

*Manuscript refereed by Professor Monika Willert-Porada, Bayreuth University*

## **Innovative Metal-Graphite Composites as Thermally Conducting Materials**

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### **Abstract**

Metal matrix composites (MMC's) made by powder metallurgy offer the possibility to tailor the thermal properties of the metal by adding carbon based reinforcements, e.g. natural graphite flakes. The microstructure, thermal conductivity (TC), coefficient of thermal expansion (CTE) and the damping behaviour of the composites based on Cu-C, Al-C, Fe-C and W-C will be displayed and discussed. The produced composites exhibit TC in the range of 300 W/ mK to 550 W/ mK combined with a reduced CTE in the range of 3 ppm/ K to 10 ppm/ K and a high mechanical damping. The tungsten- graphite composites represent a TC of 400 W/ mK and a low CTE of 3 to 5 ppm/ K. Anisotropy of the properties of metal-graphite composites due to intrinsic anisotropic properties of the graphite flake must be considered and is displayed for the CTE.

### **Introduction**

It is necessary to keep the operating temperature of thermal stressed electronically components within specified limits. The ideal thermal management material therefore working as heat sink should have a low and tailorable coefficient of thermal expansion (CTE), highest possible thermal conductivity (TC), mechanical stability, high mechanical damping, low production cost and a suitable machine ability. Carbon in the form of graphite (graphite flake, graphite fibre, expanded graphite or pyrolytic graphite) is a candidate for the use in thermal management materials. One example of a heat spreader material described by Norley [1] is chemically bonded expanded natural graphite with an in- plane TC up to 230 W/ mK and a perpendicular TC of 4.5 W/ mK. The impregnation of the porosity with resin leads to an increase of the perpendicular TC up to 70 W/ mK. Due to the low TC of non-metallic matrices metals are preferred as matrix materials to build up composites with high TC. Fukushima et al. [2] describes composites made of graphite particles and a matrix of the metals copper, silver or aluminium. The TC achieved in the composites depends on the graphite type used, the heat treatment during consolidation and the volume fraction of graphite. The composites show anisotropic properties due to the structure build up when the metal- coated graphite particles are uniaxial pressed. Commercial available aluminium/ graphite composites have a very high TC up to 750 W/ mK and a low CTE of 4 ppm/ K but have a too low strength [3 - 5].

Copper- graphite composites combine the positive characteristics of its components i.e. high thermal and electrical conductivity from the copper and low CTE from the graphite [6]. The effect of graphite with and without copper coating on consolidation behaviour and sintering of copper- graphite composites was discussed by Moustafa et al. [7]. Schubert et al. [8] manipulate the interface between copper and graphite flakes to decrease the interface thermal barrier. In contrast to diamond- copper interfaces, there the carbide formation support the heat transfer across the surface, the most promising copper- graphite composite represents a TC of 550 W/ mK in combination with a low CTE of 7-8 ppm/ K without any carbide- forming element.

In Thermal Management Applications the heat spreaders are usually parts with a thickness less than 5 mm. Calculation by Kawai et al. [9] indicated that as the thickness of the composite decreased in the direction of lower TC, the cooling performance of the anisotropic

composite approached that of pure Cu heat spreader having the same thickness. The thermal conductivity has to be highest at least in two directions.

An additional important issue for thermal management application is to reduce noise and vibration with the help of damping materials. Damping is the energy dissipation property of a material or system. It is the conversion of mechanical energy into thermal energy. The amount of energy dissipated is a measure of the material's damping level [10].

The high TC and high damping can be achieved with metal- graphite composites. The authors used as matrix metal copper, aluminium, iron and tungsten. Selected properties of these systems are described in the following paragraphs.

### Experimental

The metal powders are carbonyl iron (diameter: < 4  $\mu\text{m}$ ; BASF SE), tungsten powder (diameter: < 3  $\mu\text{m}$ ; PLANSEE SE), aluminium powder with silicon additions between 20 up to 25 wt. % (diameter: < 52  $\mu\text{m}$ ; NANOVAL GmbH & Co. KG) and copper powder (diameter: < 2  $\mu\text{m}$ ; ECKA Granulate Velden GmbH). The natural graphite flakes (Schunk Kohlenstofftechnik GmbH) have a diameter of about 100  $\mu\text{m}$  and a thickness of about 10  $\mu\text{m}$ . The volume content of graphite varies from zero up to 80 %. To achieve a homogeneous mixture of metal powder and graphite flakes a tubular mixer is used. The consolidation to a dense sinter body is carried out in Spark Plasma Sinter equipment (FCT-HP D 250/1 of the company FCT Systeme GmbH). By variation of the sinter parameter like heating rate, pressure, dwell time and different mould diameters the final metal- graphite composite is sintered. Figure 1 shows a disc of a composite made out of tungsten and 70 vol.% graphite. The diameter is 150 mm and the height is 5 mm.



Figure 1: Sintered Body with a diameter of 150 mm and a height of 5 mm of a tungsten-graphite composite with 70 vol. % graphite.

The following properties were measured and characterisation methods were applied: density with the principle of Archimedes, thermal conductivity with the flash method (Netzsch LFA447 Nanoflash), thermal expansion with dilatometry (Bähr DIL801), damping with the RFDA method (IMCE RFDA MF v6.3.0) and microstructure with optical and electron microscopy (Reichert MEF 4A, ZEISS EVO50).

### Results and Discussion

#### Microstructure

The microstructure of the sintered samples is characterized by light- and electron microscopy. Due to uniaxial pressure during SPS process the graphite flakes attain a two dimensional orientation parallel (figure 2 a) and perpendicular (figure 2 b) to the pressing direction. Along the oriented graphite planes the heat can dissipate.

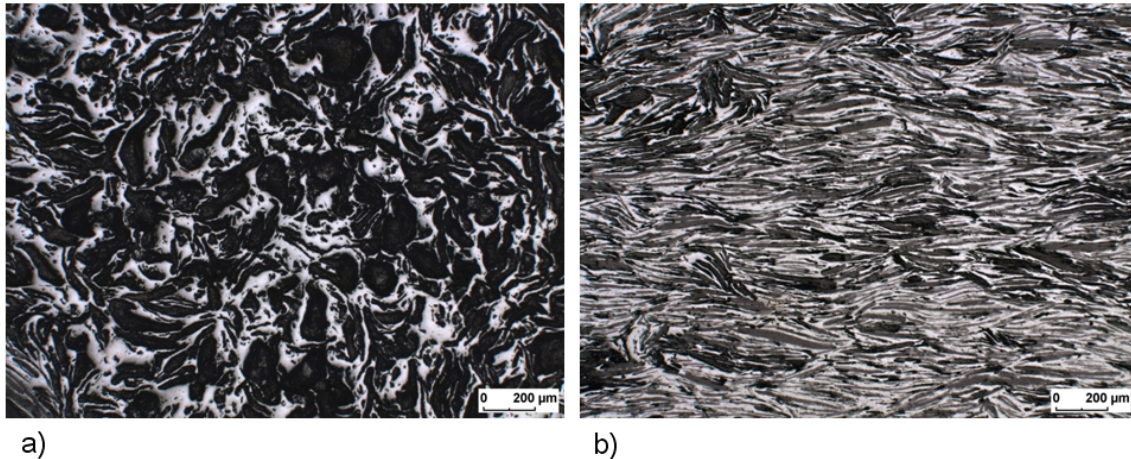


Figure 2: Typical optical micrograph of the two dimensional orientation of a metal- graphite composite made out of tungsten and 70 vol. % graphite with a density of 7.8 g/ cm<sup>3</sup>: a) parallel and b) perpendicular to the pressing direction; metal (grey), graphite (black)

The major difference between the used metal matrices is the possibility to react with carbon upon carbide formation. Using copper no reaction with carbon was detected. In the case of an aluminium matrix carbide wasn't detectable as second phase by optical or electron microscopy. By using iron and tungsten the reaction to metal carbide can be controlled by variation of sinter parameters, like heating rate, dwell time and sinter temperature. The controlled variation of the microstructure of the partially reactive systems made out of iron and 60 vol. % graphite is shown in figure 3. The carbide content and concentration differ depending upon the used dwell time, as visible from figure 3. The phase composition and microstructure of the matrix developed from ferritic with grain boundary cementite (figure 3 a) to ferritic- perlitic (figure 3 b) and at least to ferritic- perlitic with grains made out of Fe<sub>3</sub>C (figure 3 c).

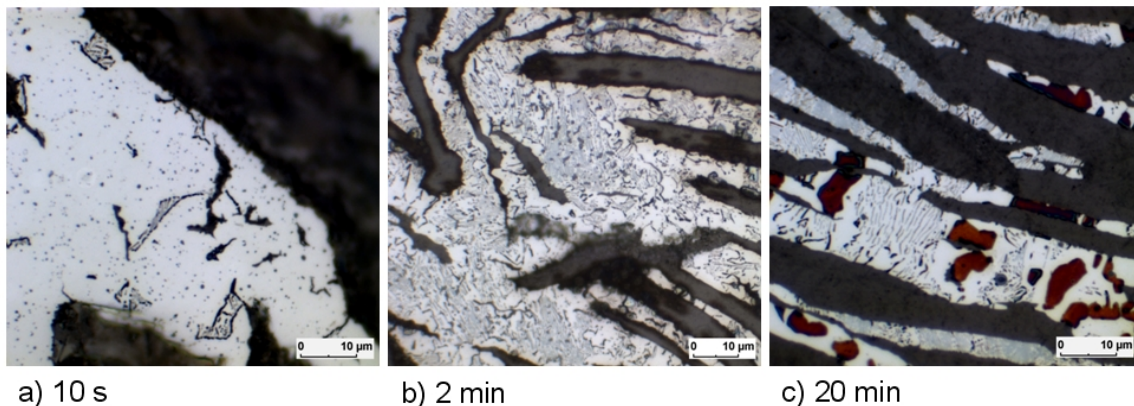


Figure 3: Dependence of the concentration and content of iron- carbide during the sintering process upon the variation of dwell time; example: Fe + 60 vol. % graphite etched with picric acid

### Thermal Conductivity

The Thermal Conductivity (TC) depends strongly on the volume content and the orientation of graphite inside the MMC. Parallel to the pressing direction the TC decreases with higher graphite content depending on the matrix metal. Perpendicular to the pressing direction TC increases with increasing graphite content and its alignment. Figure 4 summarizes the effect of graphite content of a composite with an iron matrix. To achieve a high TC in metal-graphite composites no porosity and a two dimensional orientation of the graphite flakes are required. In case of iron an increase of TC was detected up to 60 volume percent graphite. Above 60 vol. % the amount of disoriented graphite flakes increases and no further increase in TC was detected.

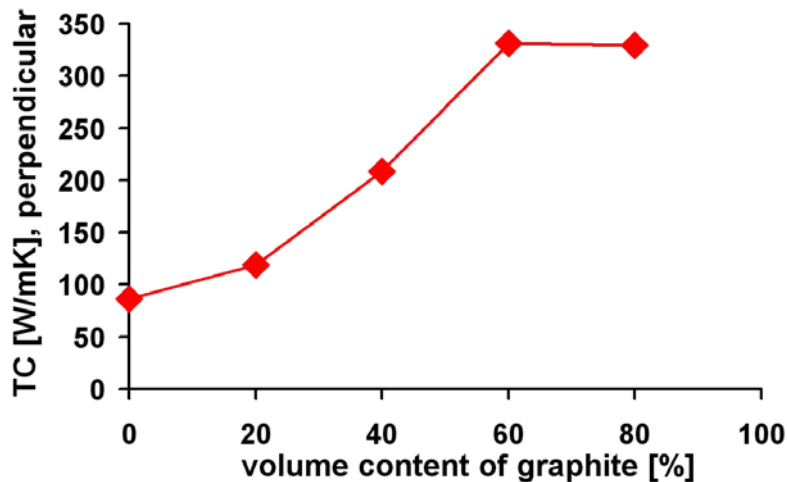


Figure 4: Effect of variation of the volume content of graphite for the composite with an iron matrix

The maximum TC values reached by powder metallurgy techniques for the used matrixes copper, aluminium, iron and tungsten are summarized in table 1. In the case of tungsten and 70 vol. % graphite was no degradation of TC after thermal cycling with 1000 cycles between -50 °C and 200 °C detected.

Matrix	Volume content of graphite [vol. %]	Thermal Conductivity [W/ mK]
Aluminium	50	300
Copper	60	550
Iron	60	340
Tungsten	70	400

Table 1: TC values reached by powder metallurgy techniques for different metal matrixes and the used volume content of graphite

#### Coefficient of Thermal Expansion

Materials for the thermal management require not only a high thermal conductivity (TC) but also a reduced coefficient of thermal expansion (CTE). In the case of metal- graphite composites increasing the volume content of graphite enables to reduce the CTE. For the composite made of tungsten and 70 vol.% graphite the value of the CTE at 50 °C is 3.6 ppm/ K perpendicular to the pressing direction and 6.0 ppm/ K parallel to the pressing direction (figure 5 a). A material that should work as heat dissipating part of a component will undergo many cycles of heating up to service temperature and cooling down. In conclusion a degradation of the composite must be avoided. In Figure 5 b) the values for CTE perpendicular and parallel to the pressing direction after temperature cycling from -50 °C up to 200 °C for 1000 cycles are shown. No degradation is detected. This is caused by the use of tungsten as matrix metal which shows a high tensile strength.

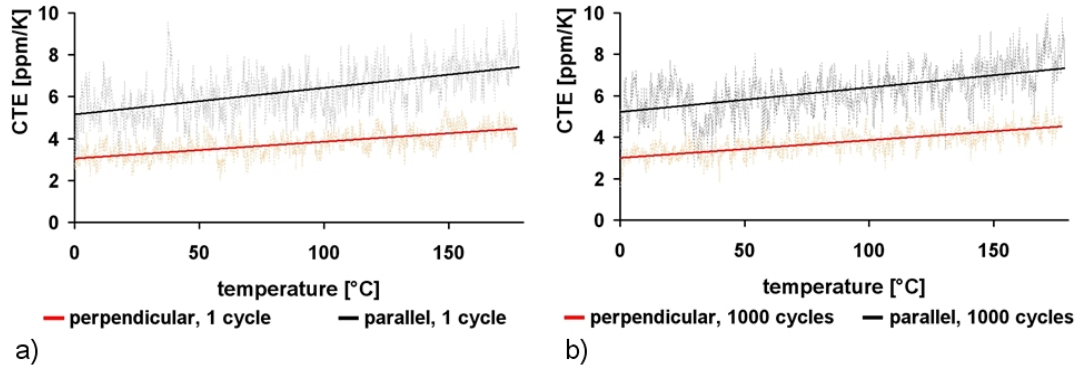


Figure 5: Coefficient of thermal expansion perpendicular and parallel to the pressing direction of a composite made out of tungsten and 70 volume% graphite a) as pressed and b) 1000 cycles; after thermal cycling treatment between -50 °C and 200 °C

In case of a copper matrix (figure 6 c) an increase of the CTE above a temperature of 60 °C was revealed. This composite undergo a plastic deformation of the matrix when heating above 60 °C, because of the lower strength behaviour of copper in comparison to tungsten. Using a matrix of AlSi25CuMg the effect of plastic deformation of the matrix can be reduced in the characterized temperature range (figure 6 b). The increase in CTE is detected above a temperature of 95 °C. In the case of an iron matrix (figure 3 a) the CTE parallel to pressing direction is reduced below the CTE perpendicular to pressing direction (figure 6 a) due to the formation of grain boundary cementite during sintering. The CTE of cementite in the directions normal to the planes (022) and (210) calculated by Rokhmanov et al. are equal to 5 and 1.3 ppm/ K, respectively [11]. An increase of CTE parallel to pressing direction is detected above a temperature above 120 °C. To avoid a plastic deformation of the matrix the use of a metal with a high tensile strength is preferred.

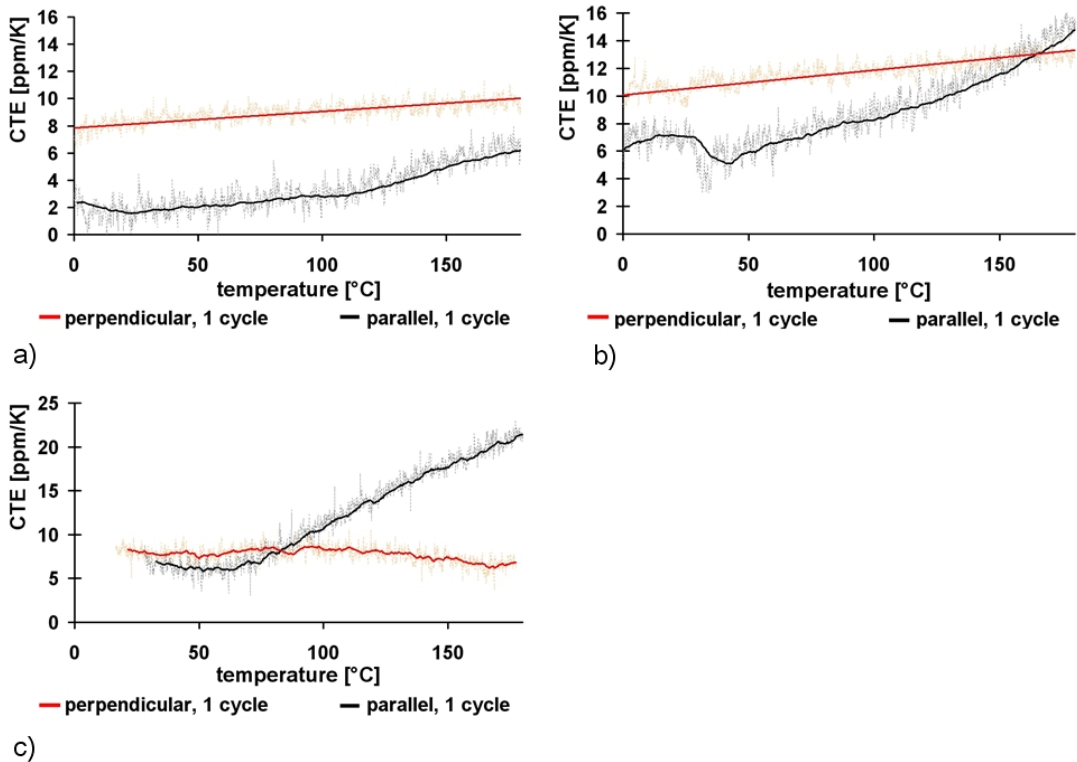


Figure 6: Coefficient of thermal expansion perpendicular and parallel to the pressing direction of a composite made out of a) iron and 60 vol. % graphite; b) AlSi25Cu4.5Mg1 and 50 vol. % of graphite and c) copper and 60 vol. % of graphite after 1 cycle between -50 °C and 200 °C

Increasing the volume content of graphite the strength decreases in comparison to the pure matrix. For iron as matrix figure 7 shows the dependence of the three point bending strength from the used vol. % of graphite. In the case of 60 vol. % the bending strength is 65 MPa. The characterisation of the tungsten- graphite composite is still in progress.

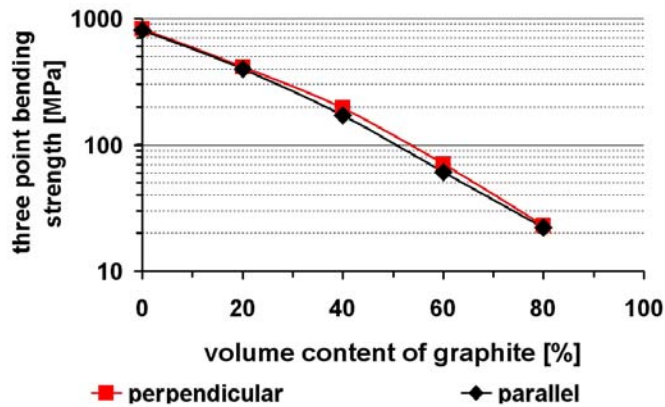


Figure 7: Three point bending strength of the iron- graphite composite for different vol. % of graphite

### Damping

Metal- graphite composites have additionally to high TC and reduced CTE an extremely high value for damping. Due to the high volume fraction of graphite the composites can reduce unwanted vibrations. In Figure 8 the combination of damping and density is shown for reference materials and the metal- graphite composites. With the help of the powder metallurgy process the high mechanical damping capability can be combined with an elastic modulus in the range from 40 GPa up to 180 GPa depending on the graphite content and the microstructure. Increasing the graphite content the elastic modulus decrease in comparison to the pure matrix. The densities of the metal- graphite composites are in the range of 2.7 up to 8.5 g/ cm<sup>3</sup> depending on the composition. To increase the mechanical damping it is possible to control the achieved porosity of the composite.

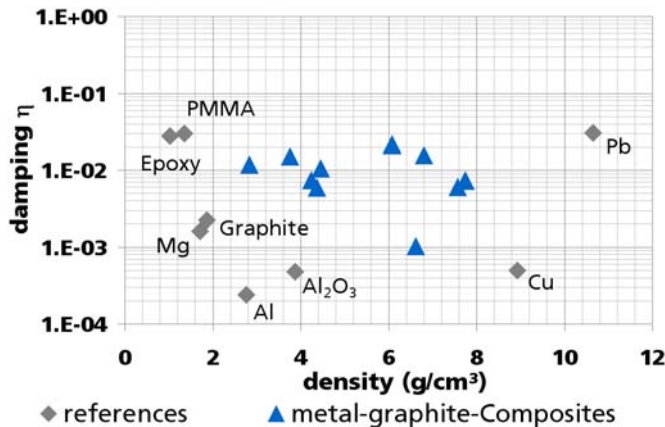
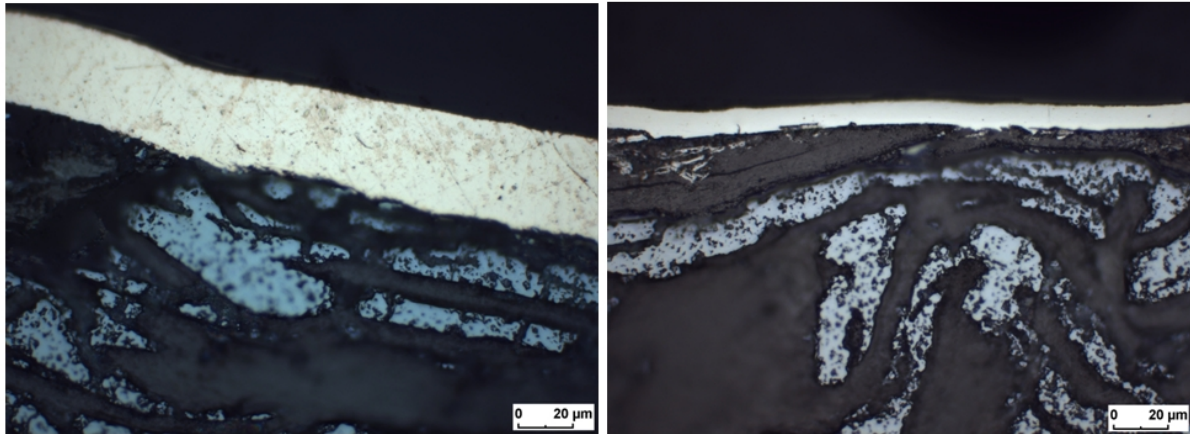


Figure 8: High damping metal- graphite composites made by powder metallurgy in comparison with reference materials

### Surface Modification

To build up heat sinks (cooling parts) it is necessary to modify the surface of the composite. Coating the surface with copper, nickel or gold is possible for metal- graphite composites. The thickness of a coating with copper and nickel is shown in figure 9 for a substrate made of tungsten and 70 vol. % of graphite. The adhesions of the coatings will investigate in further experiments.



a) b)  
 Figure 9: Optical micrograph of surface modification of a Tungsten- Graphite composite by adding a) a copper layer of 20 μm thicknesses and b) a nickel layer of 11 μm thicknesses

**Summary and Conclusion**

Metal- graphite composites have a great potential for the use as thermal management materials due to the combination of high thermal conductivity in the range of 300 up to 550 W/ mK, reduced coefficient of thermal expansion in the range of 3 up to 10 ppm/ K, stiffness and strength. Additionally the composites are well machinable with conventional techniques and have high mechanical damping capability. A modification of the surface with a coating with nickel, copper and gold is possible and enables adjustment of the necessary surface roughness. Figure 10 gives an overview about the most used materials for Thermal Management applications. The possible combinations of TC and CTE of investigated metal-graphite composites are highlighted in red. The innovative composites made out of iron or tungsten as matrix give the opportunity to generate composites with a CTE in the range between 3 and 5 ppm/ K with a TC between 300 and 400 W/ mK.

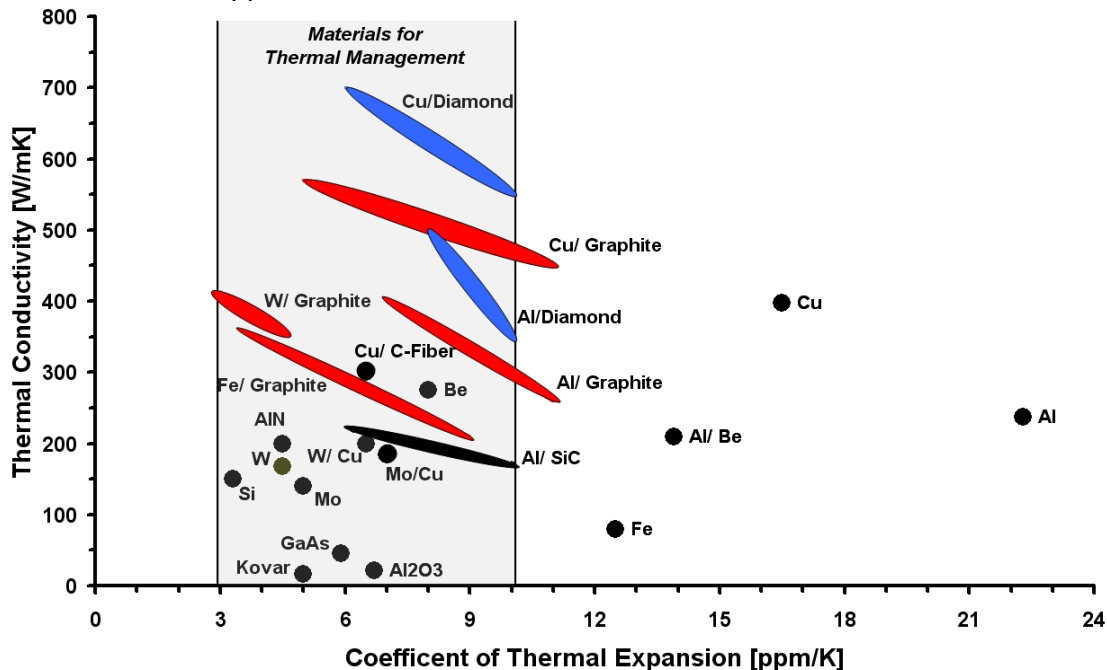


Figure 10: Overview about the most used materials for Thermal Management applications in comparison to the innovative metal- graphite composites sintered by Fraunhofer IFAM-DD

**References**

- [1] J. Norley, The Development of a Natural Graphite Heat-Spreader, 17. IEEE SEMI-Therm Symposium, San Jose, CA, March 20–22, 2001.
- [2] Fukushima, High-thermal-conductivity graphite-particles-dispersed-composite and its production method, US Patent 20090035562
- [3] MER Corporation, GraphMet350, <http://www.mercorp.com/mercorp/products3.htm>
- [4] ALG2208, <http://hos.cms.schunk-group.com/de/hos/Thermal-Management/schunk01.c.44935.de>
- [5] AlGrp, <http://www.mmccinc.com/thermal.htm>
- [6] Rajkumar. K and S. Aravindan, COPPER-GRAPHITE COMPOSITES, International Conference on Advanced Materials and Composites (ICAMC-2007), Oct 24-26, 2007
- [7] S.F. Moustafa et al., Effect of graphite with and without copper coating on consolidation behaviour and sintering of copper-graphite composite, Powder Metallurgy 1997, Vol.40 No.3, pp201 - 205
- [8] Th. Schubert et al., Carbide formation in copper-carbon composites and its effect on thermal conductivity, Advances in powder metallurgy & particulate materials - 2007. Vol. 2 : Proceedings of the 2007 International Conference on Powder Metallurgy & Particulate Materials, PowderMet 2007. May 13 - 16, Denver, Colorado
- [9] Kawai et al., Thermal conductivity and the cooling performance of Cu alloy-graphite composite heat spreaders fabricated by the powder metallurgy, Nippon seramikusu kyokai gakujutsu ronbunshi, ISSN 0914-5400 CODEN YGKSA4 , 2001, vol. 109, n 11, pp. 944-949
- [10] <http://www.sorbothane.com/blog/vibration-damping-material/>
- [11] N. Ya. Rokhmanov et al. Thermal expansion of cementite in hypereutectoid iron-carbon alloy Termicheskaya Obrabotka Metallov, No. 1, pp. 6- 9, January, 1997.