Carbon Nanotubes as Highly Conductive Nano-Fillers in Metallic Matrices

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Abstract. A baseline electroless deposition processes for Cu on CNTs has been developed. This process results in the formation of copper particles of few tens of nanometres. Using this process in a CNT loaded solution it is possible to obtain a homogeneous distribution of CNTs and Cu, even for volume fraction of CNTs as high as 17 v%. By the application of wet chemical processing it is possible to penetrate the natural felt-like structure of the CNTs and to fill the gaps with copper particles. Variations of the baseline deposition process have been established, allowing adding small amount of nickel on the CNT prior to the copper deposition to strengthen the interfacial bonding between matrix and CNTs. Hot pressing of the highly CNT loaded metal matrix composites has been developed; it allows producing bulk material that can be handled. The microstructure of these materials has been investigated and samples have been machined for further testing, i.e. mechanical characterization and thermo-physical properties.

Introduction

Potential space applications. The potential of carbon nanotubes (CNTs) is considered as tremendous both by research institutes and industry. Their intrinsic properties make them very attractive for space applications where the characteristics of the materials represent often a limit to the development of technologies. Metal as well as ceramic matrix composites were identified as promising material candidates. To better establish the potentiality of such different materials, the possible fields of application have been looked at from a space system perspective. A wide range of applications has been identified including [1]:

- Light truss structure with possibly integrated health monitoring system
- Light weight optical elements, mirrors and reflectors
- Thermal protection systems and hot structures
- Thermal control elements, heat pipes, heat sinks and improved radiators
- Components for microwave and antennas

Among the identified applications, some have a near-term priority, namely the thermal control, the stable structures and the light weight large structures. Advances in thermal management technology are required to fulfil the demands of future space missions in terms of devices having high heat dissipation rates and which, at the same time require a very accurate temperature control down to some tenths of a degree. In this context, a crucial need exists for novel thermally high

conductive materials combined with advanced thermal control technologies, such as two-phase heat transport systems. Hereunder are some clearly identified applications.

Heat sinks for laser diodes of Space LIDARS. Laser transmitters and their components such as laser diodes are typical examples for such thermal requirements, since the laser wave length emitted from space LIDARS strongly depends on the temperature of the laser diodes. An example of such system is given in Fig. 1 [2]. Densification and miniaturization of microelectronic circuits and laser diode array impose tremendous challenges on material selection for substrates and packaging that ensure effective thermal dissipation and compatible thermal expansion. Microelectronic and laser diode packaging require effective heat dissipation routes to maintain a temperature for best performance and to prevent burnout or malfunction of microelectronic circuits and quantum-well structures by thermal stress mismatch.
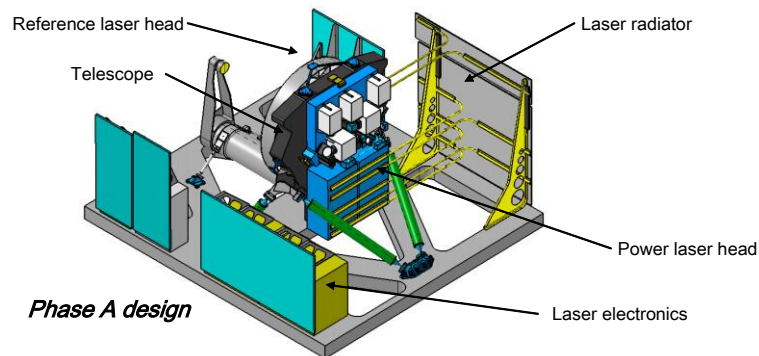

Fig. 1. ATLID Laser Subsystem, Phase A configuration [2]

Thermal Control of Densely Packed Electronics. The ultra-large-scale-integration of integrated circuits (IC), microelectronic components and devices continuously increases the power density. Power management solutions are needed to dissipate the heat generated. State-of-the-art ICs for microprocessors operated at high frequencies are routinely characterised by power densities on the order of tens of W/cm^2. Such a large density leads to highly localized heating of ICs ("hot spots") and subsequent hazard to failure. The ability to solve this problem is of utmost importance for the next-generation of IC packages, lasers and microwave generators. A most accurate and reliable temperature control of those high heat dissipating devices is mandatory for achieving the highest possible performance and instrument resolution.

Metal Composites with CNTs for thermal control. CNT based composites have the potential to provide a solution to the problem of effective thermal management of high power devices. Because of their advantageous combination of expected high thermal conductivity and adaptable thermal strain (to match the CTE of the heat dissipating device, e. g. such as gallium arsenide or alumina), and low density, CNT metallic composites let expect an attractive technical solution for advanced thermal management of future high heat-dissipative compact devices. Copper has been selected as a matrix because it has a very high thermal conductivity and can be electroless deposited, a technique that was deemed suitable for obtaining a satisfactory mixing of copper and CNT.

Experimental

The chemical electroless plating techniques method uses aqueous precursor solutions of copper compounds like Cu-nitrate or Cu-sulphate in which the CNTs are immersed by intensive stirring. By the addition of a suitable reducing agent like hydrazine hydrate or formaldehyde the copper precipitates sheathing the CNTs. As the solution penetrates the CNTs originally felty structure the copper and the CNTs can be homogeneously dispersed and mechanically bond together. To strengthen the interface additional elements like Ni can be easily introduced by the addition of a Ni-precursor to form a Cu/Ni-solution, which is processed similarly to copper. Three samples CNT2-A,

-B, and -C were processed, as well as a reference sample REF2-ABC without CNTs, but produced under comparable conditions.

The Cu/CNT mixtures and the reference sample were subsequently sintered at temperatures up to 1000°C. The sintered bodies of each batch were then hot pressed to dimensions of 52*52*8 mm at 700°C, 100 MPa and 15 minutes isothermal time.

Samples were analyzed regarding density by immersion technique and nominal composition by XRF (Philips X´Unique II); microstructure and fracture surfaces were analyzed by LOM (Olympus GX51 inverse light microscope), SEM (Quanta 200 Mk2) and FEG-SEM (JEOL JSM 6700F), microtensile test were performed on 1.5-2mm thick and 50mm long samples using an INSTRON 5kN tensile test machine. The calculation of penetration hardness H_{IT} and penetration modulus E_{IT} according ISO 14577 was determined by Nanoindenter XP, MTS Systems (Indenter: Berkovich, diamond, Penetration depth: 500 nm, penetration depth controlled procedure (25 nm/s), Dwell time at maximum force: 30 s).

Measurements of thermal conductivities in the temperature range 3.5K to 300K were performed applying a "steady-state" method in an evacuated flow cryostat on cuboids-shaped samples surrounded by three radiation shields, the innermost of which being kept on the sample's temperature to reduce heat losses due to radiation at temperatures above about 200 K. One end of the samples was anchored onto a thick copper panel mounted on the heat exchanger of the system (cryostat), whereas the other end a strain gauge was glued on to electrically establishing the necessary temperature gradient.

Dilatometric analyses were performed on a dilatometer WSK TMA 500 in the temperature range from -150°C to +150°C. The dilatometer was evacuated (0.5 mbar) during the total duration of the measurements and cooled with liquid nitrogen to a temperature around -160°C and subsequently heated with 2K/min to +150°C.

Results and discussion

All samples are close to full densification after hot pressing, except sample CNT2-C, which reveals a higher porosity (Table 1). It has to be pointed out that the calculation of a theoretical density is of course highly dependant from the value of density for the CNTs, which is in turn quite a theoretical one. Concentrations of Ni, Fe and P were also determined by XRF, indicating some small amounts of impurities for Fe < 0.05% and P < 0.01%. Ni was added in order to improve bonding between the naturally inert CNTs and the matrix, which exhibit no solubility for carbon.

Table 1. Density of hot pressed samples by immersion technique and nominal composition by XRF.

Sample	CNT [w%]	Ni [w%]	density	
			[g/cm³]	[%] theory
REF2-ABC	0	0	8.88	99.1
CNT2-A	2.9	0.721	7.71	97.5
CNT2-B	2.9	0.716	7.80	98.9
CNT2-C	3.0	0.007	7.35	93.4

Microtensile tests indicate a decrease in mechanical strength and ductility by the addition of CNT. The fracture behaviour is brittle; the strength of the C-Nanotube samples is significantly below the tensile strength of pure copper indicating that there is no strengthening effect by the nanotubes (Table 2). The fracture strains of all C-Nanotube containing samples are far below 1%, no significant differences between the individual samples can be detected. CNT2-A was measured for 2 times, indicating no significant differences; the measured differences are within standard deviation. Interestingly the tensile strength of CNT2-B is higher compared to the others, but is still below the reference one.

The penetration hardness corresponds to the maximum load measured at the maximum penetration depth (500 nm). The penetration modulus is measured from the initial slope of the unloading part of the curve when the unloading is purely elastic. Sample REF2-ABC is characterized by a much higher penetration modulus compared to the two CNT containing specimens CNT2-B and -C. The introduction of CNTs in the Cu-matrix results in a decrease of the penetration modulus of around 37%, whereas the penetration hardness increases by about 45%. This is in well agreement with the results from the microtensile tests, i.e. a significant reduction in the value of modulus for the CNT containing samples compared to the reference one.

Table 2. Mechanical properties by micro-tensile tests, hardness H_{IT} and moduli E_{IT} by recorded instrumentation penetration test.

Sample	Youngs Modulus [GPa]	Tensile strength [MPa]	Fracture strain [%]	H_{IT} [GPa]	E_{IT} [GPa]
REF2-ABC	102	220	42	1.13	127
CNT2-A	66.6/64.1	150/139	0.23/0.20	-	-
CNT2-B	64.6	192	0.33	1.62	79
CNT2-C	58.7	169	0.35	1.66	82

Nevertheless the nano-indenter hardness gives a different tendency compared to the microtensile tests: the penetration hardness H_{IT} increases while introducing CNTs in the matrix, whereas the tensile strength measured by the microtensile tests decreases in such sample. This can be explained by the fact that the nano-indenter measurements are strongly influenced by the local microstructure (homogeneity, density…), whereas the microtensile test results corresponds to an averaged microstructure across the sample. The implementation of CNTs in the Cu matrix clearly affects the mechanical properties, as the hardness increases and the penetration modulus decreases. As the first one is to be expected for strengthening the matrix, the decrease of the modulus would have to be further investigated.

Fracture surface analyses on tensile test samples reveal a homogeneous distribution of the CNT (Fig. 2). No distinct agglomerations can be found, neither area of pure Cu nor of solely CNTs. The CNTs form a continuous network throughout the complete fracture surface area. Generally the CNTs are not affected by the consolidation process, as no marked shortening is visible at all. Also no differences between the samples A, B and C have been evidenced.
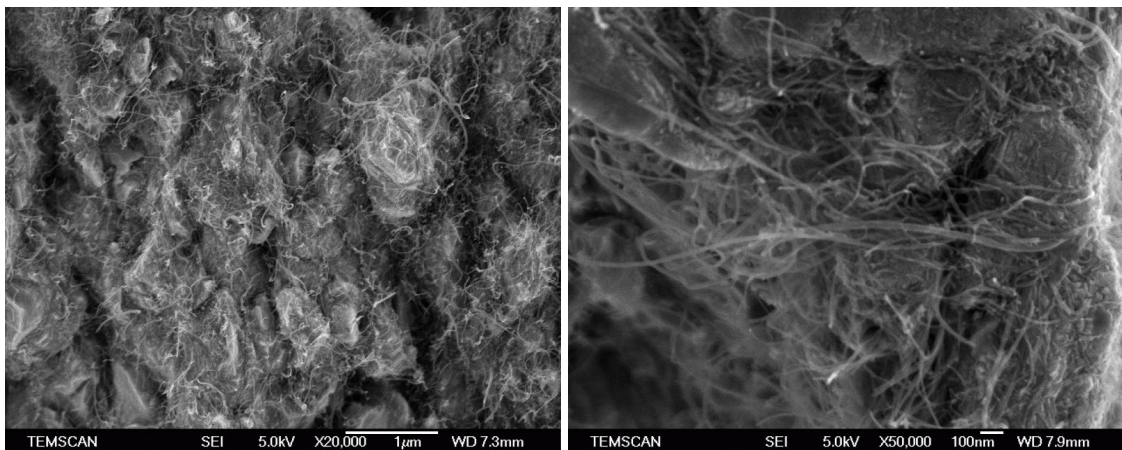

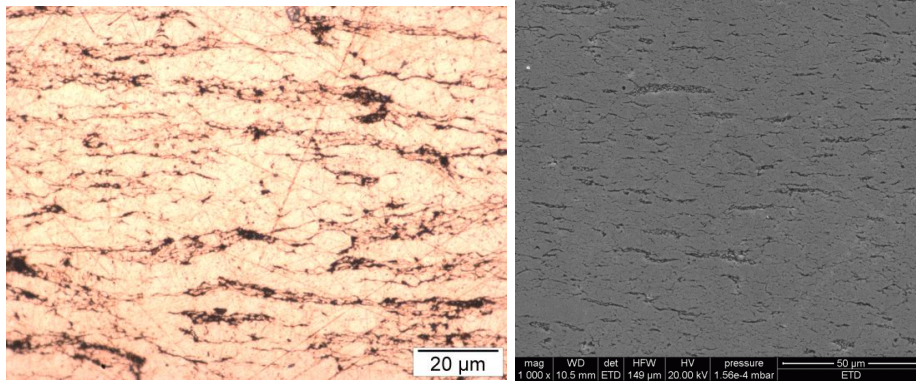**Fig. 2**. FEG-SEM analysis of the fracture surface of sample CNT2-C

Fig. 3. Microstructure of hot pressed sample CNT2-A (left image = LOM, right SEM), parallel to direction of pressing

The microstructure of the samples was intensely characterized by LOM and SEM parallel and perpendicular to the direction of pressing (Fig. 3). All samples reveal elongated areas, prolonged along the axis perpendicular to the pressing direction. Due to the cold and hot pressing, pristine Cu/CNT felted particle areas are squeezed together, forming elongated "grains" within the composite. Those areas are adjoined by regions of higher porosity (dark areas in Fig. 3, which is porosity and not agglomerates of CNTs). This is in well consistency with the results from the fracture surface analysis.

Although the CNTs affect the CTE, the effect is much less pronounced than expected (Fig. 4). Almost no difference in CTE is observable between CNT2-B and the reference sample, whereas the CTE of CNT2-C is small but significantly below the reference sample. Hence it can be concluded, that the bonding between the fibres and the copper matrix is too weak to transfer loads or simply that the concentration of CNTs in the Cu is too high to give sufficient contact between fibre and matrix.
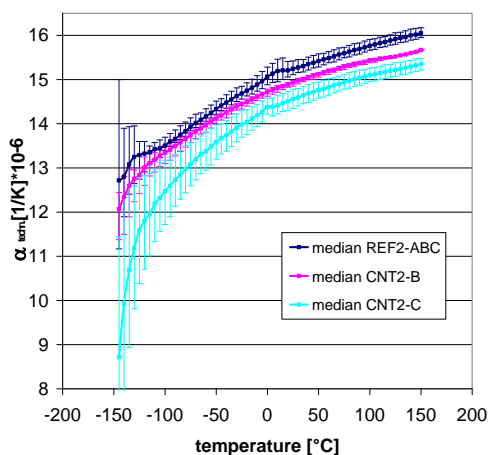

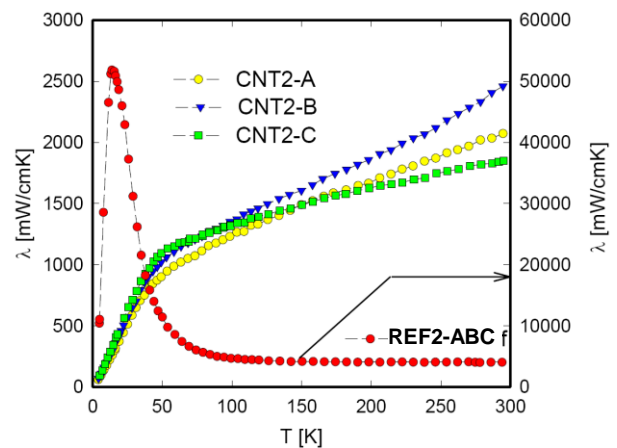**Fig. 4.** Coefficient of thermal expansion α_{tech} at T = -150°C to +150°C

Fig. 5. Thermal conductivity λ of Cu-CNT specimens by flow cryostat measurements.
Note that the scale for the pure copper REF2-ABC is on the right side of the graph while the scale for the reinforced materials is on the left

The method for measuring the thermal conductivity turned out to be reliable and accurate, as the thermal conductivity of the reference sample REF2-ABC at room temperature was estimated to be 403 W/mK (Fig. 5) and which corresponds quite well with data from literature for pure copper. Furthermore the thermal conductivity in the overall temperature range is also consistent with

literature and theory. Nevertheless all CNT containing samples reveal thermal conductivities far below the reference sample. A maximum TC of 246 W/mK was estimated for CNT2-B at room temperature, whereas CNT2-A and -C reveal 207 W/mK and 185 W/mK respectively (Fig. 5).

Theoretical considerations for the thermal conductivity (TC). The measured thermal conductivities λ of all CNT containing samples are well below the expected values. If it is assumed, that no bonding between the fibres and the matrix occur, the fibres must be treated as "porosity", hence the heat transfer between matrix and CNT approaches zero. Following this hypothesis of CNTs does not contributing to the TC, a theoretical TC for a porous body can be calculated, giving TC values of 342 W/mK for CNT2-A, 335 W/mK for CNT2-B and only 317 W/mK for CNT2-C, as this last sample reveals higher porosity. Such calculations already correlate the density and the measured thermal conductivity, but cannot explain the measured degradation of the TC. This degradation cannot solely be attributed to the porosity.

Another explanation might be found in the addition of nickel to the copper matrix and by impurities. It is well known, that traces of elements soluble in copper (like Ni is) steeply reduce the thermal conductivity, as well as phosphorus. As the reference sample does not contain any Ni or impurities, the comparison between the samples provides limited information. To rate the influence of traces elements like Fe, Ni and P on the matrix thermal conductivity and hence to compare the TC values of the CNT-MMCs to a reference containing such elements, the matrix thermal conductivity can be assumed to be in the range of 260-270 W/mK (assuming the concentrations of Ni, Fe and P according to Table 1 and considering the influence of such elements on the TC of copper by retrieving values from literature [3]). When considering both the decrease in TC due to solutes elements and that induced by the fraction densities of CNT one can see, that the measured TC values for CNT2-A und -B approach a theoretical value. As sample CNT2-C does not include any Ni, this sample should be directly comparable with REF2-ABC. But the extremely large difference between both might be attributed to the large porosity of CNT2-C.

Conclusion

Copper matrix composites reinforced with high volume fraction of CNT have been manufactured characterised and tested. On LOM micrographs, the CNT distribution appears to be not fully homogeneous and some flake shaped CNT "agglomerates" are visible. This impression is contradict by high resolution SEM-images from fractured surfaces that reveal a homogeneous distribution: CNTs are visible within the overall surface area without distinct CNT-clusters. Although local porosity seems to be present on the micrographs, the density measurements performed indicate an overall densification close to 100% of theoretical density. Loose CNT can be seen everywhere on the fracture surface, indication a very weak interface.

The mechanical properties are low and the CNT reinforced composite have a brittle fracture behavior, with less than 0.4% strain to rupture. The decrease in stiffness compared with un-reinforced copper is about 40% and the decrease in strength is in the range of 15% to 30%. When estimating the hardness and stiffness by nano-indentation, the hardness of the CNT reinforced composite increases while the stiffness decreases.

The thermal conductivity of the CNT reinforced copper MMCs is lower than that of pure copper. Differences between the expectations and the measured TC can be mainly attributed to a residual porosity which results in a low interfacial bonding between the fibres and the matrix. Also soluble additions like Ni and impurities like Fe and P reduce the overall metal conductivity. An improved interfacial bonding coupled with a decrease in residual porosities and optimizations of CNT dispersions will result in an increase of the overall thermal conductivity. The coefficient of thermal expansion is very reproducible and CTE measurements were performed in the temperature range of -150°C up to +150°C. The CTE of the CNT-containing samples is slightly lower than that of pure copper, but a much more pronounced decrease is measureable below -50°C.

Acknowledgements

References

[1] L. Pambaguian, C. Edtmaier , T. Janhsen, M. Ferrato, P. Chereau, S. Forero, T. Frey, A. Girmscheid, J. Helbig, F. Hepp, C. Laurent, A. Peiney, H. G. Wulz. Viennano´07 - 2nd Vienna International Conference on Micro- and Nano-Technology, March 14-16 (2007), Vienna, Austria, pp 31-39, Publisher: The Austrian Tribology Society, 1040 Vienna, ISBN 978-3-901657-25-2

[2] ATLID Analysis, Design and Performance Report, Doc-Nr.: EarthCARE-RP-ASF- 0001, Issue 6, 24/08/2006, Phase A Study Extension for the EarthCARE Mission

[3] E. Neubauer. PhD thesis, Vienna University of Technology (2003)