# Advanced Composite Materials for Heat Sink Applications

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## ABSTRACT

Novel heat sink materials reinforced with diamonds have been produced via powder metallurgy. As matrix, several copper alloys containing boron have been chosen. Prepared composites have been investigated regarding microstructure and the various properties such as thermal conductivity, thermal expansion, etc. Light and scanning electron microscopy have been used for observation of particle distribution in the matrix and for investigation of possible carbide formation at the matrix-diamond interfaces.

The produced composites exhibit thermal conductivities up to 600 W/mK. The copper composites with good interfacial bonding show only small decrease in thermal conductivity and a relatively stable CTE after the thermal cycling test.

## INTRODUCTION

Thermal management is an important issue in electronic packaging due to the increasing complexity, miniaturization, and high density of components in modern devices. In high-power packages, heat sinks are essential for preventing thermal damage to heat-sensitive components on the semi-conductor chip. Mismatch of the coefficient of the thermal expansion (CTE) between the various materials in an electronic package can lead to stresses degrading device reliability and lifetime. Therefore, materials having reduced CTE matching to that of semi-conductors in combination with a high thermal conductivity are required for heat sinks and heat spreaders. Comprehensive reviews of this field are given by Zweben and other authors [1,2].

Copper is one of the most important materials for thermal and electronic applications. It has a higher electrical and thermal conductivity and a lower CTE than aluminum. Unfortunately, the thermal expansion of copper is about four times higher than that of the semiconductor silicon. The CTE of copper can be tailored to the specific application by using a reinforcement with a lower CTE. Diamond has exceptional isotropic thermal properties along with a low CTE of about 1.0 ppm/K. The thermal conductivity of synthetic diamonds of Ib type can be estimated in the range of 1500-2000 W/mK.

One of the main reasons why pure copper based composite materials reinforced by high thermally conductive fillers such as diamond, graphite flakes or Pitch carbon fibres cannot exhibit the theoretical thermal conductivities can be the poor quality of the interface. Because of the lack of a reaction or dissolution between copper and carbon [3] there is only a weak mechanical bonding between the copper and the carbon based reinforcements.

It is well known that alloying of copper with a strong carbide forming element promotes wetting and bonding of carbon materials. Both during solid phase bonding (e.g. hot pressing) and liquid infiltration methods high bonding strength and/or thermal conductivity were observed for copper alloys with minor additions of e.g. Ti, Cr, Zr [4-8]. The influence of the interface formation on the thermal conductivity of these composites is not yet fully understood. Diamond/metal interfaces are also particularly interesting as the heat changes at the boundary from an only phonon to electron transport in contrast to graphite. There is some evidence that the bonding material can affect this transition [9-14]. It is assumed that a very thin interface layer of metallic ceramics can aid the necessary electron-phonon coupling.

In order to solve the interface problems between copper and diamond, the carbide former boron has been added as alloying element to the copper matrix. Boron carbide exhibits a relatively high thermal conductivity of about 40 W/mK compared to the carbides of Ti, Cr or Zr. The critical issue is to control the process parametres such that the carbide layer is not growing too strongly in order to maintain a maximum thermal interface conductance. The thermo-physical properties will be displayed and discussed as a function of the reinforcements as well as the alloying element used for composite preparation.

## EXPERIMENTAL

Elemental boron as possible carbide former was used to study the effect of this alloying element to the Cu matrix. The mean particle size of this powder is 5 µm. The pure reference copper used was a copper powder produced by wet chemical precipitation with a mean particle diameter $d_{50}$ of 6 µm and a purity > 99,9%.

The used reinforcements are synthetic diamond grit of mesh 120/140 and 70/80, respectively. This corresponds to average particle diameter of 110 and 195 µm, repectively. The synthetic (Ib-)diamond was of the MBD4 type purchased at Luoyang High-Tech Qiming Superhard Materials Co. Ltd., Luoyang, Henan, China.

Subsequently, the copper powders were mixed with the diamond particles to prepare composites with about 40-50 vol% reinforcement. These composites were fabricated by hot pressing. In order to influence the hot pressing time via heating rate a hot press with indirect resistance heating (type HPW 315/400, manufactured by FCT Systeme GmbH, Germany) or a sintering press with a direct resistance heating for very fast heating (type DSP, developed by Dr. Fritsch GmbH, Germany) were used. The rapid sintering technique is especially promising for a cost efficient manufacturing of the composites.

The bulk density of the composites was measured by using a method based on Archimedes' law and compared with the theoretical density. The measurement of the coefficients of thermal expansion (CTE) was performed in a Netzsch dilatometer under the following conditions: temperature range 25-300°C; heating rate 5K/min; argon atmosphere.

The linear CTE was measured in accordance with the equation:

$$\alpha = \frac{1}{\Delta T} . \varepsilon = \frac{1}{l_o} . \frac{\Delta l}{\Delta T} \qquad (1)$$

where $\alpha$ is the coefficient of thermal expansion, $\Delta T = T - T_o$ is the temperature interval ($T_o$ = 293 K), $\varepsilon = \Delta l / l_o$ is the relative length change, and $\Delta l$ is the expansion for $\Delta T$ , $\Delta l = l - l_o$ . The length of the sample before testing is $l_o$. The thermal conductivity was measured by Xenon pyrometry with the Nanoflash of the company Netzsch, Germany. Interfaces of the composite samples have been analysed by SEM using a EVO 50 equipment of ZEISS. In addition, diffraction patterns recorded by a Siemens-diffractometer D5000 were used to study the interfacial phases.

TEM observations of the interface structure were also performed on the thin foils prepared by Focused Ion Beam (FIB) milling.

The thermal fatigue testing for up to 1000 cycles between -55°C and 150°C, with 20 minutes storage time in each chamber, has been performed on TC and CTE samples to check the interfacial strength of the composites. The thermal diffusivity, conductivity and the thermal expansion behaviour of the composites were measured before and after thermal cycling to study any changes in the thermal properties arising from cycling thermal load.

## RESULTS AND DISCUSSION

From the first promising results obtained with the copper-boron/diamond system, composites with varied boron additions have been prepared to study this influence on the thermal properties of the composites.

An optimum boron content of 1,1 – 1,2 mas.% was found to achieve the highest thermal conductivities for diamond volume contents in the range of 40-50 % (Figure 1).

The best copper-boron composite with 50 vol.% diamond combines a thermal conductivity of 585 W/mK with a CTE (RT-150°C) of 9,0 ppm/K. Further reduction of CTE needs a higher volume content of diamonds by using bi- or trimodal particle mixtures.

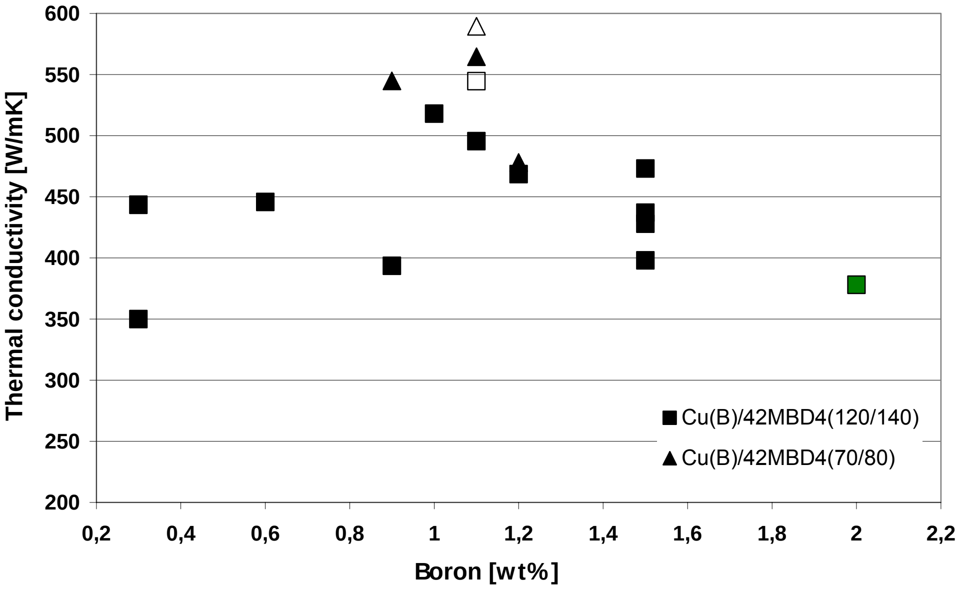

Figure 1. Thermal conductivity of 42 vol.% diamond containing composites as a function of the boron content and diamond particle size.

Another remarkable result is that a rapid sintering process using a directly heated hot press is also the preferred fabrication method of CuB based composites. The unfilled symbols in Figure 1 show the corresponding results. An increase of about 10 % of the thermal conductivity seems to be possible by the rapid sintering compared to the conventional hot pressing process. Obviously, the rapid heating can cause a smaller critical nucleus radius and higher number of nuclei for carbides, what can result in higher interfacial conductance by an more homogenously carbide formation [13].
The samples for observation in TEM were prepared using Focused Ion Beam milling. Figures 2 and 3 give the TEM overview images of the interface and high resolution micrographs of the interfacial phase respectively obtained in PHILIPS CM20 device. The TEM micrographs show a good bonding between copper and diamond. The polycrystalline copper matrix is visible, and characteristic twins can be observed in Cu grains. The matrix grain size varies. Fine, sub-micron grains are observed at the vicinity of the interface with diamond (see left image in Fig. 2) .At higher magnifications (right image in Fig. 2) an interfacial phase of some 20 nm in thickness is clearly distinguishable.
The high resolution images of that phase reveal its crystalline structure. Grains with slightly different orientation can be distinguished (left image in Fig. 3) as well as lattice deflection/nano-twins inside some grains (see right image in Fig. 3).

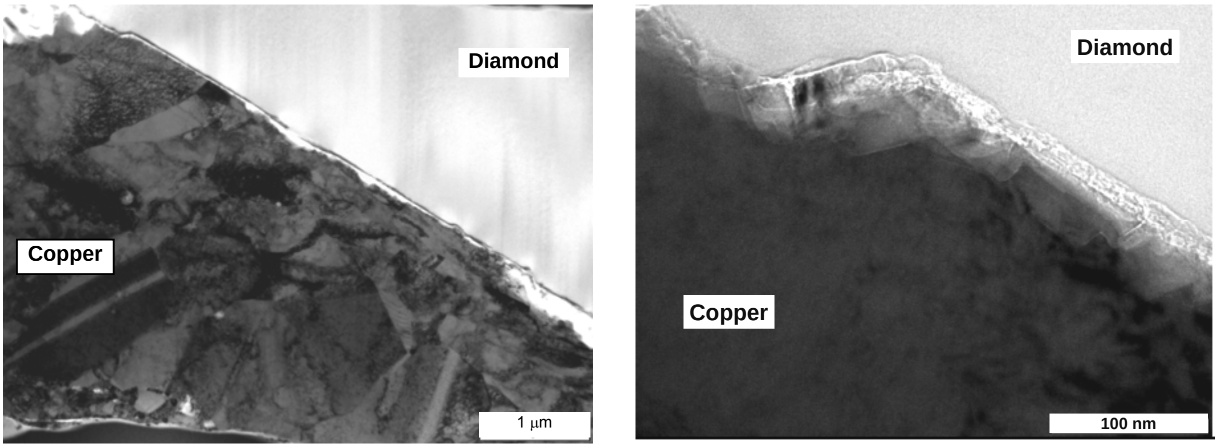

Figure 2. TEM micrographs showing the microstructure of the interface in CuB/diamond composite produced by rapid hot pressing.

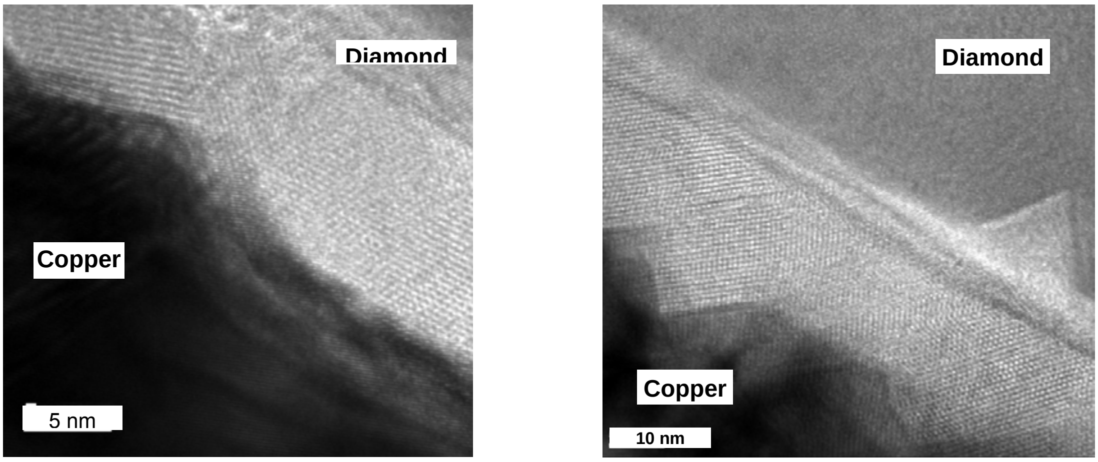

Figure 3. HR-TEM micrographs showing the microstructure of the interface in CuB/diamond composite produced by rapid hot pressing.

This lattice deflection phenomenon was reported as one of possible deformation paths in boron carbide $B_4C$ cristals [15]. Its presence in the studied material may be the effect of the interfacial residual stresses that develop during the composite fabrication.

Some more detailed study of the interfaces was done on diamonds released from the composites by a simple chemical etching.

Unfortunately, no carbide formation could be detected by X-ray analyses in contrast to the clear evidence of chromium carbide in CuCr/diamond composites [13]. A volume content of about 6% would be produced in case of a complete transformation of boron to $B_4C$. This low volume content of the assumed boron carbide can reduce the possibility of detection of the carbide phase on the diamonds.

SEM picture (Figures 4) using the SE signal of the surfaces of the released diamonds shows thin layers enriched with boron and surrounded by seemingly non-attacked surface regions. But, some loose flake-like particles suggest that a originally dense layer was destroyed and only some residual parts of the interfacial products could be found. The reason for this possible spalling of layer parts can not be given today.

Further evaluation by electron diffraction performed in future should give more information about the structural properties of this boron-enriched interfacial phase, which is obviously the key to increasing thermal conductivity in these diamond composites.

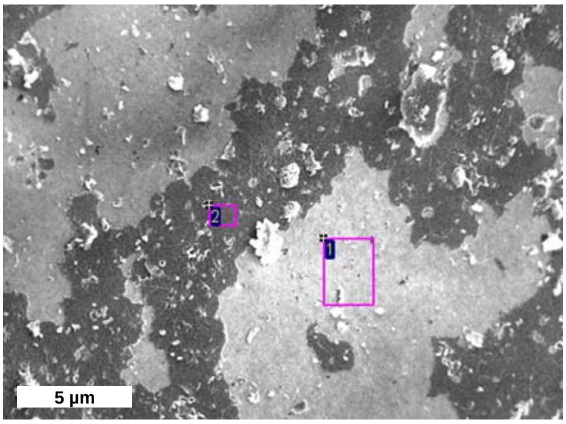

Figure 4. SEM pictures of interfaces of diamonds released from the hot-pressed composite Cu(B1,1)/42MBD4(mesh 120/140):

EDX-analyses:

1 - 100% carbon
2 - carbon + **boron**

Overall, the resistance against thermal fatigue in the diamond composites made by powder metallurgy was satisfactory. The strongest reduction was found in samples which had already shown reduced interfacial strength before the thermal cycling. Table 1 and Figure 5 show the effect of thermal cycling on the thermo-physical properties of selected composites. The thermal cycling resulted in a small reduction of thermal diffusivity of the composites between 5% to 10% and relatively stable CTE after the thermal cycling. Obviously, the diamond particle size seems to influence the resistance against thermal fatigue, smaller

Table 1. Influence of a thermal cycling on the thermo-physical properties of selected composites.

| Material | Thermal Diffusivity in mm$^2$/s | Specific heat in J/gK | Thermal conductivity in W/mK | CTE in ppm/K | |
|---|---|---|---|---|---|
| | | | | 30-200°C | 200°C |
| CuB/42MBD4(120/140) | | | | | |
| as-pressed | 209 | 0,40 | 544 | 10,4 | 11,5 |
| after 1000 cycles | 199 | 0,42 | 547 | 10,8 | 12,4 |
| CuB/42MBD4 (70/80) | | | | | |
| as-pressed | 224 | 0,41 | 589 | 10,1 | 11,3 |
| after 1000 cycles | 201 | 0,40 | 520 | 10,3 | 11,5 |

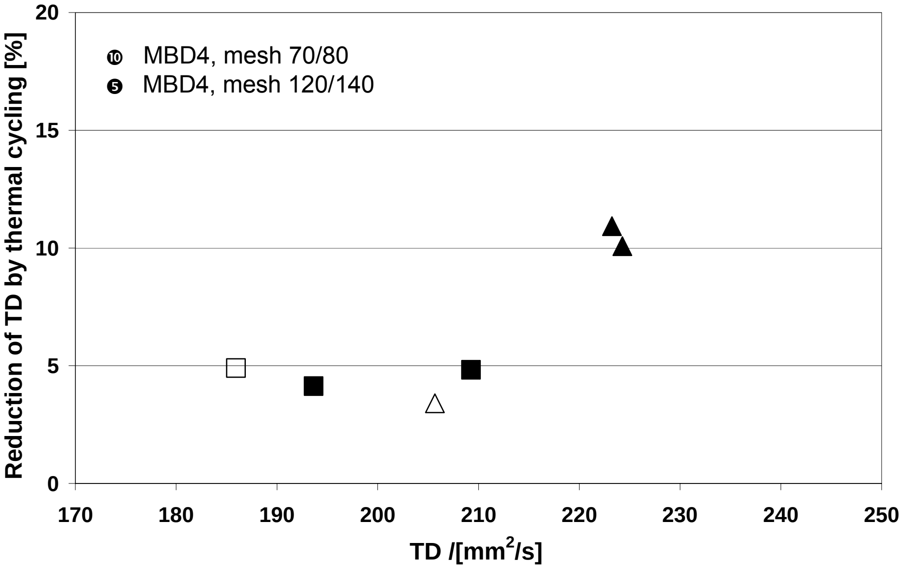

Figure 5. Reduction in thermal diffusivity TD caused by thermal cycling after 100 cycles (open symbols) and 1000 cycles (filled symbols) for different particle sizes of diamond.

diamonds (diamond grit of mesh 120/140 compared to mesh 70/80) result in a lower decrease of the thermal diffusivity and thermal conductivity of the composite.

The drop in thermal diffusivity may be attributed to the thermal expansion mismatch of the copper matrix and the diamond particles. Thermal stresses caused by this difference in CTE can result in cleavage at interface regions with a weak interfacial bonding. This cracking causes reduced thermal transfer across the interfaces between copper and diamond. Further interfacial improvements should be investigated by varying the relevant processing parameters.

## CONCLUSIONS

The use of boron for the necessary carbide formation in diamond/copper composites has been proved satisfactory. A boron content of 1,1 – 1,2 wt.% result in maximum thermal conductivities of composites with diamond contents in the range of 42-50 vol.%. A rapid sintering of the corresponding powder mixtures seems to be the preferred fabrication method. Environmental testing of diamond based composites made by powder metallurgy and its effect on thermal conductivity and CTE has been performed. Composites made by this route exhibit good resistance against thermal fatigue and corrosion.

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REFERENCES

[1] C. Zweben, "High-Performance Thermal Management Materials", *Advanced Packaging*, 2006, vol. 15, no. 2, pp. 1-5.

[2] R.M. German, k.F. Hens and J.L. Johnson, "Powder Metallurgy Processing of Thermal Management Materials for Microelectronic Applications", *The Journal of Powder Metallurgy*, 1994, vol. 30, no. 2, pp. 205-215.

[3] T.B. Massalski, *Binary Alloy Phase Diagrams*, ASM International, ISBN 0-87170-403-X

[4] H. Schmidt-Brücken and W. Schlapp, „Festhaftende Diamant/Metall-Verbindung", *Zeitschrift für angewandte Physik*, 1971, vol. 32, no. 4, pp. 307-310.

[5] B. Dewar, M. Nicholas and P.M. Scott, „The Solid Phase Bonding of Copper, Nickel and some of their Alloys to Diamonds", *Journal of Materials Science*, 1976, vol. 11, pp. 1083-1090.

[6] E. Neubauer, G. Korb, C. Eisenmenger-Sittner, H. Bangert, S. Chotikaprakhan, D. Dietzel, A. Mansanares and B. Bein, "The Influence of Mechanical Adhesion of Copper Coating on Carbon Surfaces on the Interfacial Thermal Contact Resistance", *Thin Solid Films*, 2003, vol. 433, pp. 160-165.

[7] E. Neubauer, "Interface Optimisation in Copper-Carbon Metal Matrix Composites", 2003, Ph.D. Thesis, ARC Seibersdorf Research GmbH, Seibersdorf, Austria.

[8] R. Bollina, M. Stoiber, "Ultra High Conductivity Diamond Composites*", Proc. of the 2006 POWDER METALLURGY World Congress & Exhibition*, 2006, September 24 - 28, BEXCO, Busan, Korea

[9] Th. Schubert, T. Weißgärber, "Cu-based composites prepared by Powder Metallurgy for Thermal Management of Electronic Devices", *Proc. of the 2006 Int. Conference on Powder Metallurgy & Particulate Materials*, San Diego, USA (2006), part 9, 44-52

[10] J.A. Kerns, N.J. Colella, D. Makowiecki, "Dymalloy: A Composite Substrate for High Powder Density Electronic Components. *The Int. j. of Microcircuits and Electronic Packaging*, 1996, vol. 19, no. 3, pp. 206-211

[11] P.R.W. Hudson, "The Thermal Resistivity of Diamond Heat-Sink Bond Materials", *J. Phys. D: Appl. Phys.*, 1976, vol. 9, 225-232.

[12] Th. Schubert, B. Trindade, T. Weißgärber, B. Kieback, „Interfacial design of Cu-based composites prepared by Powder Metallurgy for Heat sink applications", *Materials Science and Engineering A*, to be published.

[13] Th. Schubert, H. Weidmüller, t. Weißgärber, B. Kieback, "Carbide formation in copper-carbon composites and its effect on thermal conductivity" *Proc. of the 2007 Int. Conference on Powder Metallurgy & Particulate Materials*, Denver, USA (2007), to be published.

[14] R. Bollina, J. Landgraf, H. Wagner, R. Wilhelm, S. Knippscheer, G. Mitic, S. Levchuk, "Thermal reliability and environmental testing of advanced metal diamond composites" *Proc. of IPACK2007*, Vancouver, Canada (2007), to be published.

[15] D. Ge, V. Domnich, T. Juliano, E.A. Stach, Y. Gogotsi, „Structural damage in boron carbide under contact loading", Acta Materialia 52, (2004), 3921-3927