PREPARATION AND INTERFACE PROPERTIES OF CARBON REINFORCED COPPER-MMC'S

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Abstract

The *nanofibers are a promising reinforcement for copper based composites. The high thermal conductivity of carbon nanofibers (up to 2000 W/mK) is expected to improve the thermal properties of the composite material. The lack of any interfacial reaction between copper and carbon requires either a pre-treatment of the nanofibers and/or modification of the matrix (e.g. via alloying). The influence of both possibilities on the thermal performance (thermal diffusivity/conductivity and Coefficient of Thermal Expansion) of the material is shown. In addition microstructural analyses are carried out in order to assess the nanofiber distribution and the quality of the interface.*

1 Introduction and State of the Art

Today several materials are used as substrate, heat spreader or heat sink components in electronic devices. These materials match the thermal expansion coefficients of Si, GaAs or alumina. Materials like Mo-Cu, W-Cu, Kovar, Al/SiC, AlN, diamond, etc. are used if a low coefficient of thermal expansion (CTE) in combination with high thermal conductivity is needed for electronic packaging. Nevertheless these materials reveal several limitations or drawbacks: high density (Mo-Cu, W-Cu), limited thermal conductivity (Kovar), bad machinability (Al/SiC, diamond, AlN) or high price (diamond).

Standard copper material, which has a high thermal conductivity, has disadvantages due to its high coefficient of thermal expansion, affecting reliability and safety of products. This mainly is a consequence of the thermal mismatch (CTE) between copper and the insulating substrate. If this mismatch is too high the thermal cycling capability is reduced significantly to some hundreds of temperature cycles. In addition, for automotive or aerospace applications a second disadvantage is the high density of pure copper.

There are several promising concepts under development which overcome these limitations, e.g. by introducing filler materials into the copper matrix such as graphite flakes, carbon fibers or even carbon nanofibers/nanotubes.

For several years carbon fibers with diameters of around 7-10 μm have been used as reinforcement in various metallic matrices since they are characterized by a low CTE and a high thermal conductivity (at least in longitudinal direction). Several attempts have been made to prepare Cu based composites which are reinforced by either continuous or short carbon fibers [1-3] due to their promising high thermal conductivities combined with a low CTE. Among the used technologies for fabrication of Cu-C composites powder metallurgical processes (pressing+sintering [4,5], hot pressing or hot isostatic pressing [6-8]) are applied, as well as liquid phase infiltration methods such as gas pressure infiltration [9-11] or squeeze casting [12,13]. One of the promising powder metallurgical processes is based on the use of electrochemically coated short carbon fibers since a perfect fiber distribution can be achieved [14,15]. As mentioned above, for a full exploitation of the theoretically predicted thermal properties this is still not sufficient to provide a good thermal or mechanical interface, due to the weak bonding.

New types of carbon fibers have been brought to the market. The so called vitreous grown carbon fibers (VGCF) are characterized by a size approx. a factor 100 smaller than that of conventional short carbon fibers. The thermal conductivity reaches values up to 2000 W/mK which makes these fibers attractive as a reinforcement in metal matrix composites. With the availability of these fibers in kg batches at an affordable price they are promising candidates for the reinforcement of copper matrix

composites to achieve a material combining high thermal conductivity and improved mechanical properties with a reduced CTE. Such a combination of properties is very attractive for applications in highly thermally loaded devices, e.g. as heat sinks for high power modules or optoelectronic components. The advantage of Cu-CNF over Cu-diamond composites is the possibility to obtain a heat sink/heat spreader with high surface finish since it is easy to machine.

First attempts to prepare copper carbon nanofiber/nanotube composites have already been reported [16-18]. The used methods are basically powder metallurgical processes as well as the coating of nanofibers by copper using electrochemical deposition followed by hot pressing. One of the difficulties of this approach is to achieve a homogenous distribution of the nanofibers in the Cu matrix without destroying them. Although this can be overcome by electrochemical coating, a weak adhesion limits the thermal properties to values far below the predicted due to dewetting.

Some work has been done on copper reinforced with nano-carbon fillers. Basically Cu-CNT/CNF composites have been prepared by powder metallurgical mixing of Cu powder and CNTs/CNFs or via a coating [16]. Agood distribution of CNTs/CNFs was obtained by coating or mixing at molecular level [17]. The main problem in Cu-CNT composites prepared by pressing and sintering is the remaining porosity which can only be reduced by secondary processing such as rolling.

2 Experimental Approach

As described in the introduction there is a potential for the application of copper reinforced with carbon nanofibers, although there are several problems to solve. These problems are basically known already from the work with carbon fibers but some of them represent key problems in working with CNFs (e.g. dispersion). The goal of the present study was to identify concepts how the critical path of heat conduction between the metal matrix and the carbon nanofiber can be improved, which represents also one key step to get a material with high thermal conductivity. In order to obtain a good dispersion, the CNFs were coated with the matrix material. Table 1 summarizes the problems related to composite materials reinforced with carbon fibers and carbon nanofibers.

Within this work, two different approaches will be followed in order to address two of the key challenges in Cu-CNF composites:

a) the investigation of alloying elements on the thermal properties (thermal interface properties): Here a chemical coating process was used to individualize and coat the carbon nanofibers in order to have a defined distribution. To the coated fibers third elements (active elements) where admixed and allowed to get a modified interface during hot pressing

b) Ad-mixing alloying elements bears the risk of reducing the thermal conductivity of the matrix. Alternatively the "active" element has been introduced into the composite by PVD-coating carbon nanofibers and then mixing with copper powder. These coatings (Mo and Cr) had a thickness of 10 to 100 nm. The influence on thermal behavior was studied.

Table 1: Overview of problems in carbon fiber and carbon nanofiber reinforced composites

Problems	Carbon Fibers	Carbon Nanofibers
Selection of suitable raw materials (different suppliers & qualities)	Material properties for different carbon fibers are available; measurement of properties possible too (even for transversal direction)	Characterization of CNF properties is not easy; limited availability; there are different suppliers, but it is difficult to get reproducible quality
Separation and dispersion of short fibers in the matrix material	Optimization of conventional blending techniques is sufficient; coating of fibers provides an advanced solution; fiber breakage has to be taken into account	To coat the CNFs is one of the solutions to obtain a good dispersion in the matrix; simple mixing has limitations (especially fiber alignment)
Alignment/ Orientation/ Anisotropy	Fiber aspect ratio of 1:10 to 1:100 results in fiber alignment during PM processing => anisotropic properties	Alignment of CNFs during PM processing is not confirmed yet; alignment by extrusion is possible
Densificat. of the composite	Optimization of processing conditions with regard to densification and interfacial reactions	Remaining porosity higher; interface reactions not same as for carbon fibers; severe reactions must be avoided
Interface	Interface plays an important role for mechanical and thermo physical-properties	Interface plays an essential role to exploit the potential of the reinforcement

For carrying out the experimental work, carbon nanofibers (VGCF, CNFs) from Showa Denko have been used. These CNFs were either coated by a PVD process (sputter deposition) with an active element (Cr or Mo) or a Cu film was deposited.

To the PVD coated fibers copper powder was admixed to obtain a Cu:C weight ratio of 91.5:8.5. For the Cu coated CNF, the ratio after the coating process was determined by weighting of the coated CNFs. The ratio between Cu and CNF was found to be approx. 94:6. In a previous work it was demonstrated that the approach to use Cu coated carbon fibers and to admix the active interface element was successful to increase the thermal interface and therefore to improve the thermal conductivity/diffusivity of the composite material. Here, same as in previous work, Ti and Cr have been used since both elements showed a good diffusion through the Cu layer [18]. The critical question for the CNF material is to identify the right amount of alloying element. Due to the very(!) large surface area in the CNF material, of course a higher amount of the alloying element is necessary to get the required effect to reduce the thermal contact resistance. Therefore either 0.3–2.0wt% Ti or 0.5–3.0 wt% Cr powder was added.

The CNFs have been coated by two different ways, either by PVD or chemical coating. In general the coating of fibrous materials, especially nanofibers is a challenging task.

The main disadvantage of PVD methods is its "line-of-sight" character, which means a permanent movement of the fibers is necessary to obtain a homogenous coating. Figure 1 shows coated CNFs. Not all of the CNFs are coated. There are some areas where the material was preferably deposited. As an active layer which should form a good bonding and a good thermal transfer to the matrix, molybdenum and chromium was used. The thickness of the coating was varied, nominally between 10 and 100 nm. The coating thickness was derived from sputtering time and from correlation to reference materials. It is difficult to identify/analyze a 10 nm coating on a 200 nm fiber, and the true coating thickness might be slightly different; but this method gave a good estimate of the Ti/Cr/Mo amount.

The copper coating was done by a chemical process involving the steps of dispersion, activation and coating. The thickness of the Cu coating was controlled by the amount of Cu solution. A weight ratio Cu:C of 94:6 was realized by the coating process. This corresponds to a relatively thick coating, which means a fiber content in the order of

20 vol%. To the Cu coated fibers different amounts of Ti or Cr were added in order to enhance adhesion at the interface during consolidation.

Table 2: overview on prepared and investigated samples including material composition and manufacturing route

	Composition	Manufac- turing route	Density [g/cm³]
Cu-CNF00	Cu coated CNF	Mixing of powders, (Cu: CNF =94:6)+Ti or Cr powder, hot pressing under hydrogen	7.85
Cu-CNF01	Cu coated CNF + 0.3wt. Ti		8.03
Cu-CNF02	Cu coated CNF + 0.6wt. Ti		7.84
Cu-CNF03	Cu coated CNF + 2wt. Ti		7.37
Cu-CNF04	Cu coated CNF + 0.5wt. Cr		7.74
Cu-CNF05	Cu coated CNF + 1wt. Cr		8.20
Cu-CNF06	Cu coated CNF + 3wt. Cr		7.93
Cu-CNF10	Uncoated CNF	Mixing of powders, (Cu: CNF =91.5:8.5), hot pressing under hydrogen	6.52
Cu-CNF11	PVD coated CNF (10 nm Cr)		6.80
Cu-CNF12	PVD coated CNF (50 nm Cr)		6.84
Cu-CNF13	PVD coated CNF (100 nm Cr)		6.72
Cu-CNF14	PVD coated CNF (10 nm Mo)		6.65
Cu-CNF15	PVD coated CNF (50 nm Mo)		6.68
Cu-CNF16	PVD coated CNF (100 nm Mo)		6.56

The different mixtures (summarized in Table 2) were hot pressed under hydrogen at 1000°C for 1 hour at a pressure of about 20 MPa. At this temperature a certain degree of exudation was observed. After the compaction the density of the samples was determined, followed by polishing and microstructural analysis. For the thermal characterization a laser flash measurement technique was used to determine the thermal diffusivity. The thermal conductivity was derived from density and specific heat. The coefficient of thermal expansion was determined in the temperature range between room temperature and 300°C using a dilatometer.
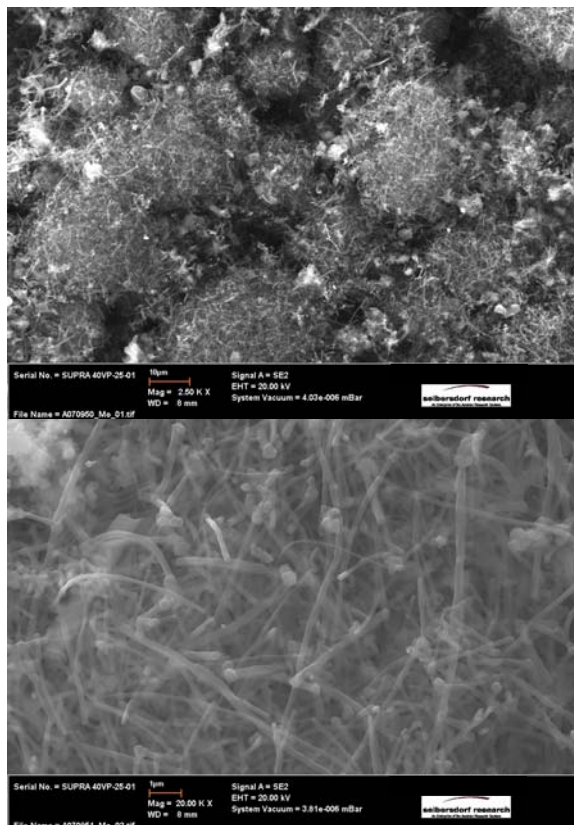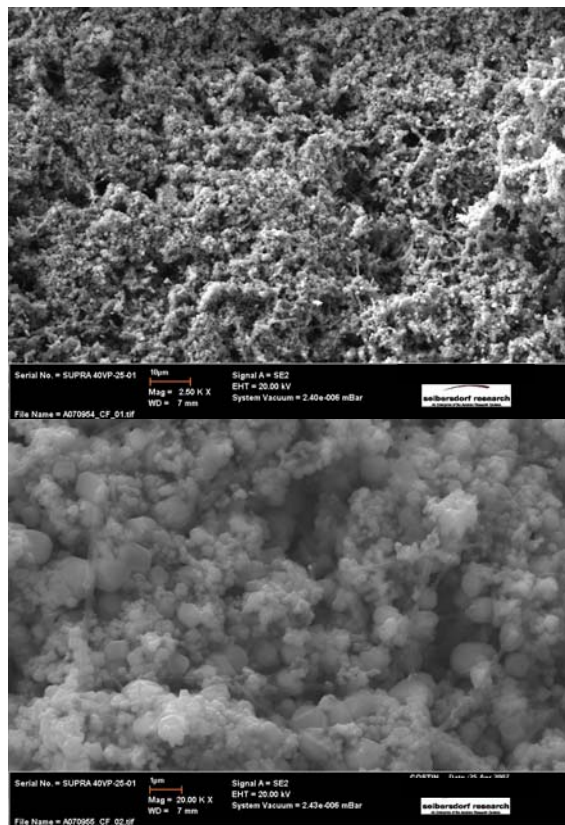
Figure 1a/b: SEM image of PVD coated CNFs (Mo)

Figure 2a/b: SEM image of Cu coated CNFs

3 Results and Discussion

Before starting with the preparation of the powder mixtures, the coated CNFs have been investigated by SEM. Especially the investigation of the PVD coated fibers is a problem since the coating thickness on the fibers is expected to be in the range of 10 to 100 nm. It seems there are clusters of CNFs, which was confirmed by SEM (BE mode). Further it was confirmed that the CNFs are coated uniformly with Mo (Figure 1a/b). The situation is different for the Cu coated CNF. Here basically (at high resolution) individual fibers are decorated with Cu islands. We cannot speak of a continuous coating on the fibers; the Cu particles rather act as a bridge between fiber clusters. So the term "composite powder" is better suited to describe the material shown in figure 2a/b.

The different powder mixtures (prepared according to table 2) were hot pressed. After consolidation the density of the samples was measured, showing that a densification to >90% TD was achieved.

In order to study the dispersion of the CNF and the homogeneity, cross sections have been prepared and studied with light microscopy and SEM. Between the two studied composites a difference in the distribution of carbon nanofibers was observed. While the coated fiber approach resulted in a homogenous dispersion of the CNF, PVD coated fibers were mixed with copper powder resulting in agglomerations.

Of course these clusters in the PVD coated CNF followed by mixing are impairing the thermal properties. But it can be assumed that for all mixed Cu+(PVD coated CNF) the dispersion is similar and therefore the role of the PVD coating thickness (10 to 100nm) or the coating element (Cr or Mo) can be studied. The main influence on the thermal properties in the PVD coated CNF composites comes from PVD coating, which should promote the heat propagation in the consolidated material.
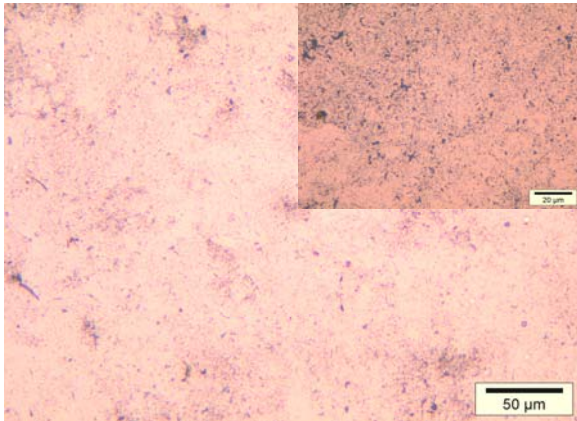
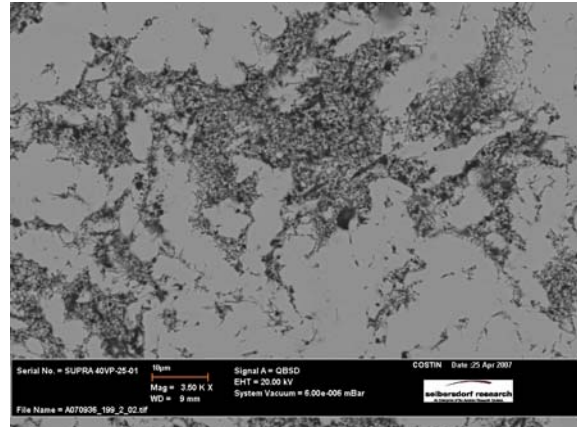Figure 3: Cross section of a Cu-CNF composite made from Cu coated CNFs

Figure 5: SEM image of agglomerates in the polished cross section
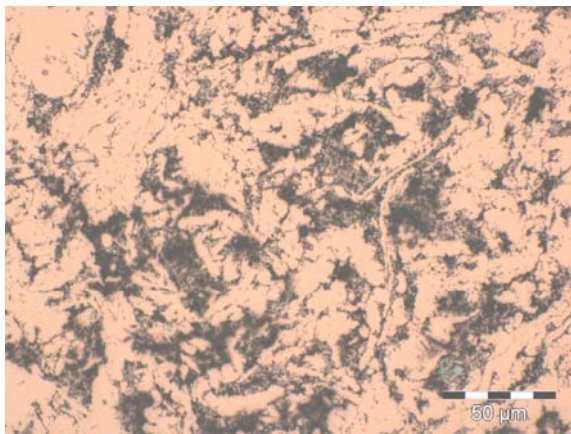

Figure 4: Cross section of a Cu powder+PVD coated CNF mixture
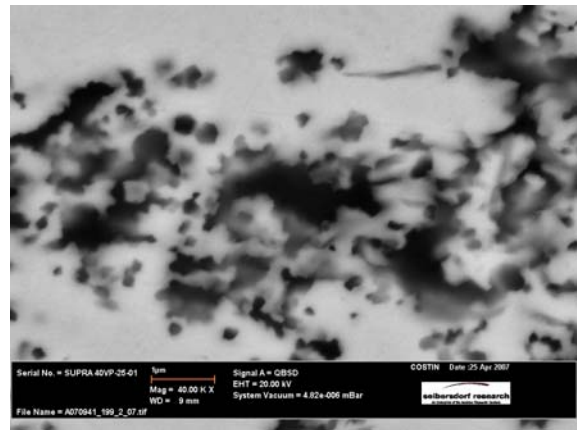

Figure 6: Magnification of Cu+CNF

Mo or Cr should act during hot consolidation as a source for carbide formation and provide good bonding to the CNF. The thickness of the coating of course will have an impact on the overall thermal performance of the composite material. If the coating is too thin it will not have an effect, if the coating is too thick a degradation of the thermal properties of the matrix material is the result.

For the Cu coated CNF basically a regular distribution of CNFs was observed with the exception of some agglomerates. The size of these agglomerates is much smaller (in the range of some micrometers) than compared to the material prepared by the mixing route (..tens of micrometers).

For the thermal analyses of the composite materials a laser flash method was used to determine the thermal diffusivity. In Figure 7 the derived thermal conductivities for the PVD coated CNF composite materials are shown as a function of the coating thickness. A thin coating (10 nm) has no effect on the properties. As the thickness increases to 50 nm a positive effect (reduction of thermal contact resistance between matrix and CNF) is observed. By further increasing the coating thickness the influence of the alloying element on the matrix properties becomes significant, because a 100 nm layer represents already a significant volume compared to the fiber volume.

In Figure 8 the thermal properties for the Cu coated CNF are shown. Here a similar situation is observed. A too large amount of Ti or Cr in the matrix has a negative effect on the matrix conductivity although the alloying element has a positive effect on the reduction of the thermal contact resistance. The maximum obtained thermal conductivity is observed at a relatively low concentration of Ti (0.2 wt%) while the amount for Cr is higher (1wt.%).
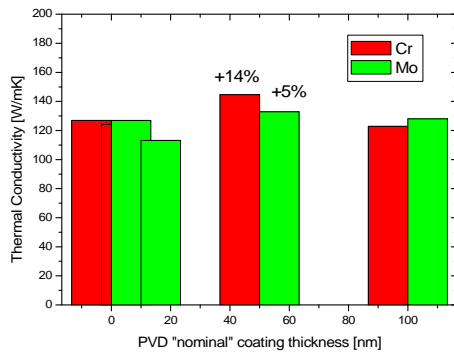

Figure 7: Thermal Conductivity for Cu+PVD coated CNF composites as a function of PVD coating thickness for Cr and Mo
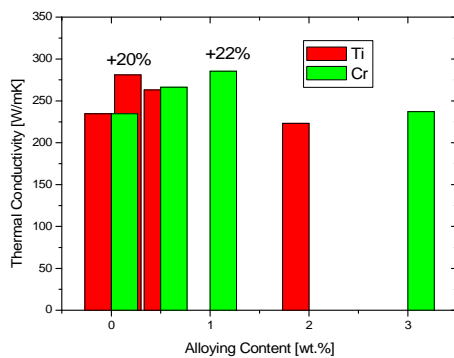

Figure 8: Thermal Conductivity for composites made of Cu coated CNF as a function of alloying content for Ti and Cr

Beside the thermal conductivity of the composite material, the second effect of the CNF reinforcement is the reduction of the CTE. Figure 9 shows the measurements of the thermal expansion behavior from the dilatometer measurements. Three cycles from RT to 300°C have been measured. The derived CTE is 12.8 ppm/K at 50°C, which is lower than the 16,5 ppm/K for pure Cu. Of course this is still beyond the required CTE of approx. 8 ppm/K or even lower. Since the actual fiber volume percentage

in this composite is around 20 vol%, a further reduction of the CTE is expected by increasing the fiber volume percentage.
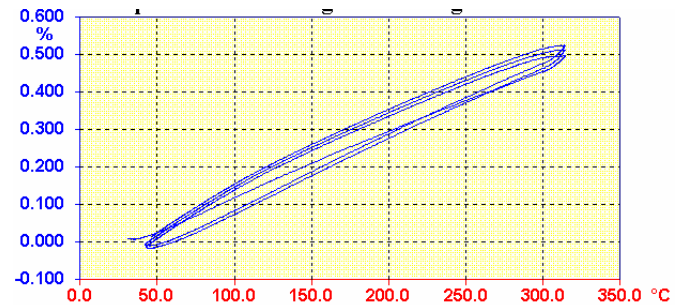

Figure 9: CTE measurement cycles (3 from RT to 300°C) of composite made from Cu-coated CNF

4 Summary and Conclusions

The first results dealing with Cu-CNF composite material with modified interface properties can be summarized as follows:

• Two different manufacturing approaches have been used to address the problem of the interface in Cu-CNF composites: the first one was based on PVD coated CNF, the second deals with the alloying of Cr or Ti to Cu coated CNFs.

• Starting from Cu coated CNF the result is a good dispersion of the CNFs.

• The thermal properties (thermal conductivity & diffusivity) are influenced by the two approaches.

As main points of future work the following topics have to be addressed:

• Optimization of the amount of alloying element, investigation of other alloying elements.

• Study the effect of hot pressing conditions on interface formation.

• Further analysis of thermal expansion and detailed microstructural analyses/carbide formation at the interface.

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