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Potential and challenges of metal-matrix-composites reinforced with carbon nanofibers and carbon nanotubes

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Abstract

With a continuous improvement of the production techniques for carbon nanofibers and carbon nanotubes along with an improvement of the available qualities of the materials, these reinforcements have been introduced into polymers, ceramics and metals. While in the field of polymers first success stories have been published on carbon nanofiller reinforcements, up to now metals containing these types of nanofillers are still a topic of intensive research. Basically a similar situation were found in those days, when micron sized carbon fibers came on the market. Today many applications of carbon fiber reinforced composites are existing, while metals reinforced with conventional carbon fibers are still only found in niche applications.

Several reasons can be identified, why the introduction of carbon based nanofillers (nanofibers/nanotubes) into metallic matrices is a difficult task. Nevertheless it is worthwhile to carry out systematic studies in this field due to the excellent and promising thermal, electrical, mechanical or tribological properties of the nanofillers.

This paper gives an overview and summarises the activities related to carbon nanotubes and nanofibers used as a reinforcement in metallic matrix materials. The main challenges and the potential with respect to material properties will be discussed.

1) Introduction

Within the past years there was a significant increase on publications related to carbon nanofiber (CNF) and carbon nanotube (CNT) reinforced composites. Most of these publications are related to polymer based composites. Up to now there has been a limited number of publications and especially of success stories, where CNTs or CNFs have been successfully introduced in metallic or ceramic matrix materials resulting in significant improvements of the properties of the matrix material.

This situation is similar to those several decades ago, when micron sized carbon fibers were already used in commercial applications in polymers while the successful introduction of carbon fibers in metal matrix composites took several additional years before showing first success.

The reason why polymer based matrix composites resulted in a faster success compared to metal based ones, is of course related to the fact that a polymer matrix is in general characterised by a rather poor thermal, mechanical, electrical or tribological performance. By introduction of a filler material, which is characterised by several orders of magnitude better/higher properties than the one of the matrix, it is much easier to generate benefits through the reinforcement. The situation is quite different when speaking about reinforcing a metallic or ceramic matrix. Here the matrix material itself exhibits good material properties already, which hampers significant improvement through the reinforcement. To take advantage of the promising properties of the filler many aspects related to the processing of materials have to be considered. Especially when using nanosized fillers with high thermal, high electrical conduc-

tivity and high mechanical strength, the compatibility of matrix and filler as well as the interface are crucial bottlenecks.

Carbon nanotubes with their – theoretically – high properties are of special interest to be introduced in metallic matrix materials. The mechanical properties of CNTs are usually reported to have an average modulus of elasticity of about 1-2 TPa. The average bending strength for MWNTs was measured at 14.2+/-8 GPa and the tensile strength is on the order of 11 to 63 GPa. Because SWNTs tend to assemble in "ropes" of nanotubes, their mechanical properties vary with the rope characteristics. In this case the modulus varies in the range of 32-1470 GPa and the tensile strength is 13-52 GPa [1].

Thermal conductivity of CNTs can be estimated using the values of the thermal conductivity of graphite. It can be expected that the axial thermal conductivity of CNTs could exceed that of II-a diamonds, with a thermal conductivity 1800-6000 W/mK. On the other hand, the radial thermal conductivity of MWNTs can be expected to be on the same order as the c-axis thermal conductivity of graphite or even lower. Home et al. [2] have measured the thermal conductivity of a loosely packed tangled mat of SWNTs in the temperature range from 8 K to 350 K. They have found that the thermal conductivity of this mat is 0.7 W/mK at room temperature. They have estimated the value of the thermal conductivity of the bulk material to be 36 W/mK. It must be noted that the mat possesses a disordered structure, when SWNTs could be aligned longitudinally, the thermal conductivity could possibly reach 6000 W/mK.

Furthermore new types of carbon fibers have been brought to the market in the past years. These so called vapor grown carbon fibers (VGCF) or carbon nanofibers are characterised by a diameter of approx. 100-200 nm. Their thermal conductivity reaches values up to 2000 W/mK, which makes these fibers attractive as reinforcement for metal matrix composites. With the availability of these fibers in kg batches and at an affordable price, they are promising candidates to achieve a metal-CNF-material combining high thermal conductivity and improved mechanical properties with a reduced coefficient of thermal expansion (CTE).

Summarising the previous considerations the introduction of nanosized carbon based fillers into a metallic matrix would have the potential

- ➢ to improve the mechanical properties
- ➢ to reduce the coefficient of thermal expansion
- ➢ to improve the thermal conductivity
- ➢ to reduce the coefficient of friction
- ➢ to improve the electrical conductivity

of the primary matrix material significantly.

These are of course results based on theoretical considerations. The following section of the paper will summarise and give examples of the main technological challenges, which have to be fulfilled at the same time and represents important aspects for being successful in taking advantage of the excellent properties of the carbon nanofillers. To demonstrate the importance of addressing all the individual challenges, examples from experimental work on copper-CNF/CNT composites will be shown.

2) Challenges in Copper-CNF composites

As described in the introduction there is a potential for the application of copper reinforced with carbon nanofibers, although several problems have to be solved. These problems are basically known already from the work with carbon fibers, but some of them turn out to represent key problems when working with CNFs/CNTs (e.g. dispersion or interface). Key problems in the metal-CNX system are listed in Table 1 and compared to those in the metal-carbon fiber system. The abbreviation CNX stands for CNF/CNT throughout the following paper.

2.1. Challenge No.1: Selection of raw materials and their characterisation

Due to the fact that there is a huge number of CNX suppliers on the market ranging from small and medium enterprises to multinational companies, it is rather difficult to select the appropriate supplier and the corresponding raw materials. In addition the production capabilities range in from some grams/hour to several hundreds of kilograms/hour. Due to the size of the CNX with typical diameters ranging from some nanometers (e.g. in single walled nanotubes) to some hundreds of nanometers in carbon nanofibers it is rather difficult to get precise datasheets of the raw materials from the producer. The direct access to the properties of the CNXs is rather difficult. While in conventional micron sized carbon fibers single fiber testing is an appropriate tool for the determination of mechanical, electrical or thermal properties, these methods cannot be applied to CNXs. Therefore today´s analytic tools have not yet reached a status, where they could not successfully carry out quality control of thermal, mechanical, tribological or electrical properties. Beside different production techniques (CVD, Laser ablation,…) for the production of these nanomaterials, the appearance of the raw material can have a broad range depending on their structure as well as dimensions.

- SWCNT (single walled), DBWCNT (double walled), MWCNT (multiwalled),..
- Nanofibers, Herringbone type (HB), Platelet CNFs (PL), Screwtype (SC)

In addition all these materials are available in different modifications such as as-received, purified, functionalised (e.g. COOH, OH), coated (e.g. with Cu, Ni), heat treated (2000°C/3000°C). These raw materials can either be directly used as a "powder" or also in form of skeleton materials (e.g. paper or felt). Figure shows the SEM image of a CNT paper (Figure 1a) and carbon nanofibers in a felt (Figure 1b).

In order to assess the quality of the raw materials, different aspects have to be checked. Scanning electron microscopy combined with statistic analysis can be used to evaluate the average aspect ratio and average diameter of the CNX materials. The purity level (remaining elements from the used catalysts from the synthesis of the CNX materials) can be determined by chemical analysis. Amorphous carbon phases can be determined by XRD or Raman Spectroscopy. The problems start when coming to mechanical, electrical or thermal properties. As already mentioned to get a direct measurement of the properties of individual nanofillers is rather difficult. Therefore attempts to correlate the thermal/electrical/mechanical properties to the structure of the CNX materials have been made.

It is indicated by Ivanov et al. [3] that a high temperature treatment (2.800°C) significantly increases the thermal properties of a carbon nanotube array. In a similar way there are indications from literature that a heat treatment in CNTs has a positive effect on their thermal properties. Up to now it requires a huge effort to characterise the thermal properties of single

CNTs. Therefore other characteristics (degree of graphitisation) are expected to be related to the intrinsic properties of the CNTs [4].

Up to now only indirect methods (via the crystallinity or the measurement of a CNX pre-form such as CNT paper or CNF felt) allow an assessment of the quality to some degree (at high statistic numbers), or even to some extent a quality control of different lots of CNXs. As an example the impact of a thermal treatment of CNT raw material on its thermal properties (thermal diffusivity) is shown in Figure 2. With the increasing temperature of the heat treatment of a CNT material a shift of the peak intensities (ratio of D/G peak is observed) is also observed as shown in Figure 3. Therefore both techniques offer a possible method for the indirect analysis of the thermal properties of CNT materials. Of course these measurements still not allow deriving the intrinsic thermal properties of the individual CNTs

2.2 Challenge No.2: Dispersion of CNX in the matrix material

Dispersion of CNXs is challenging since there are acting strong forces between them. CNXs tend to agglomerate due to their electrostatic and van der Waals forces. Therefore dispersion plays an important role to reach the theoretically predicted properties for various composites, which haven't been experimentally confirmed up to now. Several strategies were followed in literature to disperse the fillers, which can be roughly divided into the following categories:

2.2.1 Mechanical dispersion
 Of course a common way to disperse and distribute fillers in a matrix material is based on mixing and milling operations. Nevertheless the success of dispersion by dry mixing of metal powders with CNXs is rather poor. As an example Figure 4 shows the result of dry mixing of dendritically copper powders with CNFs. Here the big agglomerates, initially present in the raw materials, were not separated.

By applying high energetic mixing processes such as ball milling, better dispersions can be achieved. Of course these procedures must be handled with care and optimised very carefully in order to keep the properties of the CNXs since in some cases a damage/modification of the CNX materials due to the mixing/milling procedure was reported [5].

2.2.2 Dispersion in solvents and surfactant/ultrasonic support
Some of the solvents, which are used for dispersion of CNTs, especially for SWCNTs, are based on amides such as N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) [6]. Chen et al. reported on the dispersion of SWCNTs dissolved in organic solutions with thioylcloride and octadecylamine [7]. Another possibility is to disperse CNTs in water by using surfactants. CNTs are covered by the surfactants and help to form a stable colloidal dispersion [8]. The surfactant acts as a coupling agent and may introduce repulsive forces between individual CNTs. These repulsive forces are larger than the van der Waals attractive forces between the surfaces of the CNTs.

A promising method is to disperse high weight-fraction carbon nanotubes in water using a surfactant for this purpose. Sodium dodecylbenzene sulfonate (NaDDBS), having a benzene ring moiety, a charged head group, and an alkyl chain, dramatically enhances the stability of carbon nanotubes in aqueous dispersions compared to commonly used surfactants such as sodium dodecyl sulphate (SDS) or Triton X-100 (TX). Dispersion concentrations were improved by approximately a factor of one hundred compared to the commonly used surfactants by using a single step process which includes mixing CNTs with the surfactant in a low power, high frequency sonicator. The resulting dispersions prepared with NaDDBS remained dispersed for at least three month [9]. The positive effect of surfactants on breaking up of the agglomerations in a Cu-CNF powder mixture is shown in Figure 5.

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Nevertheless it must be mentioned that for the manufacturing of metal matrix nanocomposites the previously dispersed CNX have to stay homogeneously dispersed when admixed with the metal. In many cases surfactants are used in combination with ultrasonic support and ball milling to provide a good dispersion. Beside the selection of a suitable surfactant, the appropriate concentration and the parameters for ultrasonic mixing, a huge influence is also observed depending on the quality/purity level of the CNX raw material. As an example Figure 6 shows the results of a copper-CNFs composite using nanofibers from one supplier but with different quality/purity. The conditions of the CNFs are a) cleaned, b) after graphitisation and c) after iron free graphitisation. All the CNF raw materials where mixed by using ultrasonic support and dispersants, and the consolidation took place under identical conditions. As it can be seen from the figures, there is a difference in the achieved dispersion within the composites.

2.2.3 Dispersion in acids

In the untreated state nanotubes may be dispersed using ultrasound, but the effect of causing defects is not always clear. Chemical oxidation of their surfaces with acids can introduce oxygen containing functional groups onto the surface. During this process, open ends are formed in the oxidizing environment, which result in a well dispersed, electrostatically stabilised colloid in water and ethanol. Using HNO_3 for short period already results in a good dispersion of CNTs. Homogeneous dispersion of VGCFs (Vapor Grown Carbon Fibers) was achieved by the addition of polyacrylic acid [10]. Typically the latter procedure is also one of the first steps used for a subsequent chemical coating of CNFs.

2.2.4 Coating of CNF/CNTs

Besides conventional powder metallurgic methods of blending the powder and the CNX filler, an advanced process is based on coated reinforcements resulting in a good distribution of the CNXs in the matrix. Additionally this advanced process avoids severe mixing and milling operations. A promising coating process involves the following steps: surface modification of the reinforcement, increase of active surface sites to improve the bonding between the matrix and the reinforcement, but also to maintain the superior performance and excellent intrinsic properties of reinforcement.

The deposition of various metallic coatings (such as Cu, Ni, Co) onto short fibers or particles by electrochemical methods is emerging as a state of the art technology [11,12,13].

1) Electroless methods/Molecular Level Mixing Process have also been used to deposit various elements such as Cu [14] Au [15], Ag [16], Co-B [17], Ni [18][19] or Co[20] onto CNXs. To obtain a metallisation of a CNX several steps are necessary such as pre-treatment comprising of acid pre-clean (e.g. with nitric acid), sensitisation and activation. These steps are essential to clean and purify the CNXs and increase the catalytic sites on the CNXs for the following deposition process. During deposition the tendency of CNXs to agglomerate may hinder a continuous formation of a layer.

Depending on the selection of deposition parameters it is possible
    a) To implant the CNT/CNF in metal particles ("composite powder")
    b) To deposit metallic particles on CNT/CNFs ("decorated CNT/CNFs")
    c) To completely coat the individual CNT/CNFs

Examples of the different possibilities obtained by the controlling of the deposition parameters are shown in the Figures 7 – 9.

2) **CVD methods,** which are used to coat short fibers or particles, are based on fluidised bed reactors [21,22,23] and have been optimised during the past years [24,25]. In order to achieve uniform coatings it is necessary to have suitable precursor gases. Depending on the use of different powders – particles or short fibers – the fluidised bed conditions must be optimised for each system. The process is suitable to deposit nanometer layers of different metals, carbides, nitrides, etc., e.g. WC, TaC, Co und Ni nano-layers as well as the treatment and coating of nanofibers [26]. CVD processes (fluidised beds) are promising methods since uniform deposition of thin layers, even intermediate layers, is possible. Al, Cu or Mg have already been deposited onto CNFs and CNTs [27].

3) PVD coating of various metals on suspended single-walled carbon nanotubes (SWNT) was carried out by electron-beam evaporation [28]. TEM studies reveal that Ti, Ni and Pd coatings on the suspended tubes are continuous and quasi-continuous, resulting in nanotube-supported metal nanowire structures. In strong contrast thereto Au, Al, and Fe coatings on the suspended SWNTs only form isolated discrete particles on the nanotubes. These results shed light into the nature of metal–tube interaction, an important topic to many fundamental and practical aspects of nanotubes [29]. Of course PVD processes would offer an attractive alternative with a number of advantages such as the possibility to modify the carbon/metal interface by a plasma pre-treatment, the easy realization of interlayers or even multilayers and the broad variety of elements or alloys, which can be deposited [30]. Plasma pre-treatment and coating of carbon nanofibers (VGCFs) was already successfully demonstrated by Brüser et al. [31,32] and Seo et al., who used an atmospheric plasma for pre-treatment of nanofibers [33].

As a general remark to all dispersion and coating processes it must be mentioned that all these processes introduce additional impurities to the final compact material (e.g. coming from chemicals used in the coating process), as well all of these method are possible sources for additional carry-over of oxygen/oxides to a final product.

2.3 Challenge No.3: Processing of composite materials – Densification

The literature describes several ways for the preparation of metal matrix composites (MMCs), especially of copper based MMCs. These methods can be divided into two groups according to the state of the matrix or matrix alloy during the fabrication, namely, liquid state or solid state fabrication methods. In the following section the most important advantage and disadvantage are described.

2.3.1 Solid State Fabrication Methods:

This includes fabrication methods utilising powder metallurgical techniques. Basically reinforcement and matrix material (metal powder) are mixed together and subsequently pressed to consolidate at elevated temperatures. In many cases additional pressure is applied to achieve a composite material without or with low porosity.

For preparation of copper-carbon based composites by powder metallurgical methods in general mechanical blending of the components, cold pressing and hot consolidation such as sintering, hot pressing, hot isostatic pressing, forging or extrusion are used. When working with nano-reinforcements the final composite properties are extremely sensitive on the preparation steps before the consolidation and have to be optimised for each materials system. In the following section, several methods for consolidation of metal-CNX-composites and their advantage/disadvantage are summarised.
Pressing followed by sintering is only a feasibly processing technique, if a low concentration of CNXs is used in the composite, otherwise densification during sintering will be a problem.

The main advantage of pressing and sintering is the possibility to obtain a net shaped or near net shaped part without the need for expensive post machining processes. In addition, if a metal-CNX composite material can be successfully sintered, it would be possible to process such a composite via powder injection moulding and therefore allowing very complex shapes and structures.

For material applications where the CNX loading is larger than 5-10 vol% and full densification is the target, external pressure assisted techniques have to be employed.

Hot pressing is a commonly used process to consolidate materials either with high melting points or to achieve a fully dense part in the case of highly loaded metal matrix composites. In addition this process can be used if a material system generally has a tendency for de-wetting (as in the case of copper and carbon).

Generally the latter method uses uni-axial pressurisation. The powder mixture is filled into a graphite die and loaded with an external hydraulic system by two punches. The advanced process for the manufacturing of CNX reinforced MMCs is based on the use of pre-coated CNXs. The heating up of the filled graphite die can be achieved by different techniques such as:

> ➢ Direct heated hot pressing
> ➢ Inductively heated hot pressing
> ➢ Conventional hot pressing (indirect heated)
> ➢ Advanced hot pressing concepts, e.g. spark plasma sintering, plasma pressure compaction etc.

Figures 10 and 11 show the microstructure and the distribution of CNFs in a copper matrix for a) a simple powder mixture and b) the corresponding copper coated CNF using the same type of CNF. A clear advantage in terms of distribution as well as in terms of densification is found.

The advantage of the fiber coating process can be summarised as follows:

- Higher density compared to powder mixtures
- Continuous matrix network
- Better CNX distribution
- no reinforcement to reinforcement contact
- better interfacial contact between CNX and matrix.

2.3.2 Liquid Phase fabrication methods (infiltration processes)

The method of choice to realise high CNX volume percentages and at the same time a material with high densification is liquid phase fabrication. Here the pre-form (a CNX felt or paper) is inserted into a die and the metal or alloy is placed on top, followed by heating the set-up above the metal melting point. Depending on the wetting behaviour, spontaneous wetting and infiltration can take place. Most of the time – due to the rather poor or even non-wetting metal-carbon-system – additional pressure (either mechanical or via a gas) has to be applied to overcome the threshold pressure of the system and infiltrate the pre-form. Methods typically used are gas pressure infiltration or squeeze casting. In addition to the non-wetting system characteristics this threshold pressure becomes extremely high with a decreasing pore size (which is definitely the case for CNX pre-forms). This challenge can be solved by modifying the surface of the reinforcement to promote the wetting on the metal-carbon interface. A simple explanation for this is given by the wetting angle (solid/liquid) of the two components,

which should at least be below 90°. In the case of carbon based reinforcements and copper this promotion of the wettability can be achieved by introducing alloying elements. The CNX-metal system is extremely sensitive on the amount of alloying elements added and usually has to be optimised together with the consolidation parameters to avoid degradation of the mechanical, thermal or electrical properties of the matrix on the one hand, and to avoid too severe reactions between the alloying elements and the CNXs on the other hand. The interlayer formed by carbide formation of the alloying elements also guarantees a good internal thermal interface and reduced thermal resistance between the composite components. A careful control and optimisation of the amount of alloying elements is crucial for a successful improvement of the macroscopic composite properties.

Figure 12 shows the cross section of an infiltrated conventional carbon fiber woven with a Cu-Cr alloy. The carbon fiber woven is completely infiltrated, this means good wetting was observed. At the same time the alloying elements resulted in a significant formation of an interface zone in the range of 1 µm. By using a similar infiltration process for a CNF pre-form the infiltration was also possible, but here a gradient structure was observed (Figure 13). At the beginning of the infiltration front, due to a higher concentration of the alloying element and a longer contact time between the melt and the pre-form, already reaction – in some areas complete consumption of the CNF – was observed, while at the area of the end of the infiltration front the CNF are still present without any indication of a severe reaction with the alloying additives.

2.4 Challenge No.4: Alignment/Anisotropy of material properties

Due to a high aspect ratio of 1:10 to 1:100 of CNX during solid or liquid state processing, a certain alignment/orientation is observed. By using e.g. unidirectional pressure in hot pressing the CNT/CNF show a certain preferred alignment in x-y direction (perpendicular to the pressing direction). This is of course directly related to anisotropic material properties. The fiber alignment is not only visible from SEM micrographs but is also mirrored in the anisotropic behaviour of the thermal properties of the composite. While hot pressing results in a preferred 2D random in-plane alignment, the usage of an extrusion process can result in a longitudinal alignment of the CNX in the matrix [34]. The alignment of course is for specific application of advantage, but in most applications isotropic material behaviour is required. Figures 14 show the cross section of a Cu-CNF composite prepared by hot pressing. While Figure 14 (upper image) represents the view along the pressing direction, Figure 14 (lower image) represents the radial view (perpendicular to the hot pressing direction). It has to mentioned, that in a composite with well dispersed and randomly oriented fiber reinforcements, the exploitation of the potential increase of the composite properties is only one third compared to a composite with a 1D fiber orientation. In thermal applications this is very important, because metals themselves exhibit for example very good thermal conductivity.

2.5 Challenge No.5: Interface Design

One of the most critical challenges, when coming from micron sized fillers to nanosized fillers, is the appropriate design of the interface between the matrix and the filler. Due to the significantly increased surface/volume ratio when going to nanosized fillers, the overall interfacial area also increases significantly and therefore plays an essential role. Especially for those composite materials, where the thermal or mechanical properties of the carbon nanomaterials are of interest, a good mechanical bond as well as a low thermal contact resistance between the metal and the reinforcement must be guaranteed. The concepts to improve the mechanical

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and thermal interface are basically related to surface modifications like roughening of the surface of the reinforcement, the deposition of intermediate layers or the addition of alloying elements to ensure a certain reaction (i.e. carbide formation) at the interface. For specific matrix materials (e.g. Al) possible direct reactions with carbon filler material must be considered and controlled. Figure 15 shows the influence of various additions of carbide forming elements on the thermal conductivity in a CNF-copper MMC. As it can be seen, the addition of Ti or Cr (different amounts) increases the thermal conductivity significantly in comparison to the composite with a not-modified interface. In a similar way alloying elements have a strong impact on the thermal stability of the coefficient of thermal expansion of a metal-CNF composite during thermal cycling.

2.6 Challenge No.6: Applications

As already mentioned in the introduction, it took several years, almost decades, before products of carbon fiber reinforced metal matrix composites became available. R&D work related to metal matrix nanocomposites using CNFs/CNTs is still at the beginning and the most promising areas of applications are not yet identified. For some specific compositions a more clear picture is given, if they will succeed in specific applications or not. As an example from today´s knowledge the hurdles to realise a high thermal conductive (better conductivity than copper) combined with low CTE (approximately half of that of pure copper) for applications as heat sinks are very big. On the other hand such a material is probably of interest to be used in tribologically loaded applications. In a similar way these questions have to be addressed for other metal matrices such as Al, Mg, Ag or Ni. Probably in some of these materials the carbon nanofibers or carbon nanotubes can be used in applications with the focus on the electrical properties, in other applications to improve the mechanical material properties.

3 Conclusions and Remarks

Some general statements as conclusions and remarks to the field of metal-matrix nanocomposites:

- Within the next years there will be a "consolidation" of the many suppliers of CNF/CNT (=CNX) materials. On the one hand major producers of CNX materials are meanwhile able to produce from several tons to hundreds of tons per year such as Showa Denko, Sun or Bayer, which will significantly bring the price of nanomaterials down.
- On the other hand the quality of these high volume products is questionable. For sure it will be sufficient for polymer reinforcement, but high quality products will be needed for reinforcing metals.
- The assessment of the quality/properties of the CNX materials is an open question, which has to be addressed in the future.
- Meanwhile various methods for the dispersion of CNX have been established, which work quite well already. Coating of the reinforcement with the matrix materials is one of the most promising, but of course additional costs for the coating process have to be considered.
- The comparison of CNX reinforced metals with the unreinforced metals processed (e.g. ball milling of the pure Cu or Al powder) under the same conditions is important. Otherwise in some cases a wrong interpretation of the achieved experimental results might be the case. Some metals – if processed e.g. by ball milling – will exhibit different properties compared to those when the metal powder is consolidated without previous milling[35].

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- Due to a high surface area of the CNX material this is directly related to additional oxygen, which will be brought into the composite. As a result of this e.g. fine dispersed oxides could be formed, which could possibly have a positive impact on the mechanical properties ("dispersion strengthening effect").
- In some cases (e.g. titanium) the addition of CNX results in a refinement of the matrix grain size. So in such a case CNX indirectly effect the material properties. Probably such a grain refining effect could be also observed by the addition of other types of nanomaterials [36].
- Finally the formation of carbides from the reaction between the matrix and the CNX must be considered. In a CNX reinforced composite it has to be ensured that there are still CNXs present in the final composite.
- When bringing CNXs together with a matrix metal under high temperatures/pressures, this might also result in a modification, amorphisation or complete degradation of the CNX material [37], especially when additives are involved in a surface modification process.

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TABLE 1

Challenges	Carbon fibers	Carbon Nanofibers/Nanotubes (CNX)
Selection of suitable raw materials (different suppliers & qualities)	Data sheet of different carbon fibers are available	Lack of data from suppliers, characterisation of CNX properties is not easy, there are many suppliers, Reproducibility of data/quality?
Dispersion of reinforcement in the matrix material	Optimisation of conventional blending techniques is sufficient, coating of fibers provides an advanced solution, fiber breakage has to be taken into account	To coat the CNTs seems to be the most appropriate way to get a homogenous distribution
Densification of the composite Processing/ Reactivity with Matrix	Optimisation of processing conditions with regard to densification and interfacial reactions, Liquid phase processing allows high loading of carbon fibers/flakes	Remaining porosities are higher, maximum CNX loading is lower, liquid phase processing is difficult Reactivity of the matrix with CNX has to be considered
Alignment/ Orientation/ Anisotropy	Aspect ratio of 1:10 to 1:100 results in an orientation of the fibers/flakes during processing => anisotropy of properties	Alignment of CNXs takes place depending on the processing due to the high aspect ratio
Interface	Interface plays an important role for mechanical and thermophysical properties	Interface plays an essential role to exploit the properties of the reinforcement
Applications	Applications as heat sinks reported, companies on the market selling products	Up to now only a few products are reported – volume of sellings are not known

Table 1: Overview and summary of challenges in carbon fiber and carbon nanofiber/nanotube reinforced metal matrix composites

Table 2

Matrix	Substrate	Temperature	Contact Angle	Reference
Cu (1at% Cr)	Vitreous Carbon	1100°C	41±4	[38]
Cu (<0.2at% Cr)	Vitreous Carbon	1050°C	~130	[39]
Cu (>0.2at% Cr	Vitreous Carbon	1050°C	~45	
Cu (<0.2at% Ti	Vitreous Carbon	850°C	~150	
Cu (>10at% Ti	Vitreous Carbon	850°C	Close to 0	
Cu (10at% Ti)	VC/Pyro-C	1180°C/1150°C	Close to 0	[40]
Cu/Cu+1at%V	Vitreous Carbon	1150°C	45/62	[41][42]
Cu (1at% Cr)	VC/graphite	1150°C /60 min	50/45	
Cu	VC/Pyro-C	1150°C	136±2, 133±3	[43]
Cu	Vitreous Carbon	1100°C	139±2, 122±2	

Table 2: Influence of alloying elements in copper on the wetting behavior (contact angle) of copper and carbon substrates (VC: Vitreous Carbon)
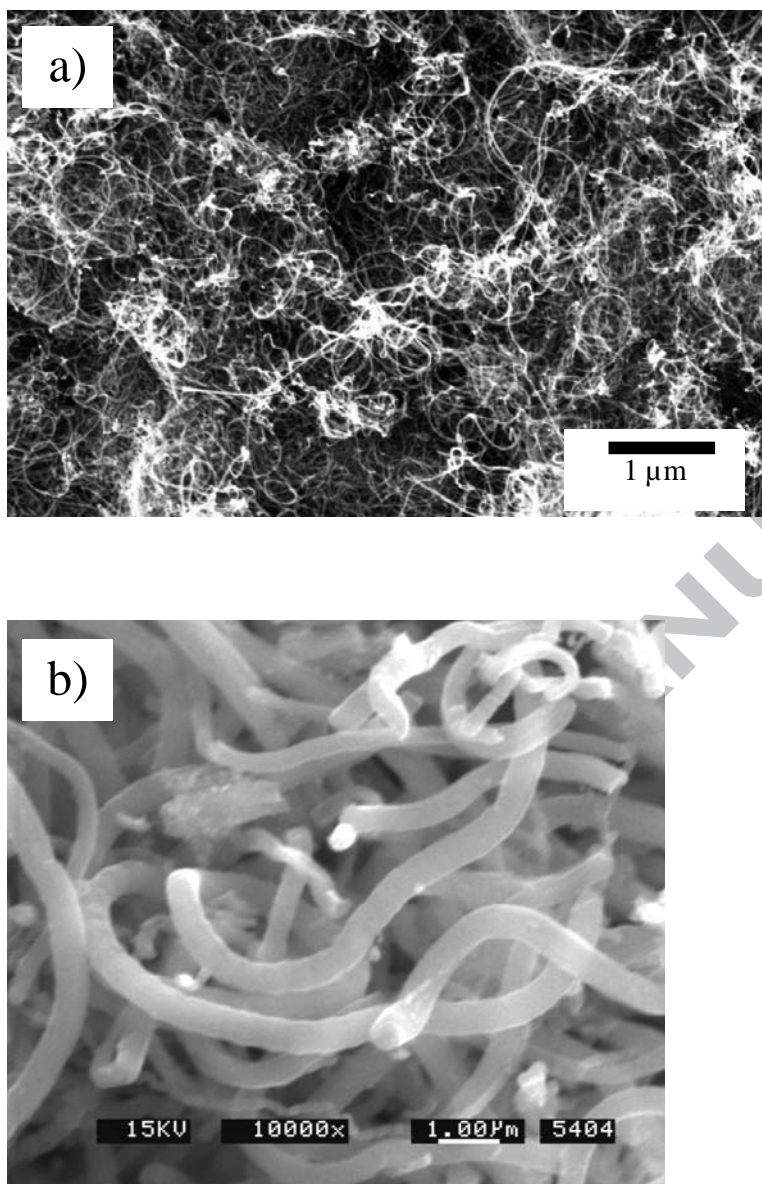
11

Figure 1

Figure 1: SEM image of a CNT paper (a); carbon nanofibers in a felt (b)
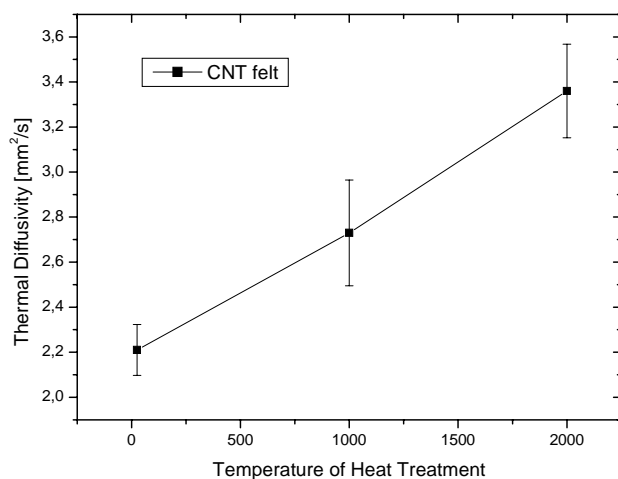
Figure 2

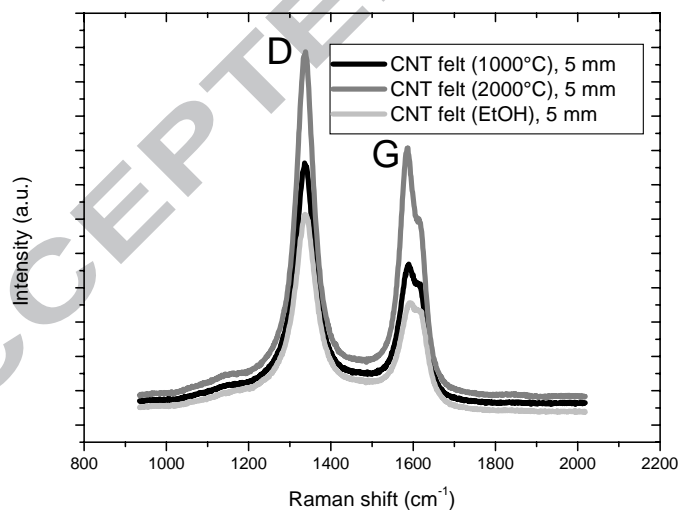Figure 2: Thermal diffusivity (@RT) of CNT felt heat treated at different temperatures

Figure 3

Figure 3: RAMAN shifts of CNT felts. With increasing heat treatment temperature of the felt the D/G peak ratio changes from 1.74 (as produced) to 1.62 (heat treated at 1.000°C) and finally to 1.34 (heat treated at 2.000°C)
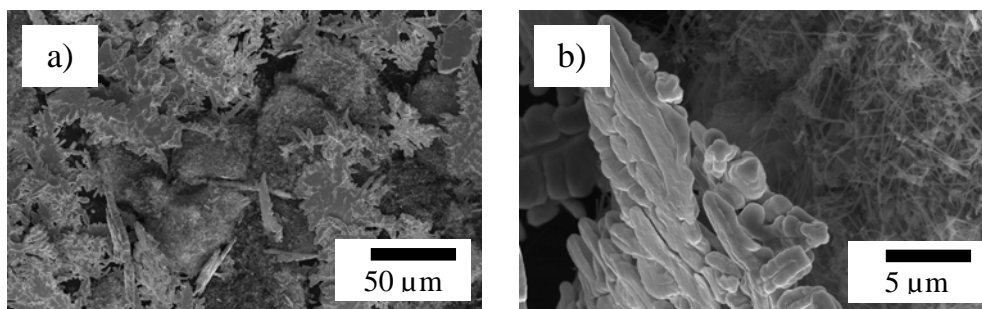
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Figure 4

Figure 4: SEM image of dentritic copper powder and CNF after dry mixing (a); magnification shown in (b)

Figure 5
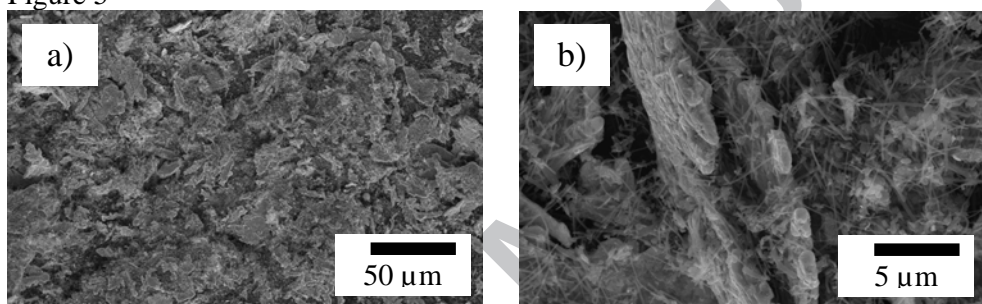
Figure 5: SEM image of dentritic copper powder and CNF after mixing using dispersion aids (a); magnification shown in (b)

Figure 6
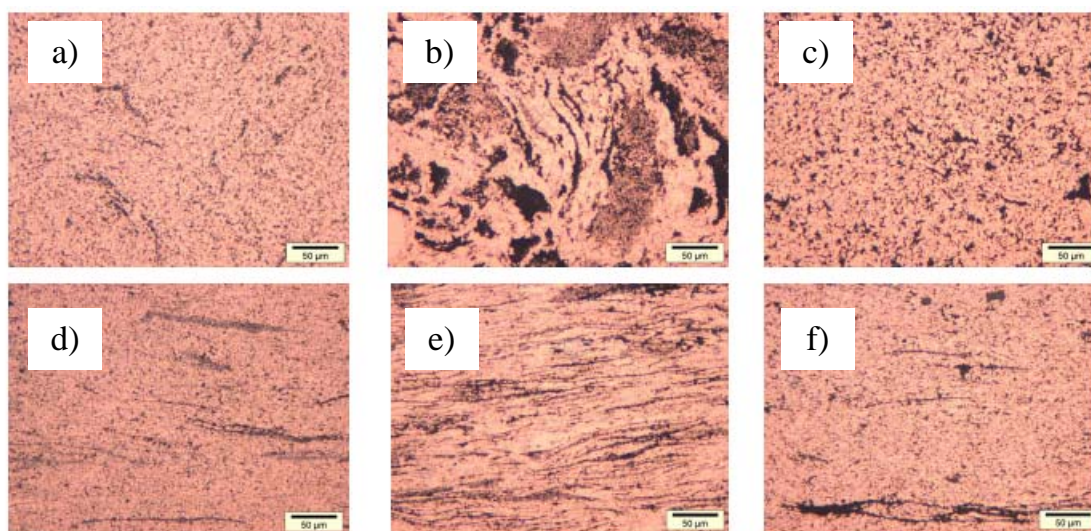
Figure 6: Light microscope image of cross sections of Cu-CNF hot pressed under identical mixing and hot pressing conditions; images in first row (a-c) show the view parallel to the pressing direction, images in the second row (d-f) show the view perpendicular to hot pressing. From left to right: cleaned CNF; graphitized CNF; iron free graphitized CNF

Figure 7
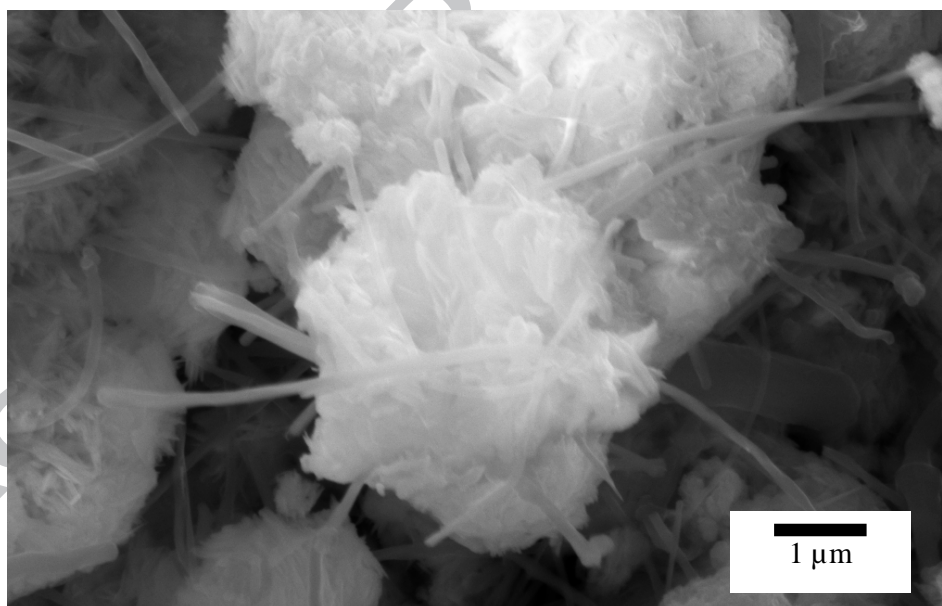
Figure 7: SEM image of "composite powder" consisting of copper particles with embedded CNFs

Figure 8
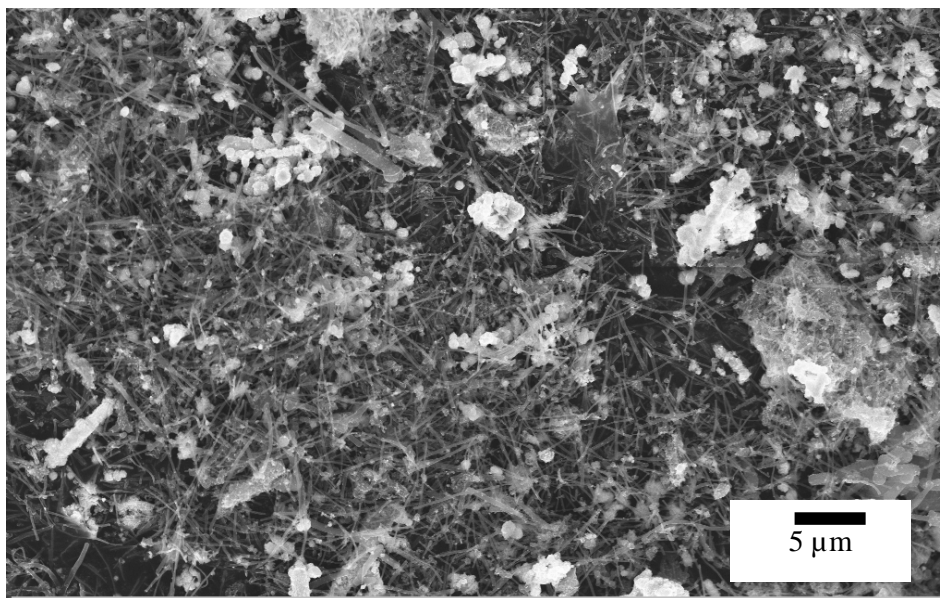
Figure 8: SEM image of partially coated ("decorated") CNFs

Figure 9
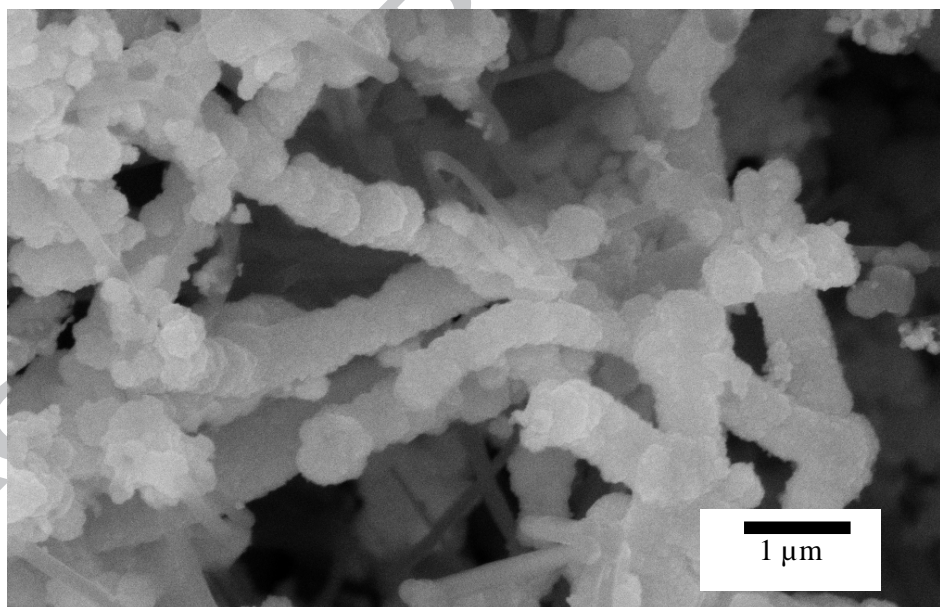
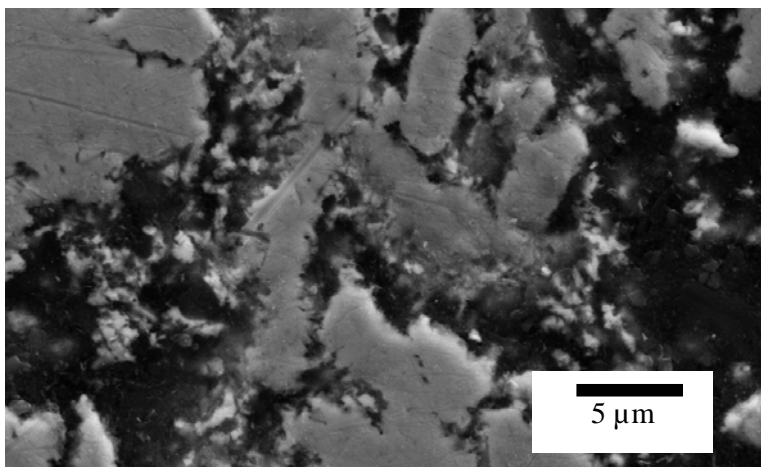Figure 9: SEM of fully copper coated CNFs

Figure 10:

Figure 10: SEM image of a cross section from a Cu-CNF composite material prepared by conventional mixing followed by hot pressing.
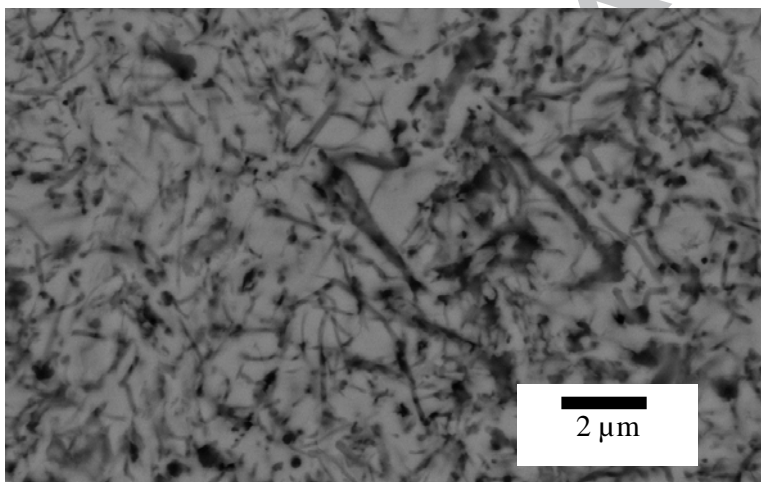
Figure 11:

Figure 11: SEM image of a cross section from a Cu-CNF composite material prepared from Cu coated CNF followed by hot pressing.
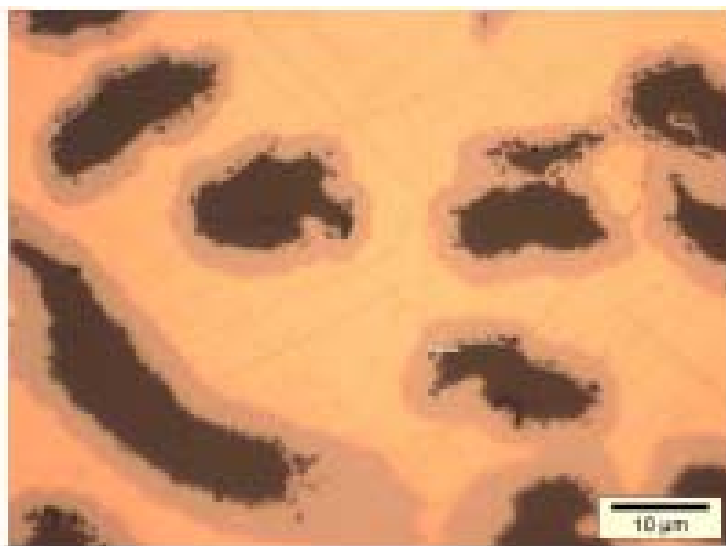
Figure 12

Figure 12: Light microscope image of a Cu-Cr infiltrated conventional carbon fiber felt
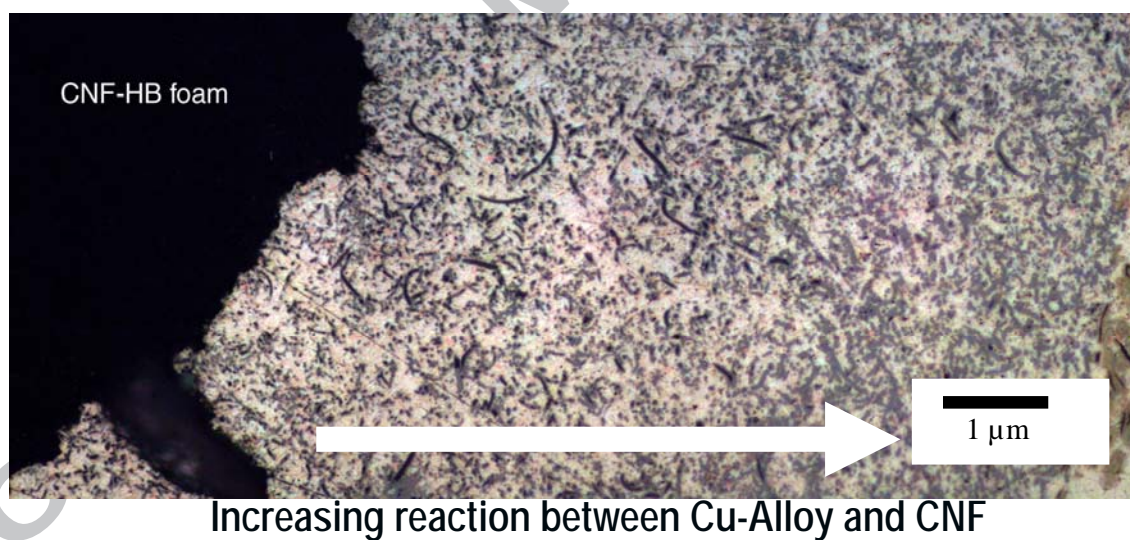
Figure 13

Figure 13: Light microscope image of carbon nanofiber felt infiltrated with a copper alloy
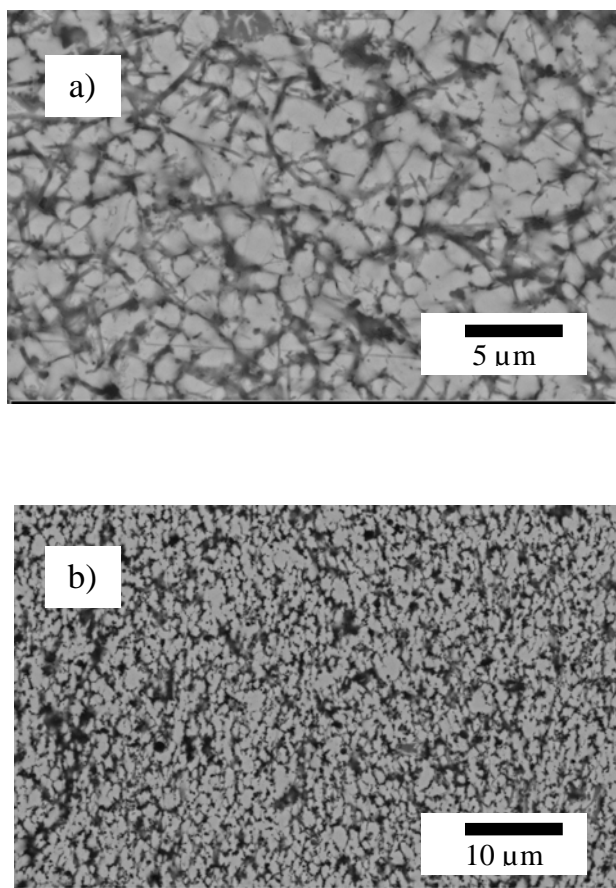
Figure 14

Figure 14: SEM image of a hot pressed copper-carbon nanofiber composite showing the pre-ferred orientation of the CNF parallel to the pressing direction (top) and perpendicular to the pressing direction (bottom)
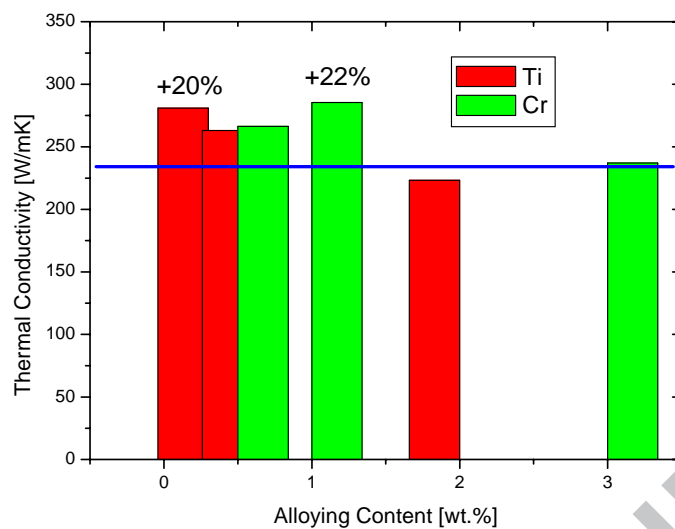
Figure 15

Figure 15: Thermal Conductivity for composites made of Cu coated CNF as a function of alloying content for Ti and Cr in comparison to the pure Cu-CNF composite (blue line)

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