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Carbon-Nanofiber Reinforced Cu Composites Prepared by Powder Metallurgy

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Abstract Electronic packaging involves interconnecting, powering, protecting, and cooling of semiconductor circuits for the use in a variety of microelectronic applications. For microelectronic circuits, the main type of failure is thermal fatigue, owing to the different thermal expansion coefficients of semiconductor chips and packaging materials. Therefore, the search for matched coefficients of thermal expansion (CTE) of packaging materials in combination with a high thermal conductivity is the main task for developments of heat sink materials electronics, and good mechanical properties are also required. The aim of this work is to develop copper matrix composites reinforced with carbon nanofibers. The advantages of carbon nanofibers, especially the good thermal conductivity, are utlized to obtain a composite material having a thermal conductivity higher than 400 W/mK. The main challenge is to obtain a homogeneous dispersion of carbon nanofibers in copper. In this paper, a technology for obtaining a homogeneous mixture of copper and nanofibers will be presented and the microstructure and properties of consolidated samples will be discussed. In order to improve the bonding strength between copper and nanofibers, different alloying elements were added. The microstructure and the properties will be presented and the influence of interface modification will be discussed.

Keywords : thermal management, thermal conductivity, copper, carbon nanofiber, composite

1. Introduction

The permanent increase in power density of electronic components caused by miniaturisation and large scale integrations requires new materials for thermal management. Heat sink materials for electronic packaging have to provide high thermal conductivities to protect electronic components against exceeding operating temperature. At the same time, the temperature changes produced by switching cycles of the electronic components generate mechanical strains if the single components possess different thermal expansion coefficients. Therefore, such heat sink materials need an adjustable thermal expansion coefficient to match those of the electronic components.

The conventional material systems like Cu-W/Mo, Al-SiC and Cu-SiC allow thermal conductivities in the range of 200-250 W/(mK) at sufficient optimisations. Such materials are not suitable for laser technology applications, because only thermal conductivities higher than 400 W/(mK) can initiate improvements in reliability and economic life time. These material systems and the known developments of Copper-

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Diamond-Composites with high thermal conductivities have another drawback that is related to the bad machinability.

Developments of composite materials with carbon nanofibers as reinforcing component in a copper matrix enable new dimensions of material properties and material combinations. Due to the excellent thermal and mechanical properties of carbon nanofibers like having thermal conductivities up to 2000 W/(mK)[1] and thermal expansion coefficients of 0 ppm/K, it is possible to get a material system with thermal conductivities higher than 400 W/(mK) and CTE lower than 10 ppm/K. It is assumed that these new materials will show a good machinability in conventional processes.

A typical carbon nanofiber property is to form agglomerates[2,3]. These agglomerates complicate the fabrication of homogeneous mixtures with submicron sized copper powder. Therefore, the development of a suitable technology to disperse carbon nanofibers in copper was one of the main problems that need to be resolved.

Furthermore, it is well-known from the carbon-copper phase diagram[4], that neither solubility nor compound formation exists between these components. Thus, the next main task is to improve the bonding strength between copper and nanofibers by using different alloying elements.

In this study, several technologies of compaction were tested for a homogeneous mixture of copper and nanofibers and the influence to microstructure and thermophysical properties of the produced samples will be discussed herein.

2. Experimental

Different delivery states of carbon nanofibers, pellets or cotton-like aggregates with low content of catalytic elements were used. The carbon nanofibers that were used had an average diameter of about 150 nm and the fiber length was generally longer than 20 μm. In addition, a special submicron-sized copper powder with a d_{50}-value of 0.5 μm was used.

It is known that post-graphitisation of the fibers is necessary in order to increase the thermal conductivity[5]. Therefore vapour grown carbon nanofibers used for these experiments have been treated at elevated temperatures (up to 3000°C) in order to decrease the catalyst content and to improve graphitisation. Graphitisation could be indirectly

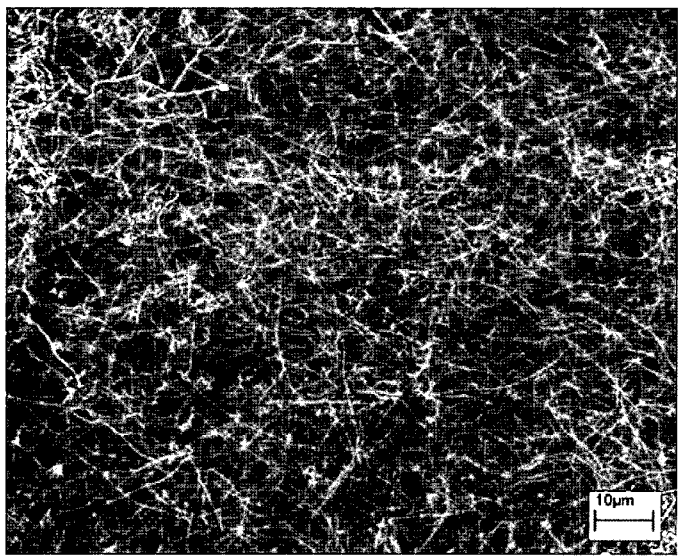


Fig. 1. Vapour grown Carbon Nanofibers (d~150 nm, l~20 μm) prepared by Electrovac Ges. mbH.

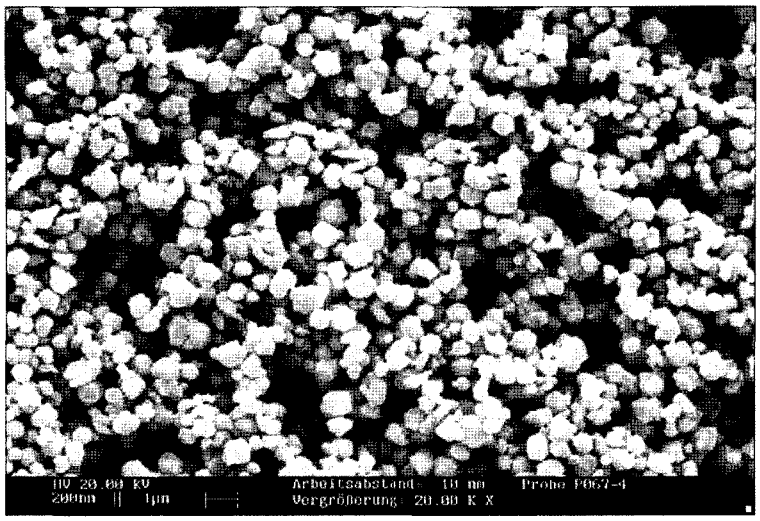


Fig. 2. Sub-Micron Cu-powder prepared by MicroMet GmbH (d_{50}~0,5 μm).

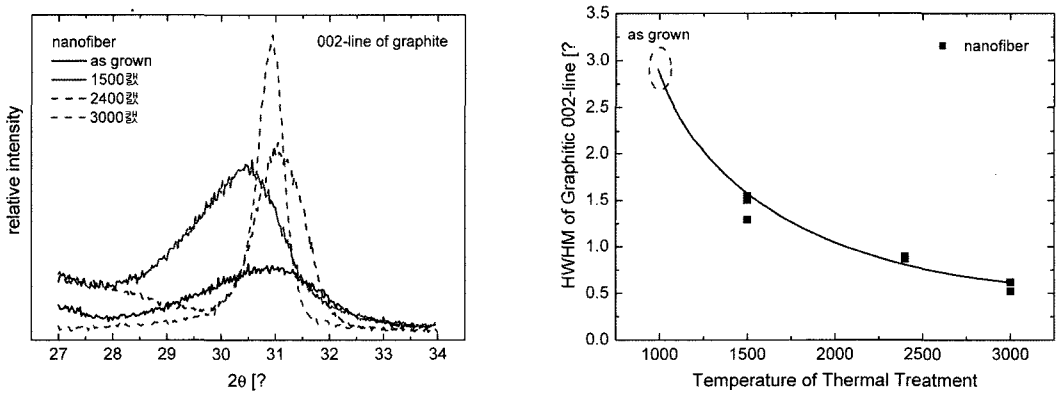


Fig. 3. XRD pattern of heat treated vapour grown carbon nanofibers (left) and calculated HWHM (right).

detected by XRD measurements. HWHM of the graphitic [002] peak decreased with increasing temperature (Fig. 3).

Several conventional mixing processes were tested to disperse carbon nanofiber agglomerates at dry or wet state. None of these processes was able to produce a homogeneous mixture with copper powder.

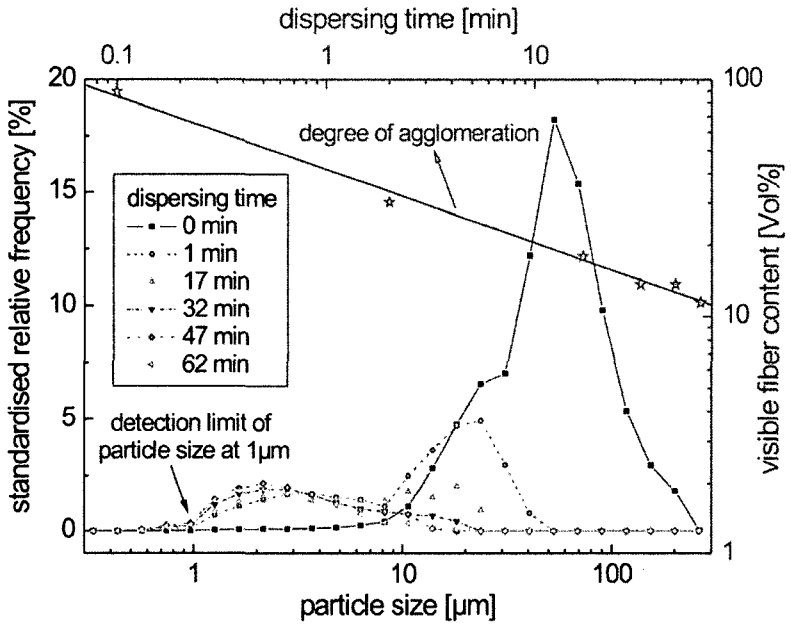
An ultrasonic flow cell allows the dispersion of carbon nanofibers in an aqueous media and the creation of a homogeneous stabilised suspension with the help of an emulsifying agent. The degree of de-agglomeration was analysed by standardised particle size measurements and scanning electron microscopy. Then, the submicron-sized copper powder was added to the suspension and the mixture was also treated with ultrasound. At the same time, different alloying elements were added. The suspensions were tried at elevated temperatures and while stirring constantly in order to preserve homogeneous mixtures. The oxidised copper particles in the mixture were deoxidised at reducing atmosphere.

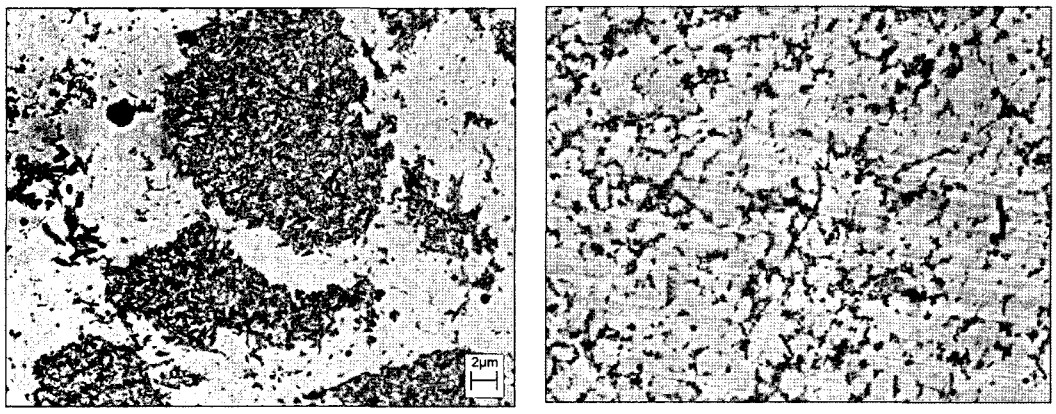
Samples were consolidated by extrusion, hot isostatic pressing and hot pressing. Physical density measurements were taken on each of the consolidated samples. Metallographic sections were prepared and analysed by scanning electron microscopy with

energy dispersive x-ray analysis (SEM/EDS). Thermal conductivity and thermal expansion coefficient were calculated from laser flash thermal diffusivity and low temperature dilatometer measurements.

3. Results and Discussion

The dispersing method with ultrasonic flow cell can be applied to each of the investigated delivery states of carbon nanofibers. Even strong agglomerated carbon nanofibers were dispersed in economically justifiable ultrasonic periods of time less than one hour. The reached degree of agglomeration was always lower than 10 percent. This can be proved either by standardised particle size measurements or by metallographic sections of consolidated samples





t_1=1 min t_2=62 min

Fig. 4. Standardised particle size distributions at different dispersing times of carbon nanofibers and degree of agglomeration depending on dispersing times (above) and SEM of hot isostatic pressed samples at different dispersing times of carbon nanofibers (20 vol%) in an ultrasonic flow cell (below).

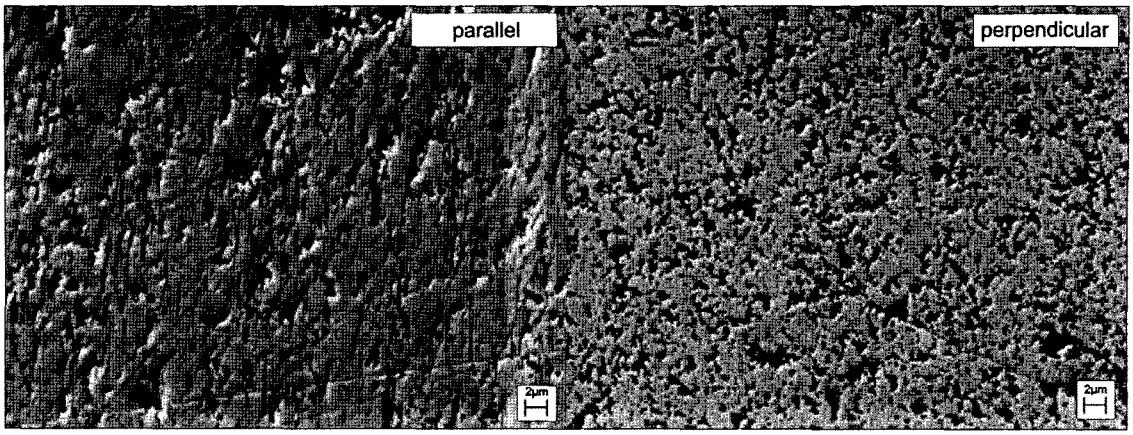


Fig. 5. SEM of extruded samples (30 vol% nanofiber content), parallel and perpendicular to the extrusion direction.

analysed by scanning electron microscopy (Fig. 4). Homogeneous mixtures of copper powder and carbon nanofibers with volume contents of 10-30 vol% and even 60 vol% are realisable via such preparing route described above.

Physical density measurements confirm a nearly complete densification, that is higher than 95% of the theoretical density, for hot isostatic pressed samples, even at a fiber content of 30 vol%. Densities higher than 90% of the theoretical density were determined for hot pressed and extruded materials.

The microstructure analysed by SEM is significantly influenced by consolidating methods. Metallographic sections of extruded samples represent a one-dimensional orientation of nanofibers (Fig. 5). A distinct fiber alignment for hot pressed materials was not detected. Hot isostatic pressed specimens possess an isotropic fiber dispersion with no distinct fiber

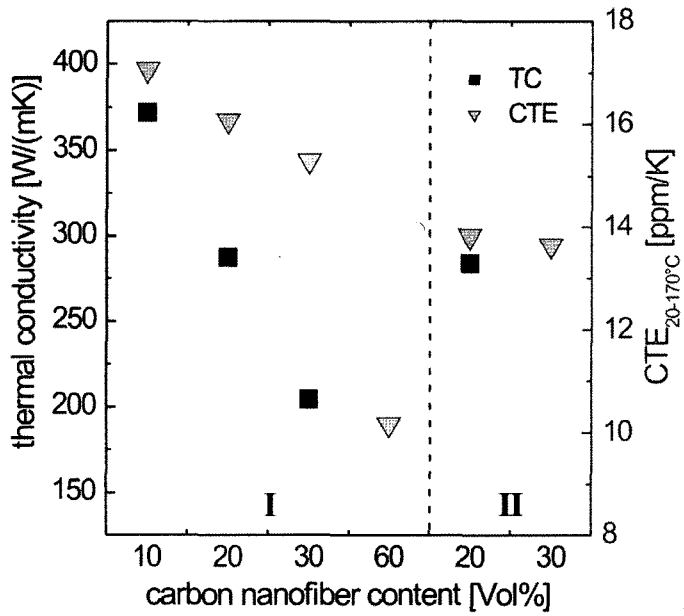


Fig. 6. Thermal conductivity (black) and the thermal expansion coefficient (grey) of hot isostatic pressed (I) and extruded (II-along the one-dimensional fibre orientation) samples with different carbon nanofiber content.

orientation (Fig. 4-t_2).

Considering specific material characteristics (Fig. 6) like thermal conductivity and the thermal expansion coefficient of numerous produced samples, the following conclusions could be drawn. Composites containing carbon nanofibers with low content of catalytic elements exhibit the highest values in thermal conductivity. Increasing carbon nanofiber contents results in a decrease in thermal conductivity of the whole sample. This fact confirms that there is insufficient bonding strength between copper and nanofibers which makes the interface modification a necessary step. Four point measurements of electrical conductivity also represent the poor bonding strength.

In the same context, the results of the measured thermal expansion coefficient should be considered. Only at high nanofiber contents (higher than 30 vol%) can a reduced thermal expansion coefficient be detected. First, the evidences for anisotropic fiber properties arise from extruded or hot pressed samples, considering material their characteristics that are dependant on sample orientation. Hot pressed materials containing nanofibers with high aspect ratio between fiber length and fiber diameter show a significant higher thermal conductivity perpendicular to hot pressed direction ($\perp$ 196.5 W/(mK) > $\parallel$ 120.1 W/(mK). Along the one-dimensional fibre orientation of extruded samples, a stronger reduced thermal expansion coefficient is determinable (Fig. 6-II).

4. Summary

Dispersion of carbon nanofibers with ultrasonic flow cell in an aqueous media is important for preparing homogeneous mixtures of nanofiber and copper powder. Excellent fiber distributions between copper particles ensure that the sample densities are higher than 90% after consolidation. SEM analyses of consolidated samples confirm homogeneous fiber distributions and anisotropic properties for hot pressed and extruded materials. The measurements of the thermal conductivity and the thermal expansion coefficient show that bonding strength between copper and nanofibers is weak. Thus, current investigations are focusing on finding ways to improve the interface by adding different alloying elements to enhance thermal conductivities to obtain a significant reduction in thermal expansion coefficients.

Acknowledgments

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