites were produced by thermal decomposition process [4] where multiwalled CNTs were first functionalized by acid treatment and polymer wrapping and subsequently decorated with copper nanoparticles (Fig. 1).

Thermal diffusivity (α) was measured and used to calculate thermal conductivity (λ) of composites following the relationship:

$$\lambda = \alpha C_p \rho. \qquad (1)$$

The experimental results show that incorporation of CNT to the metal matrix decreases its heat transport capabilities, even though the thermal conductivity of individual nanotube (3000 W/mK) is one order of magnitude higher than that of the copper matrix (400 W/mK). This observation is consistent with previous reports on thermal properties of metal–CNT composites [5]. However, it is interesting to find that composites enriched with differently functionalized nanotubes display diverse thermal behavior (Table 1). The highest α values obtained for acid-treated nanotubes, where copper nanoparticles are covalently attached to the CNTs, points to the lowest interface resistance among the produced composites. As expected, the lowest diffusivity value, and therefore, the highest thermal interface resistance exist for composites with non-chemically modified CNTs.

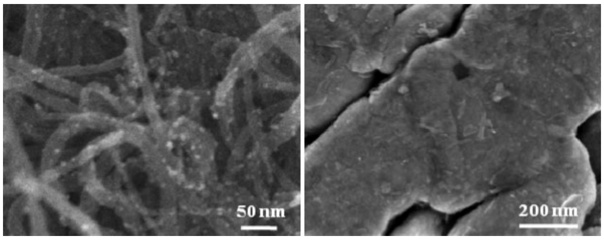


Figure 1 SEM images of CNTs decorated with Cu NPs and embedded in the copper composites.

Thermal conductivity values calculated with Eq. (1) shows analogues trend as for thermal diffusivity (Fig. 2). The polymer-wetted nanotubes display lower conductivity than acid-treated CNTs. This arises from weak van der Waals interaction forces between CNTs and the matrix. Even though the non-covalent functionalization of CNTs with polymer preserves the structure of CNTs, on contrary to destructive acid treatment, the associated presence of polyelectrolyte shields the intrinsic thermal properties of the nanotubes.

In order to understand the thermal transport behavior of different Cu-CNT composites the effective thermal conductivity enhancement (TCE) of such systems was calculated using effective medium approach [6], which accounts for contribution from thermal interface resistance at metal–CNT boundary. Accordingly, the effective thermal conductivity (λ_e) of composites with small loading of randomly dispersed,

Table 1 Thermal diffusivity in cm^2/s of copper composites with varied content of CNTs.

wt%	as-received	CNT-PSS at Cu	CNT-COOH at Cu
0.2	0.58	0.50	0.60
1	0.10	0.45	0.54
3	0.07	0.07	0.32
10	0.006	0.009	0.09

Thermal diffusivity value for pure copper 1.12 cm^2/s.

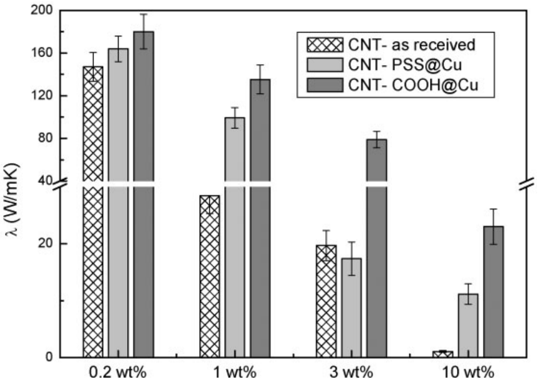


Figure 2 Effect of carbon nanotube sidewall modification on thermal conductivity enhancement of copper composites.

non-interacting CNTs can be derived as:

$$\frac{\lambda_e}{\lambda_M} = 1 + \frac{fp}{3}\,\frac{\lambda_{CNT}/\lambda_M}{p + \dfrac{2a_K\lambda_{CNT}}{d\lambda_M}}, \tag{2}$$

where radius a_K, the so-called Kapitza radius, is defined as:

$$a_K = R_K\lambda_M. \tag{3}$$

In the calculations, the thermal conductivity of copper is 230 and 331 W/mK as measured for cold-pressed and SPS Cu, respectively. The λ-value of CNTs is taken to be 3000 W/mK.

Figure 3 illustrates the influence of the thermal interface resistance on the TCE of the matrix material. It can be seen, that over a wide thermal conductivity range for the matrix material the TCE is below one and becomes greater for thermal conductivity below 25 W/mK. In case of high conductive matrix materials, like copper, the conductivity of the composites does not increase by adding CNTs. These theoretical calculations indicate that the heat transfer in composite material is governed not only by the individual thermal conductivities of the matrix and the reinforcing material but also by the thermal interface existing at the CNT–matrix interface.

Figure 4 compares measured values with theoretical predictions of TCE for various thermal interface resistances, i.e., 8.3, 20, and 80 × 10^{-8} m^2K/W. It can be seen that the experimental values are lower than the theoretic calculations. Even assuming that the thermal interface resistance is an order of magnitude higher than expected no fitting of the experimental data can be observed. This might indicate that the effective thermal conductivity of the composite might also be influenced by other factors, such as porosity of the sample caused by poor consolidation. In order to exclude the influence of sample porosity, the composite powders were fully consolidated via SPS process (see Section 2). As shown in Fig. 4, it is clear that sintering process improves the conductivity of the composites by shifting λ_e/λ_m to the higher values. For 1.75 vol% Cu-CNT, the calculated TCE (0.97) is in agreement with the experimental data (0.96). However, the effective thermal conductivity of the composites with a higher content of nanotubes is remarkable lower than predicted λ_e. One possible reason for this discrepancy is the fact that EMA is based on the assumption of perfect dispersion of individual CNTs that are in direct contact with matrix material. In the experiment, however, at high volume fraction, CNTs are entangled which has negative contribution to effective thermal conductivity of the composite.

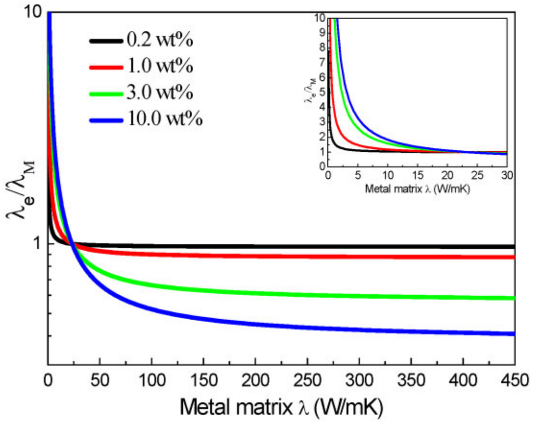


Figure 3 (online color at: www.pss-b.com) Composite thermal conductivity enhancement as a function of thermal conductivity of the matrix.

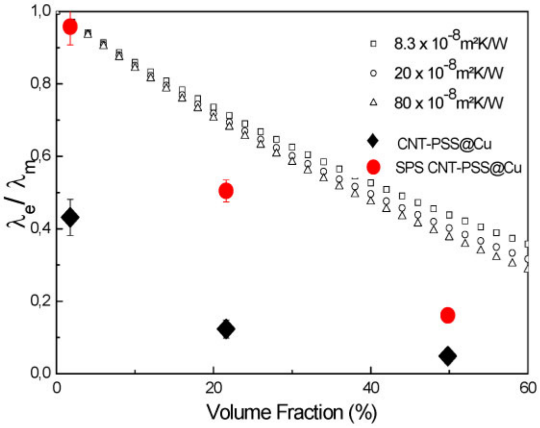


Figure 4 (online color at: www.pss-b.com) Comparison of measured (cold and SPS consolidated samples) and theoretical thermal conductivity enhancement of copper composites enriched with CNT-PSS at Cu nanohybrids.

4 Summary

In this paper we studied the dependence of CNTs chemical functionalization on the interfacial thermal resistance by measuring thermal diffusivity and conductivity of copper composites. Although no improvement in metal composite thermal conductivity could be observed, our results show that covalently functionalized CNTs are a better choice for phonon propagation in heat management composites than polymer functionalized nanotubes. We have experimentally demonstrated that decoration of CNT-COOH with Cu NPs increases the composite λ by a factor of four when comparing to pristine nanotubes. Copper nanoparticles covalently attached to the nanotubes provide strong coupling between nanotube–matrix interface, which in turn improves the interfacial thermal conductance in spite of the degradation of the tube intrinsic conductivity.

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