

Thermal expansion of Cu/graphite composites: effect of copper coating

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Received 18 August 2011, received in revised form 9 October 2011, accepted 11 October 2011

Abstract

Cu/graphite composites with 30 and 50 vol.% of graphite were prepared. Copper coated graphite particles enabled to prepare more homogeneous structure at 50 vol.% of graphite as simple powder mixture. In the case of 30 vol.% of graphite, composite prepared from mixture of coated graphite and copper powders is more heterogeneous as simple powder mixture. Measured CTE of coated composites was significantly smaller at both compositions. It is the result of the different area of copper-graphite interface that is established only by mechanical clamping. For coated composites the area of interface increases significantly due to avoiding graphite clustering. Simple model was proposed to predict this behaviour on the basis of anisotropy of graphite CTE. Further, the model can be used for calculation of the thermal expansion coefficient of the graphite reinforcement.

Key words: metal matrix composites, thermal expansion, coating

1. Introduction

Thermal considerations in the electronic package design have become critically important because electronic devices generate more heat, as the power output gets higher. The operating temperature together with the thermal stress caused by both the operation cycle and soldering limit the reliability of electronic parts. Therefore, both an efficient cooling and a reduced mismatch of the coefficient of thermal expansion (CTE) with chip materials are required. The desired thermal properties are: Thermal conductivity higher than $150 \text{ W m}^{-1} \text{ K}^{-1}$ and the CTE in the range of $4\text{--}9 \times 10^{-6} \text{ K}^{-1}$ [1, 2]. No conventional material meets these requirements.

Besides other materials, carbon or graphite reinforced copper matrix composites (Cu/C or Cu/graphite) are good candidate materials for heat sinks as they can efficiently dissipate generated heat [3–8]. The properties of the composite are given mainly by the properties of its constituents. At room temperature, copper has high coefficient of thermal expansion

$16.9 \times 10^{-6} \text{ K}^{-1}$. Graphite possesses the CTE anisotropy: for main crystal directions it is $-1 \times 10^{-6} \text{ K}^{-1}$ for basal plane, and $26 \times 10^{-6} \text{ K}^{-1}$ perpendicularly to basal plane [9]. However, polycrystalline graphite of various qualities is usually used. Then its average CTE can vary between $0\text{--}5 \times 10^{-6} \text{ K}^{-1}$ [9]. Further, by using of copper coated graphite particles instead of a mixture of copper and graphite particles, more homogeneous graphite particle distribution is expected to be achieved. Therefore the main aim of the paper is to measure the CTE of Cu/graphite composite and to show how it is influenced by the copper coating.

2. Experimental

Cu/graphite composites with 30 and 50 vol.% of graphite were prepared from the mixture of copper, graphite powder or copper coated graphite powder (Figs. 1, 2). Composites were prepared by HIP-ing at 950°C for 1.5 h under the argon pressure of 150 MPa. Used powders were pure copper (particle

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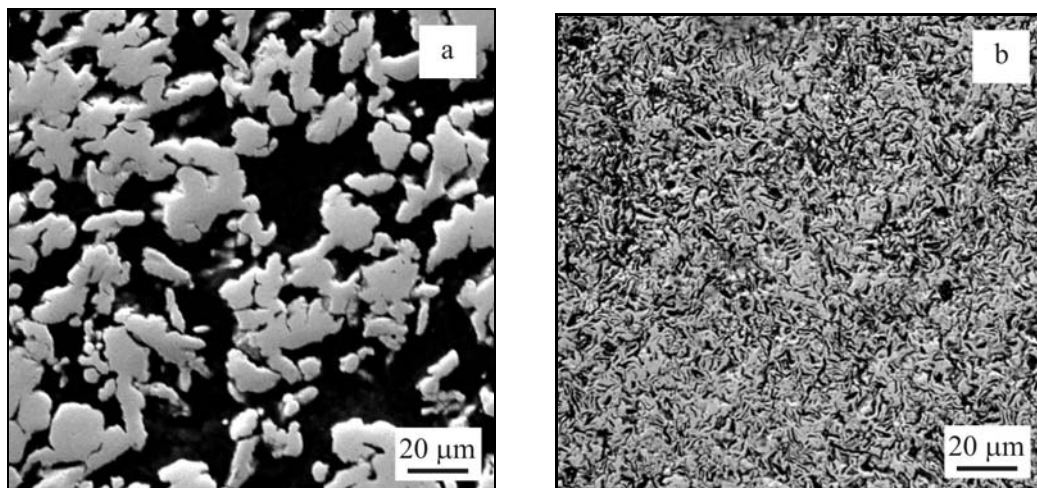


Fig. 1. SEM structures of Cu/graphite composites at 50 vol.% of graphite: left – uncoated, right – coated graphite.

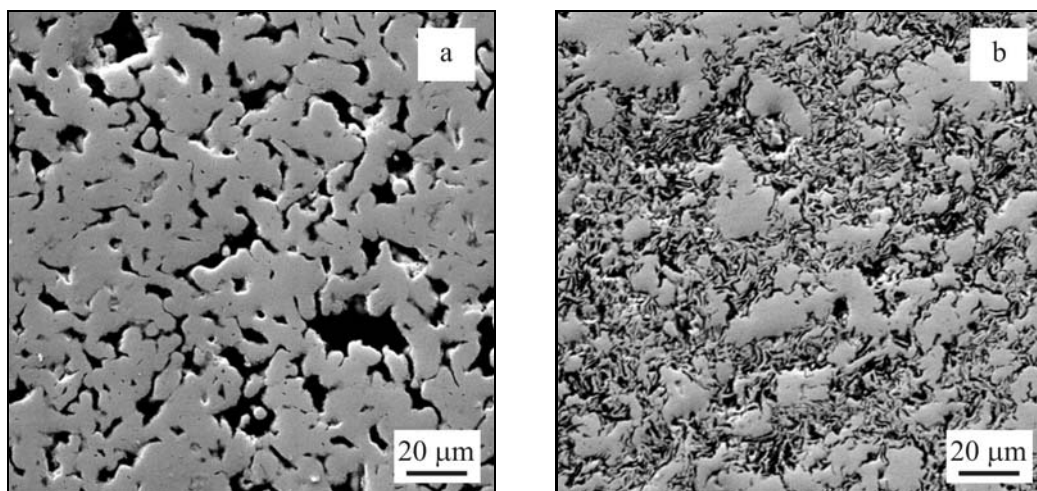


Fig. 2. SEM structures of Cu/graphite composites at 30 vol.% of graphite: left – uncoated, right – coated graphite.

size $< 63 \mu\text{m}$, average particle size $22 \mu\text{m}$, purity 99.9 %), and graphite (average particle size $16 \mu\text{m}$, purity 99.9 %) powders. The same graphite powder was copper coated by electroless coating at company Platingtech, Austria.

The copper powder has dendritic shape while graphite powder is of the flake shape. The amount of coated copper corresponds to 50 vol.% of graphite in the final composite. Cu/graphite coated composite with 30 vol.% of graphite was prepared by admixing of copper powder to copper coated graphite powder with 50 vol.% of graphite.

Thermal expansion measurements were performed in a classical mechanical push-rod dilatometer Perkin-Elmer TMS 2 dilatometer, temperature range RT – 250°C and heating rate 2.5 K min^{-1} . The linear CTE was measured as defined by the equation:

$$\alpha = \varepsilon \frac{1}{\Delta T} = \frac{\Delta l}{l_0} \frac{1}{\Delta T}, \quad (1)$$

where α is the coefficient of thermal expansion, $\Delta T = T - T_0$ is the temperature interval ($T_0 = 293 \text{ K}$), l_0 is the length of the sample before testing, Δl is the expansion for ΔT : $\Delta l = l - l_0$, and $\varepsilon = \Delta l/l_0$ is the relative length change. Samples were measured in an argon atmosphere. The calibration was performed according to DIN 51045 with NBS-Pt.

Measured samples had the shape of a disc with dimensions $\varnothing 5 \text{ mm} \times 12.0 \text{ mm}$. Parallel surfaces of samples were machined with a tolerance of $\pm 0.02 \text{ mm}$. From the known geometry and weight the density of the sample was calculated. For each composition three different samples were prepared, tested, and average values were used for analysis of coefficient of thermal expansion.

3. Results and discussion

In Fig. 3 thermal expansion behaviour of three

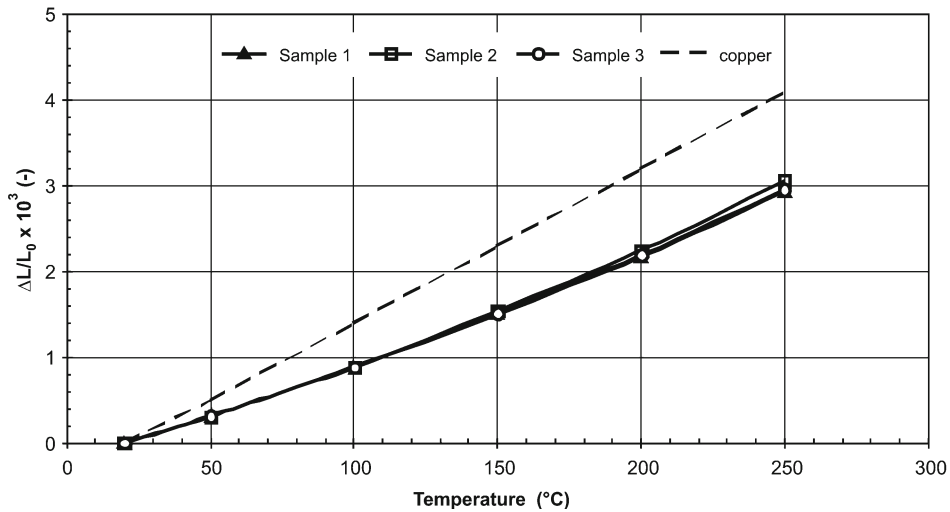


Fig. 3. Relative elongation of three Cu/graphite composite samples at 50 vol.% of graphite: copper coated graphite.

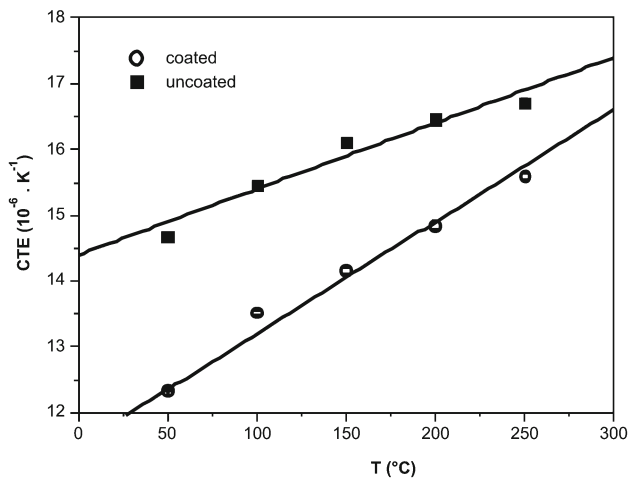


Fig. 4. Temperature dependence of the CTE for Cu/graphite composites at 30 vol.% of graphite.

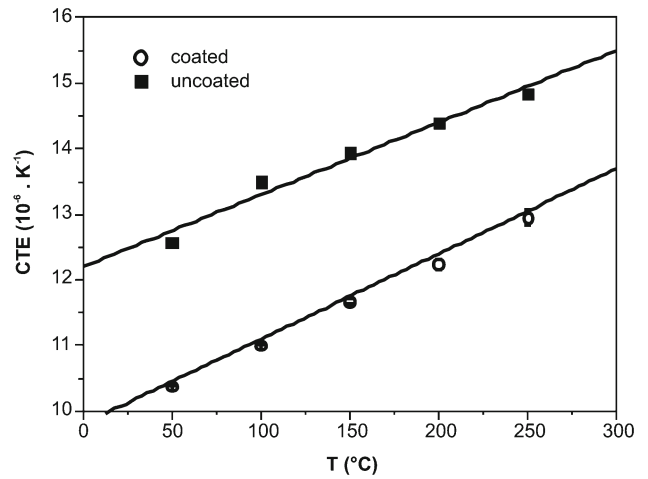


Fig. 5. Temperature dependence of the CTE for Cu/graphite composites at 50 vol.% of graphite.

Cu/graphite composite samples at 50 vol.% of graphite for copper coated graphite composite is presented. For comparison the elongation curve of pure copper is also plotted. As can be seen the curves for composite samples coincide very well. The situation was the same for all investigated compositions. From the curves temperature vs. elongation the coefficient of thermal expansion was calculated for each sample. Then the average CTE values were calculated for each composition and temperature range.

Experimental results showed that the CTE of Cu/graphite composites increased with increasing temperature (Figs. 4, 5): Thermal expansion of materials is a result of the fact that the oscillations of atoms are non-harmonic, i.e., the movement of atoms in the outward direction from the point of equilibrium is larger than the movement inwards. Therefore, the CTE of usual materials, such as copper, increases

with temperature because the atomic vibrations increase with temperature. Some materials may have different thermal expansions in the different crystal axes. Several materials, such as graphite, have not only different thermal expansions in the different crystal axes, but also positive and negative thermal expansions due to inter-atomic forces within the graphite crystal. Since the CTE of investigated composites increases with temperature, it is obvious that positive copper and graphite CTEs play a dominant role over the negative graphite CTE in Cu/graphite composites.

For both compositions, the CTE of the composite prepared from copper coated graphite powder is significantly smaller than for simple powder mixture. It is also slightly above the required limit for electronic package design. Therefore, in the case of coated composites, it will be possible to reach this limit by

Table 1. Image analysis of Cu/graphite composites for graphite phase (Figs. 1, 2)

Composition	Cu + 30 vol.% graphite		Cu + 50 vol.% graphite	
	uncoated	coated	uncoated	coated
Coating				
Number of clusters	[-]	217	64	704

varying of the graphite volume fraction. However, the thermal conductivity of Cu/graphite composite decreases with increasing graphite concentration thus limiting the usability of the composite material for heat sinks applications. The experimental results highlighted one interesting point: For the same composition, the identical graphite powder gave different values of the CTE. How to explain and model this?

It was stated above that copper had the positive CTE, while graphite showed both, the positive and the negative CTE in principal axes of its hexagonal structure. Together, these two materials form a composite that expands differently with temperature as each individual component. With increasing temperature the thermal stress occurs in the vicinity of the copper-graphite interface, because materials are not allowed to expand freely with temperature. Thus the area of the interface will rule the CTE of Cu/graphite composites.

The interface strength itself is very small because of insolubility of carbon in copper up to very high temperatures: Carbon solubility in copper does not exceed 0.02 at.% [10]. Therefore, the interface between copper and graphite can be usually established only by mechanical clamping effect.

The coating enables copper atoms to cover better the surface of graphite and invade better into the graphite micro pores. Nevertheless, the area of the interface increases significantly in comparison with simple mixture of copper and graphite particles as a result of the separation of graphite particles from themselves due to coating, thus preventing them to cluster during composite preparation. This separation is evident from Figs. 1 and 2 and is confirmed by image analysis: For all compositions, the increased number of graphite clusters indicates the separation of coated graphite particles (Table 1).

At 50 vol.% of graphite, the coated composite possesses the structure with fine and homogeneous graphite distribution. When a mixture of copper and graphite powders is used the clustering effect of powders takes place. At 30 vol.% of graphite the coated composite consists of clustered copper particles and regions containing coated graphite. This gives significantly heterogeneous composite in comparison with uncoated one, but again with significantly higher interface area.

The question is how to determine this interface

area difference quantitatively and how to model this CTE behaviour. Image analysis of the structure is very difficult in this case and it is not sure if obtained results will be exact enough. The surface area of used graphite powder can be determined experimentally, thus the only question is to determine the amount of area lost during the clustering in the case of uncoated composites.

It is possible to determine it by following gedanken-experiment:

There are a lot of models to predict the thermal expansion coefficient of composites. All of them are based on certain assumptions and simplifications [11–16]. Many of them consider a composite as a black box. Effective CTE of such black box is mainly a function of the unique combination of volume fraction, Young's modulus, shear modulus and Poisson's ratio of composite phases. In this work, the starting graphite material consisted of particles in the form of flakes. It can be expected, that graphite particles, like a graphite monocrystals, possess different physical and mechanical properties parallel and perpendicular to the powder axis. When such powder is embedded in the copper matrix their mutual interaction is also anisotropic. Thus anisotropy of graphite properties can be taken into account within the model. Due to the lack of precise property values of graphite the simple model by Schapery [13] was chosen for the CTE prediction:

$$\alpha = \frac{\alpha_a E_a V_a + \alpha_c E_c V_c + \alpha_{Cu} E_{Cu} V_{Cu}}{E_a V_a + E_c V_c + E_{Cu} V_{Cu}}, \quad (2)$$

where α , V and E are the CTE, the volume fraction and the Young's modulus, respectively. The properties of graphite in the direction perpendicular and parallel to the main powder axis are denoted as a and c (Fig. 6). Cu subscripts denote the properties of the copper.

For the investigated Cu/graphite composites, the properties of the raw materials are almost the same; the main difference is in the interface area. In the case of uncoated graphite powder clustering takes place, i.e., the graphite powders are more or less packed together. As a result, the interface area between copper and graphite phases decreases significantly in comparison with coated composites. The higher is the degree of clustering, the lower is the interface area. Due to

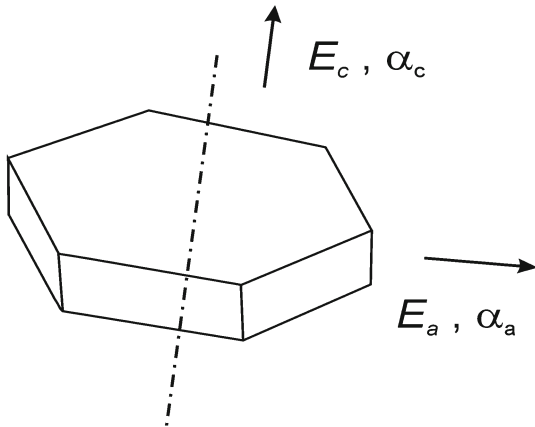


Fig. 6. Definition of graphite powder anisotropy used in the model: a – means perpendicular to main axis, c – parallel to main axis.

anisotropy of graphite properties (positive and negative CTE) different clustering (Fig. 7) can produce different CTE of composite.

Principally, the overall volume of graphite can be divided into two parts, one corresponding to copper-graphite interface with prevailing positive CTE of graphite and second one with prevailing negative CTE of graphite. It can be assumed that $V_a = c_a V_G$ and $V_c = c_c V_G$, where c_a and c_c represent the fraction of graphite volume V_G acting in the resulting composite with negative and positive CTE, respectively. $c_a + c_c = 1$, because $V_a + V_c = V_G$. Using these assumptions,

the model changes to

$$\alpha = \frac{(\alpha_a E_a c_a + \alpha_c E_c (1 - c_a)) V_G + \alpha_{Cu} E_{Cu} V_{Cu}}{(E_a c_a + E_c (1 - c_a)) V_G + E_{Cu} V_{Cu}} \quad (3)$$

The proposed model was used to calculate the CTE of composites at room temperature (Table 2): The value of c_a was varied to obtain similar value of composite CTE as measured. Graphite CTE values were used according to [9]. Values of the mechanical properties of graphite were roughly estimated according to the work of Korb et al. [16].

In coated composites the coefficient $c_a \approx 0.5$ confirms separation of graphite particles. On the contrary, clustering of graphite in uncoated composites is confirmed by the value of $c_a \approx 0.265$.

At this point it is necessary to end the gedankenexperiment and to analyse the results from the point of view of surface area.

It is evident, that there is 50 % less of the volume connected to the negative CTE in the case of uncoated composites. This can be connected to the copper-graphite interface area in the direction perpendicular to basal plane of graphite flake-type particle. It indicates that the clustering in the form of the stacking of graphite particles similar to the conditions illustrated at Fig. 7 – centre takes place at uncoated composites. Table 1 indicates that there is really at least 50 % difference in the number of graphite clusters within coated and uncoated composites. As a result, the CTE of uncoated composites is higher than that for coated composites at the same volume fraction of graphite.

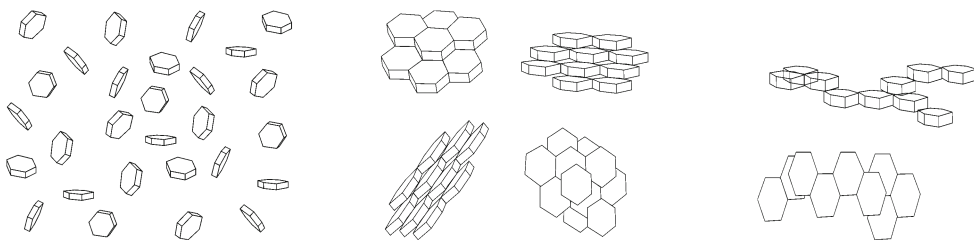


Fig. 7. Sketch of various possible fillings of the copper matrix with graphite: left – fully separated, centre – clustered predominantly in c-direction, right – clustered predominantly via a-direction.

Table 2. Measured CTE, model parameters and calculated CTE for the investigated Cu/graphite composites at room temperature

		α_{meas}	α_a	α_c	α_{Cu}	E_a	E_c	E_{Cu}	c_a	α_{calc}
		($10^{-6} K^{-1}$)	($10^{-6} K^{-1}$)	($10^{-6} K^{-1}$)	($10^{-6} K^{-1}$)	(GPa)	(GPa)	(GPa)	(-)	($10^{-6} K^{-1}$)
50 vol.%	coated	10.4							0.435	10.39
	uncoated	12.6							0.270	12.59
30 vol.%	coated	12.4	-1	26	16.9	200	20	125	0.535	12.41
	uncoated	14.7							0.260	14.68

Further, the proposed model for the CTE of composite enabled to estimate the CTE of pure graphite powder to be approximately $2.1 \times 10^{-6} \text{ K}^{-1}$ ($c_a \approx 0.435$).

4. Conclusions

Cu/graphite composites were prepared with 30 and 50 vol.% of graphite from both uncoated and the copper coated graphite powder. The graphite powder used for the preparation of all composite types was identical. For copper coated particles, the material with 50 vol.% of graphite revealed homogeneous isotropic structure. In the case of 30 vol.% of graphite, the composite has more heterogeneous structure as simple powder blend.

The CTE of composites was measured in the temperature range between RT – 250 °C, where the CTE of composites increased almost linearly with temperature. The obtained CTE of coated composites is significantly lower than the CTE of uncoated ones for both compositions. It was showed that the interface between copper and graphite governed the coefficient of thermal expansion of the composites as there is only mechanical clamping that usually establishes at the copper-graphite interface. In the case of coated composites the area of interface increases significantly as a result of coating which prevents clustering of graphite particles during composite preparation. Therefore fine and homogeneous graphite distribution without any clustering is the key factor for lowering the CTE not only of Cu/graphite composites, but also Cu/carbon fibres and Cu/carbon nanotubes composites. The proposed model was successfully used to estimate the area of the interface and enabled to predict the CTE of pure solid graphite of $2.1 \times 10^{-6} \text{ K}^{-1}$.

Acknowledgements

Authors thank the Slovak Grant Agency – VEGA grants No. 1/0114/10 and 2/0191/10 and APVV VMSP-II-0009-09 for funding this work. Š. E. thanks AMTT program for funding the CTE measurement (Austrian Research Centres, Seibersdorf, LSF contract No. HPRI-1999-00024).

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