

## ABOUT THE EFFECT OF CARBON NANOTUBES ON THE OVERALL THERMAL CONDUCTIVITY IN Cu–Ti/CNT COMPOSITES

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### **Abstract**

*Copper matrix/Carbon Nanotubes (CNTs) composites and titanium as “active” element were considered and their room temperature thermal conductivities measured using a steady state heat flow method. The evolutions of the thermal conductivity as a function of CNT and titanium concentrations in Cu–Ti/CNT composites are presented. As opposed to expectations, the thermal conductivity of the composites was below pure copper. However, a positive effect of the CNT additions was clearly detectable as the thermal conductivity is higher than unreinforced Cu–Ti alloys.*

**Keywords:** *carbon nanotubes, MMCs (Metal Matrix Composites), fibre/matrix bond, thermal properties*

### **INTRODUCTION**

In recent past decades the proposed outstanding intrinsic properties of Carbon Nanotubes CNTs (mainly multi-walled Carbon Nanotubes MWNTs) have inspired researchers and fired speculations (and stimulated several project proposals as well), as to whether CNTs could be used in metal matrix composites MMCs to raise the overall thermal conductivity of the composite bodies [1,2]. Highly conductive filler materials like CNTs as well as diamonds came into the focus of MMC research, as heat producing components in modern micro-, and power-electronics demand improved cooling efficiencies [3]. While improvements in thermal properties (thermal conductivity and CTE) in diamond MMCs seem to be rather easily attainable and technologically advanced, scientific results of CNTs in MMCs are rather scarce and mostly disappointing. Although the outstanding intrinsic (thermophysical) properties of CNTs are undoubtable, the scientific question is still not answered, if CNTs can positively contribute to an enhancement of composite thermal conductivity. Few works using Carbon Nanofibres (CNFs) were performed and show no enhancement, respectively, a pronounced degradation in thermal conductivity [4,5].

This unexpected behaviour can be attributed to a number of challenging problems one has to face during implementation of the extremely tiny fibres in a metallic matrix: difficulties arising by the high aspect ratio of CNT–fibres compared to the relatively large scale diamond crystals, thus leading to problems in uniform distribution of the phases (also aqueous based ones), bundling of the naturally entangled and tortuous CNTs in their as-produced condition, surface and interface problems, alignment of the fibres and equal contaminations with catalyst particles and carbon/graphitic by-products as well.

Although many approaches exist to overcome those problems, many seemed to be unsolved. The formation of homogeneous dispersions might be supported by coating the nanofibres with the matrix metal followed by hot pressing compaction. Due to the lack of chemical reactivity and wetting between carbon and the matrix metal, the investigation of

methods to adjust the interface between the metal and the carbonaceous inclusion towards excellent thermal and mechanical behaviour plays an essential role. Several potentially interesting reactive matrices degrade the fibres at high temperatures by severe reactions and therefore development has concentrated on matrices chemically inert towards carbon, such as copper. In order to address the thermal conductance between metal/inclusion conductors interfaces have to be improved, if a layer of electron-conducting material is introduced at the interface between the two phases. This intermediate layer must have high bond strength to the fillers and the matrix.

Titanium was identified as an appropriate candidate element to address the interfacial bonding between copper and carbon nanotubes. Titanium can either react with the carbon to give titanium-carbide or be dissolved within the copper matrix. It has to be considered, that any dissolved Ti in Cu significantly reduces the thermal conductivity of the matrix.

Here we present results on the influence of titanium additions in copper/multi-walled carbon nanotubes composites on the evolution of thermal conductivity. We further compare the amounts of CNTs and titanium needed to confer good bonding within the Cu–Ti/MWNT couple.

## EXPERIMENTAL PROCEDURE

Multi-walled carbon nanotubes fabricated by a chemical vapour deposition process were used in stable aqueous dispersions (FutureCarbon GmbH, Bayreuth, Germany). Titanium metallization was performed by the addition of titanium hydride  $\text{TiH}_2$  powders to the CNT suspensions, drying and subsequent heat treatment under a constant flow of hydrogen gas ( $1 \text{ L} \cdot \text{min}^{-1}$ ) at temperatures up to 1273 K. Those as-metallized CNTs were re-dispersed in an aqueous solution of 1M copper nitrate. An aqueous solution of 1M oxalic acid was slowly added to the copper nitrate Ti-metallized CNT suspension under vigorous stirring. A constant temperature of 353 K was adjusted during unification. Copper oxalate with incorporated CNTs is formed instantaneously. The precipitate was subsequently filtered off, dried and decomposed to metallic copper–Ti/CNTs composite powders under a constant flow of hydrogen gas ( $1.5 \text{ L} \cdot \text{min}^{-1}$ ) at temperatures up to 773 K.

An overall volume fraction of CNTs was adjusted between roughly 0.7 and 2.5 vol.%, titanium content was varied between 0.2 and approximately 3 vol.%. However, the composition of the composite powders and the consolidated composite samples were controlled by C-analysis (induction furnace combustion) and ICP-OES measurements respectively.

The composite powders were consolidated by die pressing, sintering under a constant hydrogen gas stream ( $1 \text{ L} \cdot \text{min}^{-1}$ ) 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 hours.

Pure copper (99.99 wt.%), Cu–Ti alloy and Cu–TiC samples were prepared as reference materials. Cu–Ti alloys were produced by two different methods: first by vacuum induction melting of the pure substances, second by the same method described above for the preparation of Cu–Ti/MWNT samples by decomposing Cu-oxalate/ $\text{TiH}_2$  composite precursors, and consolidated by hot pressing. Cu–TiC reference materials were produced by decomposing Cu-oxalate–TiC mixtures under  $\text{H}_2$  and hot pressed as well. The TiC powders used had a mean particle size of 2  $\mu\text{m}$ .

Consolidated samples were characterized by LOM, SEM and the condition of the MWNTs embedded in the matrix was followed by FEG-SEM analysis.

Thermo-physical properties were determined on cuboid-shaped samples. In the case of CNT containing samples the direction of measurement was perpendicular to the direction of hot pressing (cast and hot pressed reference samples are assumed to behave isotropically). The thermal conductivity  $\kappa_{c/m}$  was measured by a steady state, equal heat-flow comparative method against a brass reference. To this end, the temperature gradient in the samples was compared to that in the reference by means of two Pt100 elements in both sample and reference. The system was calibrated with measurements on 5 N pure silver, aluminium or copper reference samples. We evaluate the overall uncertainty of the measured thermal conductivities to within  $\pm 2\%$  of the indicated values.

## RESULTS

Two different series of Cu–CNT composites were fabricated: the first attributed the influence of the CNT concentration in Cu and Cu–Ti matrix samples, the later realizing a constant Ti concentration of 0.25 vol.% Ti. The second series intended to study the influence of the Ti concentration at a constant CNT concentration (0.7 vol.% CNTs). This series was compared to matrix reference samples of Cu–Ti and Cu–TiC with increasing Ti and TiC content.

Carbon analysis revealed some divergences between desired and effective amounts of CNTs in the range of  $\pm 5\%$  (rel.) and might be attributed to the appearance of agglomerates in the delivered CNT dispersions. However, the measured concentrations by C-analysis were subsequently used as effective CNT concentrations in the composites and displayed in the graphs.

The titanium concentration in the samples was varied roughly between 0.2 and 3 vol.%.

The density of the consolidated composites is close to 100% for low CNT loaded samples. High volume fraction of CNTs in the composites can cause porosities up to 5%.

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

The FEG-SEM analysis of the matrix etched surface in a Cu–Ti /CNT composite is given in Fig.1. The evolution of the thermal conductivity for Cu/CNT and Cu–Ti/CNT composites at a constant Ti concentration of 0.25 vol.% vs. CNT-concentration and Cu–TiC samples in Fig.2. Note that the Cu–TiC graph is displayed against its C content and the CNT concentration is given as a carbon concentration. Figure 3 shows the evolution of the thermal conductivity for Cu–Ti–, and Cu–TiC reference samples respectively, and Cu–Ti/CNT composites; the CNT concentration is constant at 0.7 vol.%; the shown Cu–TiC line is displayed by its Ti content. Figure 4 displays the numeric evolution of the composite thermal conductivity following the DEM scheme for a Cu–TiC composite, assuming  $h_b = 4.2\text{E}^7 \text{ Wm}^{-2}\text{K}^{-1}$ ,  $\kappa_{\text{Cu}} = 405 \text{ Wm}^{-1}\text{K}^{-1}$ ,  $\kappa_{\text{TiC}} = 30 \text{ Wm}^{-1}\text{K}^{-1}$ . The 2D and 3D-models of Hattataya were applied to calculate the evolution of Cu/CNT composites, assuming a matrix thermal conductivity  $\kappa_m = 360 \text{ Wm}^{-1}\text{K}^{-1}$ , a longitudinal fibre conductivity  $\kappa_i^{33} = 2000 \text{ Wm}^{-1}\text{K}^{-1}$  and a transversal conductivity  $\kappa_i^{11} = 2.4 \text{ Wm}^{-1}\text{K}^{-1}$ . The thermal conductivity data measured were normalized using a  $\kappa_m$  value of  $360 \text{ Wm}^{-1}\text{K}^{-1}$  for Cu–Ti/CNT composites and  $405 \text{ Wm}^{-1}\text{K}^{-1}$  for Cu–CNT composites.

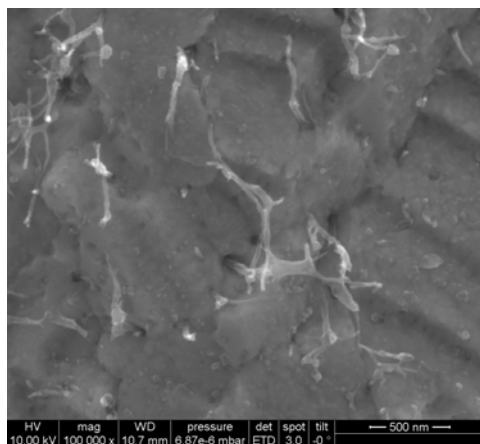


Fig.1. FEG-SEM image of Cu-Ti/CNT composite (2 vol.% CNT, 0.25 vol.% Ti), matrix etched by hot nitric acid.

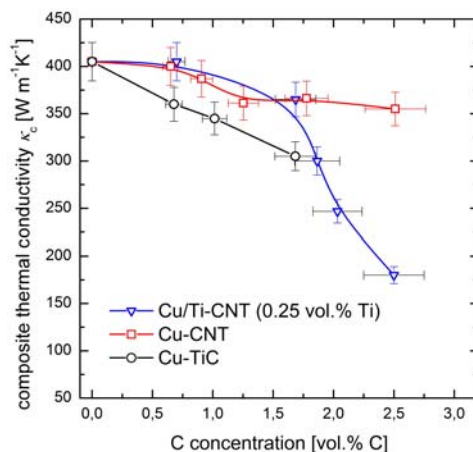


Fig.2. Evolution of the thermal conductivity for Cu/CNT and Cu-Ti/CNT composites; the Ti concentration is constant at 0.25 vol.%; the shown Cu-TiC line is displayed by its calculated theoretical C content, the CNT concentration is given as carbon concentration.

## DISCUSSION

The consolidated samples (surface etched by nitric acid) were analyzed by FEG-SEM (Fig.1) showing that the CNTs are still present and not totally consumed during metallization processing, although bundles of CNTs are still visible in cases where no titanium was added (not displayed).

Sporadic individualized MWNTs can be observed sticking out of the copper matrix, whereas areas of uncovered MWNTs bundles are visible in other areas. Obviously the presence of an active element like titanium enhances the deposition of copper on the primarily metallized CNTs and incorporates the nanotubes more easily. The active elements might act as nuclei resulting in a preferred deposition of the matrix on those sites.

Recent reports of Cho [6], Chu [7], Kim [8] (and more recent of Yamanaka [9] on Ni-CNT composites), on the successful fabrication of CNT-reinforced Cu matrix composites by means of a particle-compositing method followed by spark plasma sintering (SPS), fed speculations about the contribution of CNTs to an increase in thermal conductivity at low volume fractions.

Their thermal conductivities, however, showed either no enhancement or quite limited contributions at volume fractions of up to 1.5 vol.% (Cho et al). Although they stated a maximum increase of roughly 2.5%, the enhancements could be concealed by the uncertainty of the measured thermal conductivities to within  $\pm 5\text{--}10 \text{ W m}^{-1} \text{ K}^{-1}$  of the indicated values, which is evident in laser flash measurements. At higher volume fractions, Cho et al. observed a decrease in thermal conductivity which they attribute to the increasing difficulties in dispersing bundled CNTs with an increase in the CNT content.

Other researchers reported similar disappointing results for ceramic composites (CMCs) or for MMCs with CNFs, see references in [6].

In addition to problems of dispersion, the interface between CNTs and metal matrix plays a crucial role for  $\kappa_c$ , the thermal conductivity in composites, even when CNTs are well dispersed. It is well known that the interfacial thermal resistance causes a size effect in the overall composite thermal conductivity, which makes it difficult to increase  $\kappa_c$  when the size of the inclusions is below a certain limit, even if highly conductive fillers are used [10]. CNTs are clearly small enough to create such an effect [6].

However, from all above-mentioned reports, the question whether CNTs can contribute to the overall thermal conductivity in a composite is still not fully answered, as they do not address the role of interfacial elements. They are essential, as pure Cu and carbonaceous allotropes show no mutual reactivity.

With this contribution we wanted to clarify if the combination of carbide forming elements and CNTs could ever contribute to  $\kappa_c$  the overall thermal conductivity of composites.

On a first sight, Fig.2 indicates similar results to other research groups: no contribution of the CNTs to  $\kappa_c$  with increasing volume fractions; first the conductivity remains constant up to 0.5 vol.% CNTs and then slowly decreases with increased CNT content. Samples with titanium additions show a similar conductivity evolution up to roughly 1.7 vol.% CNTs, whereas increasing volume fractions of Ti metallized CNTs give a pronounced decrease in  $\kappa_c$ . We first assume that this is a result of the matrix solid solution formation between copper and titanium, responsible for a sharp decrease in  $\kappa_m$ , the matrix thermal conductivity. A very small increase (compared to a pure copper matrix) in  $\kappa_c$  might be interpreted at a very low volume fraction (up to 0.5 vol.%), but is more or less concealed by the uncertainty of the measured thermal conductivity values.

Special emphasis was put on the preparation of reference samples, as Cu–Ti/CNT samples should not be stringently rated against pure copper, as is often done. In this context it was also of interest to evaluate the possible formation of TiC in Cu–Ti/CNT composites and determine their possible contribution to thermal conductivity degradation in copper composites.

However, the matrix reference samples in Fig.3 show the expected TC evolution of copper with increasing titanium content, in line with data reported elsewhere or similar reported data [4], whereas a different behaviour is notable between molten samples and hot pressed ones. This can be attributed to a better dissolution of titanium in the case of liquid processing, whereas by powder metallurgy the condition of the titanium is important, as natural oxidation layers of powders used and oxidation during handling respectively must be considered. Therefore the Ti content in solid solution is lower, thus resulting in an increase of thermal conductivity compared to a fully dissolved Ti in Cu by liquid metal processing of bulk substances.

Cu–TiC samples generally exhibit a much higher thermal conductivity compared to all reference samples and the Cu–Ti/CNT composites. As TiC is not soluble in the Cu lattice the thermal conductivity degradation is much lower compared to the reference samples and thus mainly driven by the intrinsic thermal conductivities of TiC (around 30 Wm<sup>-1</sup>K<sup>-1</sup>) and Cu and their proportion.

If we assume mutual dissolubility between the TiC phase and Cu, the thermal conductivity of such composites can be calculated – in the simplest form – by the rule of mixture (ROM) or more sophisticated by the DEM scheme (see details and formulation in [10]). However, in both cases the theoretical thermal conductivity of Cu–TiC composites should be much higher than the experimental values reflect (see Fig.4).

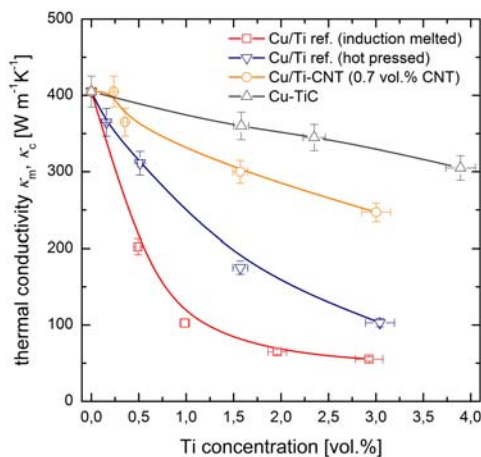


Fig.3. Evolution of the thermal conductivity for Cu–Ti, and Cu–TiC reference samples respectively, and Cu–Ti/CNT composites; the CNT concentration is constant at 0.7 vol.%; the shown Cu–TiC line is displayed against its Ti content.

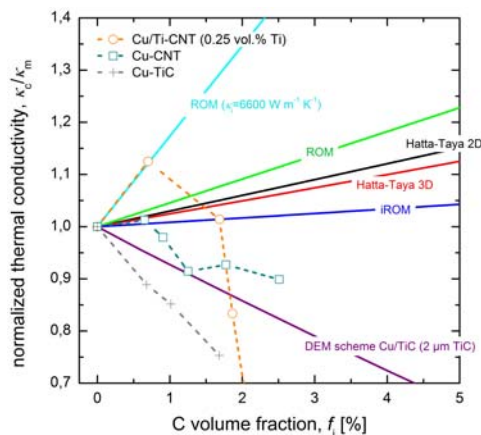


Fig.4. Numeric evolution of the composite thermal conductivity for CNT composites following the 2D and 3D-models of Hatta-Taya according eq. (1) and (2), and the ROM and iROM models, assuming  $\kappa_m = 360 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\kappa_i^{33} = 2000 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\kappa_i^{11} = 2.4 \text{ W m}^{-1} \text{ K}^{-1}$ . A second graph is displayed for the ROM model using  $\kappa_i^{33} = 6600 \text{ W m}^{-1} \text{ K}^{-1}$ . The DEM scheme was applied for a Cu–TiC composite, assuming  $h_{bd} = 4.2 \text{ E}^7 \text{ W m}^{-2} \text{ K}^{-1}$ ,  $\kappa_{Cu} = 405 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\kappa_{TiC} = 30 \text{ W m}^{-1} \text{ K}^{-1}$  according formulations given in [10]. The measured thermal conductivity data were normalized using a  $\kappa_m$  value of  $360 \text{ W m}^{-1} \text{ K}^{-1}$  for Cu–Ti/CNT composites and  $405 \text{ W m}^{-1} \text{ K}^{-1}$  for Cu–CNT composites.

However, the remarkable feature of Fig.3 is that with increasing Ti concentration all Cu–Ti/CNT composites' samples (constant CNT concentration of 0.7 vol.%) possess a significant higher thermal conductivity compared to matrix reference samples. Hence it is verified, that CNTs can positively contribute to the overall composite thermal conductivity, with the constraint that an active element like titanium must be present. Additionally, the



comparison of Cu–Ti/CNT and Cu–TiC composites verifies that the CNTs are not fully consumed and converted to TiC, as the conductivity of the CNT composites is lower.

### Theoretical considerations

Generally predictive schemes for physical properties of two- or even multi-phase materials are an important tool for assessing the potential of, and then tailoring of composite materials for specific applications. There are several predictive schemes described in literature, among the most powerful for predicting the thermal conductivity of fibre composites is the model of Hatta-Taya [11] and which is based on the Eshelby method: here the elastic problem with stress ( $\sigma_{ij}$ ), strain ( $\varepsilon_{ij}$ ) and stiffness ( $C_{ijkl}$ ) tensor correspond to the thermal problem with heat flux ( $q_i$ ), temperature gradient ( $T_i$ ) and the thermal conductivity ( $\kappa_{ij}$ ) respectively. Following the Hatta-Taya model, the composite thermal conductivity for a completely random distribution and a 2D (circular cylindrical) inclusion misorientation can be calculated by:

$$\kappa_c = \kappa_m \left( 1 + \frac{f_i (\kappa_i^{33} - \kappa_m) [0.5 (\kappa_i^{33} - \kappa_m) + 2\kappa_m]}{0.5\kappa_m (\kappa_i^{33} - \kappa_m) (2 - f_i) + 2\kappa_m^2} \right) \quad (1)$$

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

$$\kappa_c = \kappa_m \left( 1 - \frac{f_i (\kappa_m - \kappa_i^{33}) [0.5 (\kappa_i^{33} - \kappa_m) + 3\kappa_m]}{R\kappa_m (\kappa_i^{33} - \kappa_m) (2 - f_i) + 3\kappa_m^2} \right) \quad (2)$$

$$R = 1.5 - f_i \quad (3)$$

Note that the shape tensor  $S_{ij}$  - given in the original paper of Hatta & Taya - for a cylindrical fibre derives to  $S_{11} = 0.5$  and  $S_{33} = 0$  simplifying the equations in the way given above. 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 well-known formulation by Hasselman and Johnson, which is described in detail elsewhere and not considered here.

Calculations were performed assuming a copper–titanium matrix composite with 0.25 vol% Ti ( $\kappa_m = 360 \text{ Wm}^{-1}\text{K}^{-1}$ , an approximated value, estimated by the experimental results in Fig.3) and a theoretical intrinsic CNT thermal conductivity in longitudinal fibre direction of  $\kappa_i^{33} = 2000 \text{ Wm}^{-1}\text{K}^{-1}$ .  $\kappa_i^{11}$ , the radial fibre (CNT) thermal conductivity was assumed to be in the typical order of graphite fibres ( $2.4 \text{ Wm}^{-1}\text{K}^{-1}$ ). An additional graph for the ROM model is displayed using  $\kappa_i^{33} = 6600 \text{ Wm}^{-1}\text{K}^{-1}$ , a value often cited for single wall nanotube SWNTs.

The DEM scheme was applied to calculate the theoretical conductivity for a Cu–TiC composite; details of formulations are given in [10]. The calculations were performed assuming  $h_{bd} = 4.2 \text{ E}^7 \text{ Wm}^{-2}\text{K}^{-1}$ ,  $\kappa_{Cu} = 405 \text{ Wm}^{-1}\text{K}^{-1}$ ,  $\kappa_{TiC} = 30 \text{ Wm}^{-1}\text{K}^{-1}$ .

Note that the measured thermal conductivity data displayed in Fig.4 were normalized using a  $\kappa_m$  value of  $360 \text{ Wm}^{-1}\text{K}^{-1}$  (Cu–Ti/CNT composites) and  $405 \text{ Wm}^{-1}\text{K}^{-1}$ , respectively (Cu–CNT composites). Results presented in Fig.4 consider the different models described by equations (1) – (2) and by the ROM and iROM models to illustrate the influence

of MWNT additions on the overall composite's conductivity and the models. Both are compared with experimental results.

In general the highest increase in conductivity with increasing nanotube content is predicted by the ROM model, the least by iROM, thus both represent the extreme boundaries. Considering the steric orientation of the CNTs within the matrix, represented by the 2D and the 3D models, results in a degradation of thermal conductivity. The corresponding graphs are, as expected, between the ROM and iROM model.

Comparing the theoretical calculations and the experimental results shows that the few composites with very low CNT loadings fit the models, especially the one with the highest conductivity, which perfectly narrows the ROM model using  $\kappa_i^{33} = 6600 \text{ Wm}^{-1}\text{K}^{-1}$ . In this case we can imagine being quite close to the uppermost boundary theoretically possible in such systems. Hence, we can describe the heat transfer capability at the matrix/fibre interfaces being optimal, if low inclusion loadings and concomitantly additions of titanium are fulfilled.

Nevertheless, with increasing CNT content the conductivity contribution of the CNTs diminishes rapidly and all model predictions fail.

At high MWNT content 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.

To rate the influence of larger titanium additions, we have to face the possibility of severe reactions between the CNTs and the Ti, possibly fully consuming the fibres or the formation of undesirable thick TiC layers, acting as physical thermal barrier to the heat flow across the interface due to the low intrinsic thermal conductivity of TiC. In order to reduce and exclude excessive TiC formation, the amount of titanium should be strictly limited.

## CONCLUSION

Investigations presented here indicate that the presence of MWNTs in Cu-Ti/CNT composites can contribute to an increase in composite thermal conductivity. This finding is restricted to the additional presence of an "active" element like titanium in the matrix. If no carbon affine elements are added, the thermal conductivity is not positively influenced. It must be also clear, that the thermal conductivity of a pure copper reference will be not (under any circumstance) be exceeded.

At high CNT contents the impact of the presence of an active element 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. The same effect is visible for increasing Ti content, as the composite conductivity rapidly decreases due to the low intrinsic conductivities of Ti and TiC.

FEG-SEM investigations were performed at the university service institution for transmission electron microscopy USTEM within the Vienna University of Technology, Austria.

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