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Thermo-physical properties and TEM analysis of silver based MMCs utilizing metallized multiwall-carbon nanotubes

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ABSTRACT

Metal matrix composites with embedded multiwall-carbon nanotubes (MWNT) are attractive because MWNTs exhibit high intrinsic thermal conductivity. Thus to improve the thermal conductivity of a metal matrix, silver matrix composites with MWNT were prepared by "chemical" mixing, different active elements were introduced enhancing the bonding between inclusions and matrix. The evolution of the thermal conductivity and the coefficient of thermal expansion CTE as a function of the MWNT concentration and the presence of active elements cobalt, molybdenum or nickel in the silver matrix in Ag–X/MWNT composites are presented. A transition from weak to strong matrix/MWNT bonding is observed by adding active elements, the latter leading concomitantly to an increase in thermal conductivity and a decrease in CTE. The thermal conductivity was found to increase by up to 10% for a composition of 0.2 wt.% MWNT and cobalt as active element and a 6% decrease in CTE compared to a pure silver reference.

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1. Introduction

Heat dissipating systems like micro- and power electronic devices, LEDs and CPUs require an efficient heat removal to avoid possible damage or delamination due to thermal stresses. Therefore effective heat removal is in need for materials with high thermal conductivity and low coefficient of thermal expansion tailored to the substrates. Composites containing fillers with highest intrinsic thermal conductivity and concomitantly a very low coefficient of thermal expansion CTE could fulfil the requirements.

The idea of using carbon nanotubes (multiwalled carbon nanotubes MWNTs) as such highly conductive filler has drawn great attention both from industry and academia. Research mainly concentrated on polymer composites to enhance the electrical conductivity as well as mechanical properties [1], minor investigations concern metallic or ceramic composite systems [2–4]. CNT/polymer composites can exhibit very low percolation thresholds owing to the high aspect ratio of CNTs. Consequently the composites have an improved electrical performance relative to the host matrix without compromising other properties. Many matrix polymers have been investigated and very low percolation thresholds have been achieved with some of those systems [5]. However few investigations concentrated on CNT/metal composites so far, although comparable behaviour can be expected.

To fulfil the demand as heat sink material it is naturally positive to start from a high level of thermal conductivity, therefore copper and silver are candidate matrices. Unfortunately, carbon nanotubes - like all carbon allotropes - have a weakly bond with silver or copper, as no mutual solubility, wetting or reaction by carbide formation is evident. Hence, either concept exist using so called "active elements" utilizing small concentrations in matrix alloys [6-8]. Others follow the idea of coating the filler particles by thin intermediate layers, simultaneously enhancing the wetting behaviour and addressing the interface thermal conductance [9]. Both are a necessity for tailoring the interface between the matrix and the fillers, decreasing the interfacial thermal resistance or generally improving the wetting behaviour for infiltration methods. However, the concentration of active elements soluble in the metallic matrix must be limited in order to maintain the high intrinsic matrix thermal conductivity thus excluding many elements.

The use of carbon nanotubes (MWNTs) in a composite material is in so far a challenge, as they are non-straight, entangled and tortuous in their as-produced condition. However the surface of MWNTs is also generally tremendously large, resulting in increasing difficulties to end in homogeneous dispersion, also aqueous based ones. Furthermore differences in thermal conductance between metal/phonon conductor interfaces have to be considered in general. It is known from theoretical considerations as well as experimental work [10] that an interfacial thermal conductance between two metallic conductors can be in the range of one to three orders of magnitude higher than in case of metal/phonon

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interfaces. Nevertheless it is also known, that the interface thermal conductance between a metal and a dielectric could be improved if a layer of electron-conducting material is introduced at the interface between the two phases aiming at the necessary electron-phonon coupling. This intermediate layer must have high bond strength to the fillers and the metal and might be formed epitaxial on the fillers. Candidates for such layers in case of diamond MMCs exist as, e.g. nickel, chromium- and boron-carbide [6].

In order to address the interface between silver and carbon nanotubes, two different approaches were investigated. Within the first concept electroless deposited cobalt and nickel layers were investigated. Cobalt and nickel do not form carbides, but have a maximum solubility of 4.1 at.% for carbon at 1593 K (cobalt) and 2.7 at.% at 1600 K, respectively (nickel). A classical carbide former like molybdenum was added within a second approach.

Here we present results on the influence of composites preparation as well as cobalt, nickel or molybdenum additions in silver/ multiwalled carbon nanotubes composites on the simultaneous evolution of thermal conductivity and CTE. We further compare the amounts of MWNTs and active elements X needed to confer good bonding within the Ag/X–MWNT couple.

2. Experimental procedure

Multiwalled carbon nanotubes fabricated by a chemical vapour deposition process and either cobalt metallized or non-metallized MWNTs were delivered by Future Carbon GmbH, Bayreuth, Germany in stable aqueous dispersions. Molybdenum metallization was performed by the addition of molybdenum oxide MoO_3 to the MWNTs, drying and subsequent heat treatment under a constant flow of hydrogen gas ($1 L min^{-1}$) at temperatures up to 1273 K. Those as-metallized MWNTs have to be re-dispersed in an aqueous solution for further processing. Nickel metallization was done by nickel-hydroxide precipitation by the addition of sodium hydroxide to nickel-sulphate, which was dissolved in the MWNT-dispersion.

The dispersed metallized carbon nanotubes were added to an alkaline bath comprising hydrazine hydrate, ammonia and ammonium carbonate under sonication. Simultaneous prepared aqueous alkaline solutions of silver nitrate AgNO₃ (Oegussa-Umicore Austria, purity 99.94%, metals basis) were added drop by drop to the MWNT containing dispersion under vigorous stirring and again sonication. Instantaneously the silver is reduced by the reducing agent hydrazine hydrate while added, leaving behind a MWNT/Ag composite powder which can be filtered off and dried at the end of the unification of both solutions and the completion of the reaction.

An overall volume fraction of MWNTs was adjusted between 0.15 and 3 wt.%. However the composition of the composite powders and the consolidated composite samples were controlled by C-analysis (induction furnace combustion) and WXRF measurements respectively. Pure silver (99.99 wt.%) was prepared as reference material for thermal properties measurements.

The composite powders were consolidated by die pressing, sintering under a constant hydrogen gas stream (1 Lmin^{-1}) at temperatures up to 1173 K, followed by hot pressing in graphite dies at a maximum temperature of 1173 K and a maximum pressure of 42 MPa. The isothermal time was set to 5 h. In order to minimize residual porosity the samples were finally hot isostatic pressed at 1173 K and 130 MPa at an isothermal heating of 3 h. Consolidated samples were characterized by LOM, SEM and the condition of the MWNTs embedded in the matrix was followed by FEG-SEM and HR-TEM analysis.

Thermo-physical properties were determined on cuboidsshaped samples perpendicular to the direction of hot pressing. The coefficient of thermal expansion was measured in a vertical differential Netzsch DIL 402C dilatometer in two cycles between 293 and 673 K at a nominal heating and cooling rate of 5 K min⁻¹ under Helium gas atmosphere. The reported CTE is the slope of the $\Delta l/l$ vs. *T* curves averaged over the two heating ramps.

The thermal conductivity was measured by a steady-state, equal heat-flow comparative method against a brass reference. To this end the temperature gradient in the 6×6 mm cuboids-shaped sample (overall length 30 mm) was compared to that in the reference by means of two thermocouples in both sample and reference. The system was calibrated using pure silver, aluminium or pure copper reference samples. Repeatability of the measured value was assessed to be far smaller than 2%.

3. Results and discussion

The FEG-SEM analyses of some composite Ag/MWNT powders are given in Figs. 1–3. The results of the thermal conductivity measurements and the coefficient of thermal expansion are given in Fig. 4, with details on the evolution of thermal conductivity (RT) of 0.1 < x < 0.3 wt.% MWNT/Ag-composites utilizing non-metal-lized and cobalt metallized MWNTs respectively in Fig. 5. HR-TEM analysis representing the status of the MWNTs in the matrix is given in Figs. 7 and 8.

Carbon analysis revealed some divergences between desired and effective amounts of MWNTs in the range of $\pm 10\%$ (rel.) and might be attributed to the appearance of agglomerates in the delivered MWNT-dispersions. However the measured concentrations by C-analysis were subsequently used as effective MWNT concentration in the composites and displayed in the graphs. Concentrations for active elements are in the range of few 100 ppm, mostly between 200 and 400 ppm (note: no distinctive context between the different samples and their active element concentrations can be deduced). The density of the consolidated composites is close to 100% for low MWNT loaded samples. High volume fraction MWNTs in the composites can cause porosities up to 5%.

We generally note that the carbon nanotubes used in the experiments are multiwalled carbon nanotubes MWNTs with outer diameters up to about 50 nm have large but finite aspect ratios and are not straight. A theoretical density of 1.65 g cm^{-3} was used for calculating the volume fraction from the used weight fractions in experimental investigations.

3.1. FEG-SEM analysis

The as-processed Ag–X/MWNT composite powders were analyzed by FEG-SEM (Figs. 1–3) showing first, that the MWNTs are



Fig. 1. FEG-SEM image of sample Ag-0.2 wt.% MWNTs using non-metallized MWNTs.



Fig. 2. FEG-SEM image of sample Ag-0.5 wt.% MWNTs, using cobalt metallized MWNTs.



Fig. 3. FEG-SEM image of sample Ag-0.7 wt.% MWNTs, using molybdenum metallized MWNTs.

still present and not consumed during metallization processing, being particularly important for the molybdenum metallized nanotubes. Secondly the images reveal different appearance between metallized and non-metallized MWNTs. Those ones using metallized nanotubes are obviously better enwrapped by silver particles, even composites having higher loadings of MWNTs. Thus sample Ag/Co–C0.5 has no isolated bundles of MWNTs, all bundles are covered by silver particles. Sporadic individualized MWNTs can be observed sticking out of the silver, whereas areas of uncovered MWNTs bundles are visible in sample Ag–C0.2. Obviously the presence of an active element like cobalt enhances the deposition of silver on the primarily metallized MWNTs. The active elements might act as nuclei resulting in a preferred deposition of the matrix on those sites.

3.2. Thermo-physical properties

The coefficient of thermal expansion CTE starts off at a value of 20 ppm K⁻¹ (20–200 °C) and 21 ppm K⁻¹ (30–400 °C) respectively being characteristic for a pure silver matrix. Concurrently the ther-



Fig. 4. Evolution of thermal conductivity (RT) k_c and CTE_{tech} (20–200 °C and 30–400 °C) of 0.2 < x < 3 wt.% MWNT/Ag-composites as a function of the active element contents, i.e. cobalt, nickel or molybdenum.



Fig. 5. Details on the evolution of normalized thermal conductivity (RT) κ_c/κ_m of 0.1 < x < 0.3 wt% (0.6 < x < 3.1 vol.%) MWNT/Ag-composites utilizing non-metallized and cobalt metallized MWNTs respectively. For comparison reasons two high volume MWNT fraction experimental data were included (14.5 and 16.4 vol.% MWNTs).

mal conductivity κ_m is close to the value expectable for pure silver. Fig. 4 then shows the evolution of both thermo-physical properties by the addition of MWNTs. Precisely the CTE is unaffected (or even higher than the reference sample) at low (0.2 wt.%) and high (3 wt.%) MWNT concentrations. However by the addition of active elements the CTE can be decreased. As the concentrations of those active elements are small, the reported CTE decrease can be solely attributed to a MWNTs effect and not to a solid solution effect caused by the active elements. Implications of different active elements on CTE are difficult to evaluate, but a tendency to a higher impact on CTE for low MWNT volume fractions can be interpreted. Generally all tested active elements – nickel, cobalt and molybdenum – show an impact on CTE. The most pronounced effect can be

seen for the element cobalt at 0.5 wt.% MWNT concentration: the reduction of CTE is in the range of 6%.

In parallel the evolution of the thermal conductivity is different to the evolution of the CTE. For example additions of active elements can significantly reduce the thermal conductivity of the composites (Fig. 4): compare Ag–C3 (i.e. a MWNT concentration of 3 wt.%) with samples Ag/Ni–C2.7 and Ag/Co–C2.6. Two exceptions exist, of which both include low volume fractions of MWNTs: the molybdenum and the cobalt metallized samples. Both having high thermal conductivities, sample Ag/Co–0.5 wt.% MWNTs features a value of 440 W m⁻¹ K⁻¹. This is fairly above the pure silver reference of 425 W m⁻¹ K⁻¹. Obviously high MWNT volume fractions result in a significant degradation of conductivity, but a low volume fraction does not cause per se higher thermal conductivities. The enhancement of the conductivity is also associated with the presence of active elements, e.g. comparing Ag–C0.2 and Ag/ Co–C0.5 or Ag/Mo–C0.7.

Summarizing those results, the thermo-physical properties CTE and thermal conductivity can be enhanced by the addition of active elements and along with the realization of low volume fractions of MWNTs. It is instructive to compare the levels of MWNT and concomitantly the presence of the active element cobalt at which the transition from a weak to a strong bonding between the fibres and the matrix appears.

In order to verify those results and to clear the dependence of the thermal conductivity by the MWNT fractions, additional samples were prepared realizing a cobalt metallization at MWNT weight fractions of 0.1 < x < 0.3 wt.%, i.e. 0.6 < x < 3.1 vol.% (Fig. 5).

At a MWNT-content of roughly 0.1 wt.% (0.6 vol.%), the thermal conductivity starts increasing, with a maximum at around 0.2 wt.% (1.26 vol.%). The maximum thermal conductivity derives to 470 W m⁻¹ K⁻¹. At higher MWNT-contents up to 0.5 wt.% (3.1 vol.%), the thermal conductivity saturates at a value of roughly 440 W m⁻¹ K⁻¹. However, the rise in thermal conductivity is limited: at MWNT-contents >0.5 wt.% (3.1 vol.%) a significant decrease is observed, although the exact limit cannot be verified for the moment, as no samples exist in the range of 0.5 and 3 wt.% (16.4 vol.%) MWNTs. A marked difference between cobalt metallized and not metallized MWNTs is observable, showing again the importance of active elements being present in the composites.

The high value of the CTE and degradation of thermal conductivity for Ag/MWNT composites indicates very weak bonding between the matrix and not metallized MWNTs. Improved bonding due to active elements results in both increased heat transfer and improved load transfer between the matrix and the MWNT. This explains the increase in thermal conductivity and the drop in CTE. At high MWNT-contents the impact of active elements diminishes and results in the observed degradation. This can be attributed to the non-straight, entangled and tortuous nature of CVD as-produced MWNT-fibres. Hence the necessary contact between fibres and matrix for heat and load transfer cannot be established, as the matrix cannot penetrate the fibre bundles thoroughly. This is also reflected by an increasing porosity of the samples with increasing MWNT concentration thus contributing to the contact problems between fibres and matrix.

3.3. Theoretical considerations

Several theoretical calculations for thermal conductivity enhancements in fibre composites are well documented throughout literature [11–14], partly including C-nanotubes as inclusions, e.g. by Nan et al. [15] or Deng et al. [16]. In what follows we summarize different analytical models for predicting the thermal conductivity for MMCs and as special case MWNT composites with high and low loadings of randomly oriented CNTs. It is clear, that in case of high loaded composites, interactions among the inclusions must be considered. So far, this is currently outside the theoretical possibilities.

In its simplest form, a composites' thermal conductivity can be calculated following the rule of mixtures according:

$$\kappa_c(\|\text{heat flow}) = \kappa_m f_m + \kappa_i^{33} f_i \tag{1}$$

where κ denotes the thermal conductivity, f the volume fraction, the indices c, m and i the composite, isotropic matrix and the inclusions (fibres) respectively. κ_i^{33} is the inclusion longitudinal thermal conductivity, parallel to the x_3 (longitudinal) axis. The fibres are oriented parallel to a steady-state flow of heat and assumed to be infinite long. The overall thermal conductivity κ_c is then in the longitudinal direction (along x_3 axis).

Note, that Eq. (1) does neither consider the non-straightness of fibres like CVD grown MWNTs, nor an interfacial thermal resistance, nor a random 2D or 3D fibre distribution. The last might be the most important issue, as the highly anisotropic thermal conductivity behaviour of the MWNT-fibres in radial and axial direction must be considered.

The model of Hatta–Taya [12] is based on the Eshelby method: here the elastic problem with stress (σ_{ij}), strain (ε_{ij}) and stiffness (C_{ijkl}) tensor correspond to the thermal problem with heat flux (q_i), temperature gradient (T_i) and the thermal conductivity (k_{ij}) respectively. Following the Hatta–Taya model, the composite thermal conductivity for a completely random distribution and a 2D inclusion misorientation can be calculated by:

$$\kappa_{c} = \kappa_{m} \left(1 + \frac{f_{i} \left(\kappa_{i}^{33} - \kappa_{m}\right) \left[0.5 \left(\kappa_{i}^{33} - \kappa_{m}\right) + 2\kappa_{m} \right]}{0.5 \kappa_{m} \left(\kappa_{i}^{33} - \kappa_{m}\right) \left(2 - f_{i}\right) + 2\kappa_{m}^{2}} \right)$$
(2)

For the 3D orientation case the model is defined by:

$$\kappa_{c} = \kappa_{m} \left(1 - \frac{f_{i} (\kappa_{m} - \kappa_{i}^{33}) \left[0.5 (\kappa_{i}^{33} - \kappa_{m}) + 3\kappa_{m} \right]}{R \kappa_{m} (\kappa_{i}^{33} - \kappa_{m}) (2 - f_{i}) + 3\kappa_{m}^{2}} \right)$$
(3)

$$R = 1.5 - f_i \tag{4}$$

Note that the shape tensor S_{ij} – given in the original paper of Hatta and Taya – for a cylindrical fibre derives to S_{11} = 0.5 and S_{33} = 0 simplifying the equations in the above given way. For inclusions others than fibres, the formulation given can be described in a general way, details in [12,13]. The model is also based on the assumption that the inclusions are completely surrounded by the isotropic matrix; therefore it is only valid up to an intermediate range of fibre volume fraction, $f_i \leq 0.5$. Other effects such as fibre non-straightness, thermal interface conductance and inclusion size can be incorporated by modifying the effective inclusion thermal conductivity. The limited heat transfer capability at the interface can be considered by the presence of a very thin interfacial barrier layer, described by the thermal interface conductance h_{bd} . This barrier layer reduces the equivalent thermal conductivity of the fibres. The effects of the thermal interface conductance h_{bd} give rise to the formulation by Hasselman and Johnson [17], which is described in detail elsewhere and not considered here.

Similar relationships have also been obtained by Nan et al. [15] and Deng et al. [16], describing composites considering nonstraight C-nanotubes and a limited thermal interface conductance. For composites with low loadings of randomly oriented (but straight) MWNTs of average length *L* and diameter *d*, an analytical estimate for the effective thermal conductivities κ_c , of the CNT composites is given by Deng et al. [16]:

$$\kappa_{c} = \kappa_{m} \left(1 + \frac{f_{i}}{3} \left[\frac{1}{\left(\kappa_{i}^{33}/\kappa_{m} - 1\right)^{-1} + H} + \frac{2}{\left(\kappa_{i}^{11}/\kappa_{m} - 1\right)^{-1} + (1 - H)/2} \right] \right) (16)$$
(5)

where *H* denotes the influence of the aspect ratio p = L/d (details see [16]).

Calculations were performed assuming a silver matrix composite ($\kappa_m = 425 \text{ W m}^{-1} \text{ K}^{-1}$) and two theoretical intrinsic MWNT thermal conductivities of $\kappa_i^{33} = 2000 \text{ W m}^{-1} \text{ K}^{-1}$ and 6000 W m⁻¹ K⁻¹ respectively. Results presented in Fig. 6 consider the different models described by Eqs. (1)–(4) to illustrate the influence of different intrinsic MWNT conductivities on the overall composite's conductivity and the models. Both are compared with experimental results. For the model of Deng (formulation (5)), an aspect ratio *p* of 2000 was assumed resulting in a value of 1.8E^{-6} for factor *H*.

In general the highest increase in conductivity with increasing nanotube content is predicted by the ROM model, Eq. (1). All other models show a smaller increase in conductivity. Including the experimental data (only cobalt metallized MWNT-samples displayed) shows that the intrinsic thermal conductivity of the MWNTs must be relatively high at very low loadings of nanotubes; the data are closely described by the 2D-model and κ_i^{33} = 6000 W m⁻¹ K⁻¹ (Fig. 6). For higher MWNT volume fractions the 2D- and 3D-model fit conveniently to a MWNT thermal conductivity of 2000 W m⁻¹ K⁻¹. This is in good agreement with values given in literature for nanotubes. However the model predictions fail the higher the MWNT-content, as $\kappa_c/\kappa_m \ll 1$ is observed.

Comparing the different models with experimental data, the correlation between cobalt metallized MWNTs and model Eqs. (1)-(4) is high for small MWNT concentrations, thus indicating a thermal interface close to optimum. Using non-metallized MWNTs obviously results in imperfect interfaces over the total range of MWNT concentration and thus a large discrepancy to the modelling.

3.4. TEM analysis

Two divergent ways of preparing a TEM conditioned sample (sample Ag/Co–C0.5) were followed: cutting by FIB (DualBeam-FIB Quanta 200 3D), subsequent thinning by ion milling (Gentle-mill) or ultra-microtome cutting (Leica Ultracut E). Fig. 7 highlights the FIBed and ion milled structure, which feature divergent thin areas. Arrows mark the possible former position of individualized



Fig. 6. Prediction of the normalized thermal conductivity κ_c/κ_m as a function of different analytical models (Eqs. (1)–(5)) and of different theoretical thermal conductivities for MWNTs assuming $\kappa_m = 425$ W m⁻¹ K⁻¹, $\kappa_i^{33} = 2000$ and 6000 W m⁻¹ K⁻¹ respectively. For formulation (5), an aspect ratio *p* of 2000 was assumed resulting in a value of $1.8E^{-6}$ for factor *H*.



Fig. 7. HR-TEM image of the ultra-microtome cut sample Ag/Co–C0.5; the insert represent the high resolution image of the tagged area.

MWNTs. Nanotubes cannot be detected directly and might be removed from the structure during preparation. Nevertheless there is the impression of a "replica" visible within the microstructure, commemorating on the curled structure of a nanotube.

The second preparation method - ultra-microtome cutting gives a different imagination of the sample (same sample Ag/Co-C0.5). First it shows a constant thickness over a large area (Fig. 8). The microstructure shows some "holes", representing former areas of agglomerated or less penetrated MWNTs. No individual MWNTs can be detected within the matrix. This is rather a hint for the non-existence of MWNTs in the silver matrix, but can be attributed to the two involved constituents - C and Ag -, two materials of each quite large divergent atomic numbers Z and therefore transmission behaviour. Therefore this is simply not an easy task to separate both and detect them in a TEM image. The only areas where MWNTs are visible are the cavities. At the "interface" or intersection between the cavity and the MWNTs one can interpret the outgrowing of them respectively the continuation of the MWNTs into the matrix, although not directly visible. It appears to be fairly implausible that those observations concern a bundle of MWNTs lying on top or beneath the thin foil. It is also notable that many particles are visible on top of the MWNTs. Up to now it was not possible to verify their exact nature. Neither EDAX nor EELS analysis yielded reliable results. The spectra gave silver, carbon, as well as copper (TEM-grid), but no cobalt at all.

Note in particular cobalt does not even form thermodynamically stable carbides. Yet even with high resolution TEM and neither EDX nor EELS analysis revealed layers of cobalt at the interface to the MWNT. A possible explanation for increasing the thermal conductivity by cobalt additions is that cobalt might exhibit a tendency to segregate to grain boundaries or to the interface due to the high positive enthalpy of mixing with solid silver. It may thus be that a very thin adsorption layer of a few atoms covers the MWNTs in the metal matrix, with which the MWMT bonds much more strongly than with a pure silver matrix.

4. Conclusion

Investigations presented here indicate that in Ag–X/MWNT composites the thermal conductivity can increase and the coefficient of thermal expansion can decrease if two preconditions are fulfilled:

- (a) The concentration of MWNTs is low and concomitantly.
- (b) An active element X is present (in low concentration).

We furthermore note that these materials can have a thermal conductivity up to 10% higher than pure silver concomitant with

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Fig. 8. HR-TEM images of the ultra-microtome cut sample Ag/Co-C0.5, the inserts represent the high resolution images of the tagged areas.

a 6% decrease in coefficient of thermal expansion making them very interesting materials for heat sinks. Improved bonding is notable due to active elements resulting in both increased heat transfer and improved load transfer between the matrix and the MWNT. This explains the increase in thermal conductivity and the drop in CTE. At high MWNT-contents the impact of active elements diminishes and results in a pronounced degradation of thermo-physical properties. This can be attributed to the non-straight, entangled and tortuous nature of CVD as-produced MWNT-fibres. Hence the necessary contact between fibres and matrix for heat and load transfer cannot be established, as the matrix cannot penetrate the fibre bundles thoroughly.

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