THERMAL PROPERTIES OF Cu-GRAPHITE COMPOSITES

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Cu-graphite composites were prepared by HIP-ing at 50 vol.% of graphite. Coated composite was made from copper coated graphite powder. Uncoated one was made from the same graphite powder mixed with copper powder. Specific heat, thermal diffusivity and conductivity of both composites were measured and compared. While specific heat of composites is similar, thermal diffusivity and conductivity of coated composite is significantly lower. It was assumed to be the result of the different microstructure and thermal resistance of copper-graphite interface.

Key words: metal matrix composites, hot isostatic pressing, coating, thermal conductivity

TEPELNÉ VLASTNOSTI KOMPOZITOV Cu-GRAFIT

Kompozity Cu-grafit s 50 obj.% grafitu sme pripravili *HIP-ovaním.* Povlakovaný kompozit sme vyrobili z pomedeného grafitového prášku a nepovlakovaný kompozit zo zmesi toho istého grafitového prášku a prášku medi. Namerali a porovnali sme merné teplo, teplotnú a tepelnú vodivosť oboch kompozitov. Kým merné teplo kompozitov je porovnateľné, teplotná a tepelná vodivosť povlakovaného kompozitu je výrazne nižšia. Predpokladáme, že je to dôsledok rozdielnej mikroštruktúry a tepelného odporu rozhrania meď-grafit.

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1. Introduction

In the case of low voltage and high current densities, typically for welding applications, it is reasonable to employ materials with a high specific electrical conductivity, satisfactory thermal conductivity and low friction coefficient. Such conditions are fulfilled by copper-graphite (Cu-graphite) composite material [1–5]. There, copper matrix shows high electrical conductivity while graphite in the form of particles creates the secondary phase in the matrix thus ensuring high sliding properties. Both phases are good thermally conductive.

At present the Cu-graphite material is mainly produced from powders, which are mixed and sintered and their average diameter is in the range of ten to hundred micrometers. By using copper coated graphite particles instead of a mixture of copper and graphite particles a better particle distribution is expected to achieve. This results also in a continuous copper network at high vol.% of graphite for a good electrical conductivity. Another benefit is the improved interface between the matrix and the inclusions due to mechanical clamping effect between the coating and the particle. To investigate how copper coating will affect the thermal conductivity of Cu-graphite particulate composite is the main aim of the paper.

2. Experimental

Composites with 50 vol.% of graphite (Fig. 1) were prepared from the copper coated graphite powder and from the mixture of copper and graphite powder. Composite materials were prepared by HIP-ing using pure copper (particle size $< 70\ \mu$m, average particle size 22 μm, purity 99.9 %), and graphite (average particle size 16 μm, purity 99.9 %) powders. The same graphite powder was copper coated using a conventional electroless coating process at company Platingtech, Austria. The starting powders were wet mixed (if necessary) and dried afterwards. Then the mixture was cold compacted to a pellet, put into a steel tube, evacuated and sealed. The sample was HIP-ed at 950 ℃ for 1.5 hour under the pressure of 150 MPa.

The thermal conductivity of Cu-graphite composites was measured by the transient laser flash method [6]. In this method the laser beam supplies a flash of energy on the front face of a thin disc and the thermal diffusivity is computed from the resulting temperature response on the rear face of the sample. Calculation of the thermal diffusivity from measured data is based on the knowledge of the half time ($t_{0.5}$), i.e., the time, which corresponds to temperature rise into the half of its maximum value. The thermal diffusivity a is given from the thickness of the sample l and specific time $t_{0.5}$ according to the formula:

$$a = \frac{0.139 \cdot l^2}{t_{0.5}}. \tag{1}$$

The thermal diffusivity was measured in the temperature interval from room temperature (RT) – 250 ℃. Sensitivity of the measurement was ± (3–5) % in the measured temperature range. The conventional experimental formula was corrected by

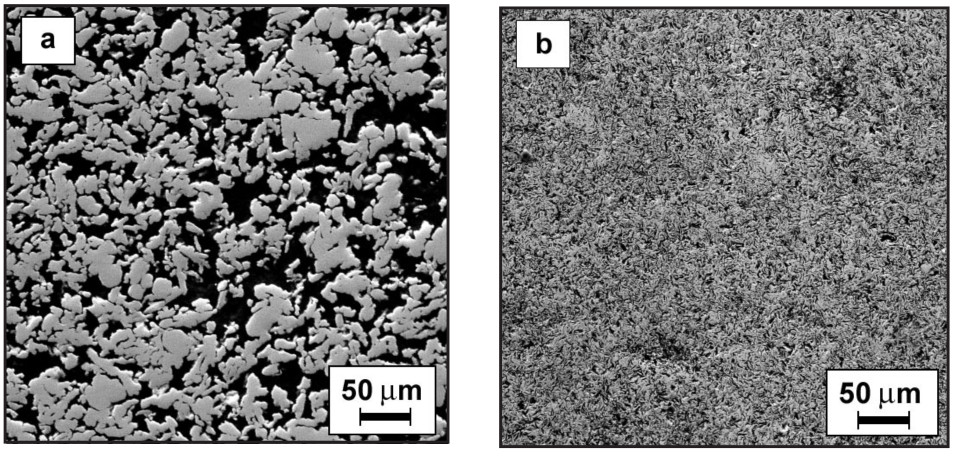

Fig. 1. Structures of Cu-graphite composites at 50 vol.% of graphite (black colour): a) uncoated, b) coated graphite composite (SEM).

using the method according to Clark and Taylor [7] or Degiovanni [8]. For equipment calibration, both stainless steel and Poco-graphite were used. A time interval of the flash was short compared with the time required for the resulting transient flow of heat to propagate through the sample. Measurements were performed according to ISO 9001 and ISO 45001.

Thermal conductivity λ can be calculated from

$$\lambda = a \cdot c_{\mathrm{p}} \cdot \rho, \tag{2}$$

where a is thermal diffusivity, ρ and c_{p} is the density and specific heat at constant pressure of the sample. Specific heat represents the quantity of heat required to produce a unit temperature rise within material under conditions of either constant volume (c_{v}) or constant pressure (c_{p}). Specific heat can be measured by using a drop calorimeter. A sample of known mass is heated to a known temperature and it is then transferred to the calorimeter. From the calorimeter the curve of the temperature – enthalpy is recorded and the slope of the curve at a given temperature is the specific heat. The specific heat at constant pressure was determined using Differential Scanning Calorimetry. The measurement was performed between 50 and 250 ℃ in inert gas atmosphere in the Perkin Elmer DSCII.

The measured samples had the shape of a disc with dimensions $\phi\ 10 \times 2.7$ mm. Parallel surfaces of samples were machined with a tolerance of $\pm\, 0.02$ mm. From the known geometry and weight the density of the sample was calculated. For each composite and property three different samples were prepared, measured, and average values with errors were used for analysis of thermal properties.

3. Results and discussion

3.1 Specific heat

Specific heat is one of important parameters for thermal conductivity calculation. For the composites, where matrix and filler are mutually non-reactive, insoluble and only wetting occurs between them, the specific heat can be calculated directly by the following:

$$c_{\mathrm{p}}^{\mathrm{comp}} = \frac{1}{\rho_{\mathrm{comp}}} \cdot (V_{\mathrm{Cu}} \rho_{\mathrm{Cu}} c_{\mathrm{p}}^{\mathrm{Cu}} + V_{\mathrm{gr}} \rho_{\mathrm{gr}} c_{\mathrm{p}}^{\mathrm{gr}}), \tag{3}$$

where V is volume fraction of components, ρ is density and c_{p} is specific heat at constant pressure. Symbols comp, Cu and gr denote the composite, copper and graphite properties, respectively. The non-reactivity takes place for the investigated Cu-graphite composites, because carbon is insoluble in copper up to very high temperature; its solubility does not exceed 0.02 at.% [9].

Figure 2 confirms cubic dependence of the specific heat of composites upon temperature according to the Debye phonon model. This is due to the fact, that Debye's temperature for pure copper is 343 K (70 °C); and even much higher Debye's temperature can be expected for graphite: Debye's temperature of diamond is about 2230 K (1960 °C). Similar temperature dependence of specific heat was obtained by Koráb et al. [10] for Cu-carbon fibres composite at 50 vol.% of carbon.

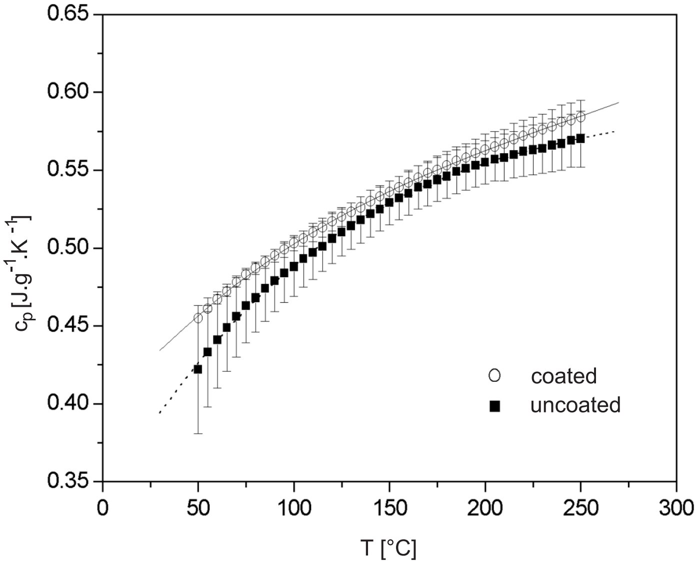

Fig. 2. Temperature dependence of the specific heat at constant pressure for Cu-graphite composites at 50 vol.% of graphite.

Table 1. Specific heat of the composite at 50 ℃ and estimated specific heat of graphite according to Eq. (3): Specific heat of copper 0.385 $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$ [10], density of copper 8.93 $\mathrm{g \cdot cm^{-3}}$, density of graphite 1.88 $\mathrm{g \cdot cm^{-3}}$ [12]

Coating		Uncoated	Coated
Density of composite	$[\mathrm{g \cdot cm^{-3}}]$	5.41 ± 0.02	5.50 ± 0.09
Measured c_p	$[\mathrm{J \cdot g^{-1} \cdot K^{-1}}]$	0.422 ± 0.041	0.455 ± 0.001
Calculated c_p	$[\mathrm{J \cdot g^{-1} \cdot K^{-1}}]$	0.422	0.454
c_p of graphite	$[\mathrm{J \cdot g^{-1} \cdot K^{-1}}]$	0.60	0.83

High scatter of the specific heat data was observed for uncoated composite. It is surprising because higher scatter of the composite density was found for the coated composite (Table 1). Using the experimental values of specific heat for composite and specific heat data for copper, we can estimate the specific heat of used graphite powder. The results in Table 1 indicate that specific heat of the used graphite powder at constant pressure is in the interval 0.6 – 0.83 $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$ and is consistent with specific heat data range of commercial graphite materials: 0.71 – 0.83 $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$[11].

3.2 Thermal diffusivity

Thermal diffusivity data (Fig. 3) showed significant difference between coated and uncoated composites. In this case high scatter of the data is consistent with higher scatter of the composite density for coated composite (Table 1). Thermal diffusivity of both samples decreases almost linearly in the investigated temperature range. The experimental data are significantly lower than thermal diffusivity of pure copper $111.6 \cdot 10^{-6} \cdot \mathrm{m^2 \cdot s^{-1}}$ [11].

The observed difference of thermal diffusivity data can have different origin, such as measurement method, copper-graphite interface properties, and anisotropy of graphite.

At this point we shall discuss the suitability of the measurement method: The laser flash method is usually used to avoid time consuming and tremendous measurements of the thermal conductivity by stationary methods. The method is based on measuring of temperature rise on the rear surface of the sample, when the front surface is irradiated with a high-energy laser pulse. The temperature rise follows the propagation pattern of the heat pulse. Mathematical solutions for this method assume homogeneous materials.

Kerrisk [13] obtained a general criterion for the homogeneity of composite in the case of the flash method. It requires, that the particle size d of dispersed phase ought to be much smaller than the sample thickness l in following way:

$$d \cdot V^{-1/3} < \frac{l}{M}, \tag{4}$$

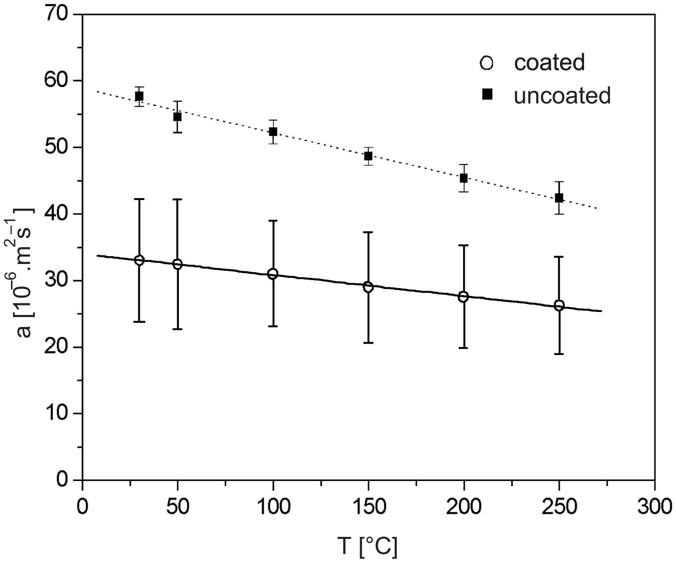

Fig. 3. Temperature dependence of the thermal diffusivity for Cu-graphite composites at 50 vol.% of graphite.

where V is a volume fraction of dispersed phase and M is a parameter which is usually $100 < M < 1000$.

Image Pro Plus (Media Cybernetics, USA) software was used to determine the diameter of particle size of the investigated composites. Cu-graphite composites consist of different microstructures (Fig. 1): Coated composite possesses fine structure of graphite particles encapsulated within continuous copper network. On the contrary, uncoated one consists of clustered copper within graphite matrix. For this reason different dispersed phases were used to evaluate the homogeneity of composite for laser flash method. While coated composite fulfils the criterion (Table 2), the uncoated one is slightly above the required limits. Summarizing, we can with certain error accept that the laser flash method is a proper measurement method in this case.

Table 2. Homogeneity criterion evaluated according to Eq. (4): volume fraction of dispersed phase $V = 0.5$, sample thickness $l = 2.7$ mm

M	[–]	1000	100
l/M	[μm]	**2.7**	**27**
Composite		uncoated	coated
Dispersed phase		copper	graphite
d	[μm]	38	23
$d.V^{-1/3}$	[μm]	**27** < 30.2	**2.7** < 18.3 < **27**

3.3 Thermal conductivity

While temperature dependences of the thermal conductivity of investigated Cu-graphite composites are almost identical, their magnitude is different (Fig. 4). Coated composite showed significantly lower value of thermal conductivity than uncoated one. Most probable explanation for this is the different microstructure of composites.

Composites consist of good thermal conductors, from which copper has thermal conductivity in the range of 360–400 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, while graphite conductivity is between 1–150 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ according to the degree of graphitization. Therefore, the heat flows primarily via copper phase and is dissipated on the copper-graphite interface. The microstructure and interface effects on the thermal conductivity of composites are usually characterized [14] by non-dimensional parameter α:

$$\alpha = \frac{d_{\mathrm{k}}}{d}, \tag{5}$$

where d is the average radius of dispersed particles and d_{k} is Kapitza radius defined as

$$d_{\mathrm{k}} = R_{\mathrm{Bd}} \lambda_{\mathrm{m}}, \tag{6}$$

where λ_{m} is the thermal conductivity of the matrix, and R_{Bd} is the thermal boun-

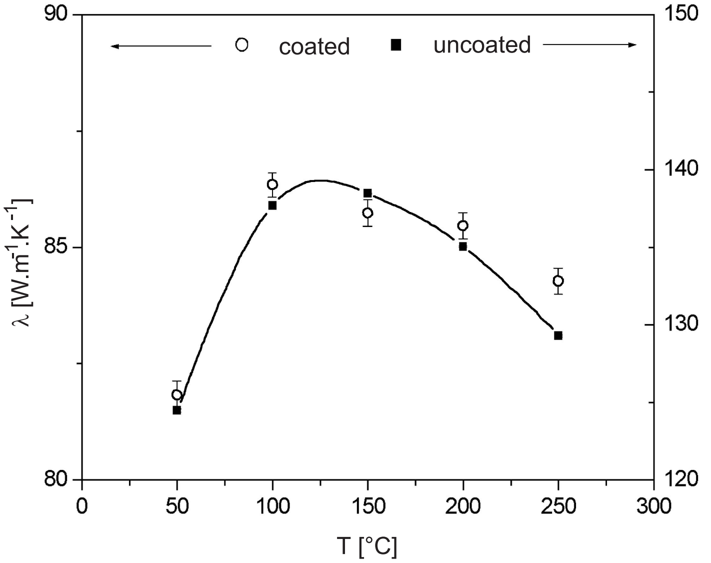

Fig. 4. Temperature dependence of the thermal conductivity for Cu-graphite composites at 50 vol.% of graphite.

dary resistance. Using a simple Debye model Kapitza radius can be estimated using

$$d_{\mathrm{k}} = \frac{4}{3} \cdot \frac{b}{\eta}, \tag{7}$$

where b is the phonon mean free path and η is the average probability for the transmission of the phonons across the interface from matrix into particle.

Copper coating of graphite particles prevents clustering of graphite, thus the radius of the dispersed particles is significantly smaller than for uncoated composite. Further coating increases significantly also the area of copper-graphite interface. The higher is the area of interface the higher is the thermal boundary resistance effect on the thermal conductivity of composite. Finally, due to small dispersion of graphite within continuous copper matrix, the mean free path of electrons and phonons in copper significantly decreases when compared with uncoated composite.

The value of α for the investigated composites can be estimated from Hasselman and Johnson [15] and Benveniste [16] model. They modified Maxwell's theory for the dispersed spherical particles of radius d, of a material having a thermal conductivity of λ_{d}, occupying a volume fraction V, embedded in a matrix with conductivity λ_{m}. Their result for the effective conductivity of composite λ_{comp} can be written in the following form:

$$\frac{\lambda_{\mathrm{comp}}}{\lambda_{\mathrm{m}}} = \frac{\left[\lambda_{\mathrm{d}}\left(1+2\alpha\right)+2\lambda_{\mathrm{m}}\right]+2V\left[\lambda_{\mathrm{d}}\left(1-\alpha\right)-\lambda_{\mathrm{m}}\right]}{\left[\lambda_{\mathrm{d}}\left(1+2\alpha\right)+2\lambda_{\mathrm{m}}\right]-V\left[\lambda_{\mathrm{d}}\left(1-\alpha\right)-\lambda_{\mathrm{m}}\right]}. \tag{8}$$

We tried to fit the experimental data to Eq. (8) with the thermal conductivity of copper matrix λ_{m} set to 375 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. However, varying of non-dimensional parameter α from zero to infinity gives no possibility to obtain the experimentally observed value of the thermal conductivity of composite.

For both composites there is the same graphite phase: The same graphite powder was used for composite preparation – uncoated and coated. Thus, besides copper-graphite interface the only other difference can have origin in copper phase. As was mentioned above, small dispersions of graphite in copper significantly decrease the electron and phonon's mean free path within copper. Hence, thermal conductivity of copper decreases as well. Therefore, thermal conductivity of copper matrix ought to be smaller for the coated composite. This was confirmed by results in Table 3. Besides uncertainty in the determination of λ_{m} and α, the $\alpha > 1$ indicates that the contribution of the graphite dispersions to the effective thermal conductivity of composite is dominated by the copper-graphite interface. This is due to the low solubility of carbon in copper, carbon material is not cohesive with copper and existing gaps decrease the resulting thermal conductivity of composite.

Thermal conductivity of composites can be modelled in various ways. As the values of the thermal conductivity of both phases are almost comparable, one can use also the effective medium theory (EMT). EMT considers a spherical entity consisting of a single phase embedded in the surrounding effective medium. For

Table 3. Non-dimensional parameter α and conductivity of copper matrix λ_m estimated according to Eq. (8) at 50 ℃: thermal conductivity of graphite $\lambda_\mathrm{d} = 10\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$, $V = 0.5$

Composite		Uncoated	Coated
λ_comp	$[\mathrm{W \cdot m^{-1} \cdot K^{-1}}]$	124.5	81.4
λ_m	$[\mathrm{W \cdot m^{-1} \cdot K^{-1}}]$	297	190
α	[–]	7.6	6.1

a two-phase composite in 3D, it gives [17]:

$$V_\mathrm{Cu} \cdot \frac{\lambda_\mathrm{Cu} - \lambda_\mathrm{comp}}{\lambda_\mathrm{Cu} + 2 \cdot \lambda_\mathrm{comp}} + V_\mathrm{gr} \cdot \frac{\lambda_\mathrm{gr} - \lambda_\mathrm{comp}}{\lambda_\mathrm{gr} + 2 \cdot \lambda_\mathrm{comp}} = 0, \tag{9}$$

where indices comp, Cu and gr indicate the thermal conductivity and volume fraction of composite, copper and graphite, respectively. Barta and Dieška [18, 19] investigated the problem of conductivity in particulate and fibre reinforced composites. They derived similar EMT formula as Eq. (9) for composites made from matrix and coated particles [19]. Their approach can be used to determine thermal conductivity of coated graphite particle or particle encapsulated by delaminated copper-graphite interface.

Equation (9) provides for uncoated composite $\lambda_\mathrm{comp} = 124.5\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and $\lambda_\mathrm{Cu} = 375\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ the thermal conductivity of graphite of $\lambda_\mathrm{gr} = 17.5\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ which is reasonable value. However, for the coated composite the experimental thermal conductivity ($\lambda_\mathrm{comp} = 81.4\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$) can be obtained only with negative thermal conductivity of "coated graphite".

Instead, one can use the estimated value of thermal conductivity of graphite to determine thermal conductivity of the copper matrix for coated composite. The thermal conductivity estimate $216.9\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ is remarkably below the thermal conductivity of copper $375\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. It can be considered, that thermal conductivity of coated composite can be influenced by the impurities rested in copper matrix due to electroless coating. However, using Jeol JSM 5310 microscope no additive elements above 1 at.% of additives in copper were observed. Furthermore, the estimated value coincides with the thermal conductivity of copper ($190\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$) determined by previous model for the coated composite.

Summarizing, both models indicate that the size of graphite particles influences copper-graphite interface properties.

4. Conclusions

Cu-graphite composites with 50 vol.% of graphite were prepared by HIP-ing. They were made either from the mixture of copper and graphite powders or from copper coated graphite. The same original graphite powder was used (uncoated and copper coated). Due to coating, the structure of coated composite consists of homogeneous dispersions of small graphite phase in continuous copper phase.

The mixture of graphite powder with copper powder has homogeneous but coarse dispersion of clustered copper and graphite phases.

The cubic temperature dependence of specific heat was observed according to the Debye phonon model. The estimated specific heat of used graphite is in the range $0.6-0.83\ \mathrm{J \cdot g^{-1} \cdot K^{-1}}$ that is consistent with data for commercial graphite materials: $0.71-0.83\ \mathrm{J \cdot g^{-1} \cdot K^{-1}}$.

Thermal diffusivity and conductivity of composites showed important difference between coated and uncoated composite. It is revealed that it is the result of the structure and the thermal resistance of copper-graphite interface. Thanks to the low solubility of carbon in copper the contribution of the graphite dispersions to the effective thermal conductivity of composite is dominated by the copper-graphite interface as confirmed by non-dimensional parameter $\alpha > 1$.

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REFERENCES

[1] EMMER, Š.—HAVALDA, A.—BIELEK, J.: J. Phys., *IV 3*, 1993, p. 1799.
[2] KOVÁČIK, J.—BIELEK, J. : Scripta Mater., *35*, 1996, p. 151.
[3] EMMER, Š.—NEUBAUER, E.—KORB, G.: In: Materials Week. Munich 2001.
[4] ŠEBO, P.—MARUNOVÁ, G.—ŠTEFÁNIK, P.—KAVECKÝ, Š.: Kovove Mater., *41*, 2003, p. 248.
[5] MOUSTAFA, S. F.—EL-BADRY, S. A.—SANAD, A. M.—KIEBACK, B.: Wear, *253*, 2002, p. 699.
[6] PARKER, W. J.—JENKINS, R. J.—BUTLER, C. P.—ABBOTT, G. L.: J. Appl. Physics, *32*, 1961, p. 1679.
[7] CLARK, L. M.—TAYLOR, R. E.: J. of Appl. Physics, *46*, 1975, p. 714.
[8] DEGIOVANNI, A.: Rev. Gen. Therm., *185*, 1977, p. 417.
[9] DORFMAN, S.—FUKS, D.: Composites A, *27A*, 1996, p. 697.
[10] KORÁB, J.—ŠTEFÁNIK, P.—KAVECKÝ, Š.—ŠEBO, P.—KORB, G.: Composites A, *33A*, 2002, p. 577.
[11] TAYA, M.—ARSENAULT, J. R.: Metal Matrix Composites – Thermomechanical Behavior. New York, Pergamon Press 1989.
[12] EMMER, Š.: unpublished results.
[13] KERRISK, J. F.: J. Appl. Phys., *42*, 1971, p. 267.
[14] EVERY, A. G.—TZOU, Y.—HASSELMAN, D. P. H.—RAJ, R.: Acta Metall. Mater., *40*, 1992, p. 123.
[15] HASSELMAN, D. P. H.—JOHNSON, L. F.: J. Comp. Mater., *21*, 1987, p. 508.
[16] BENVENISTE, Y.: J. Appl. Phys., *61*, 1987, p. 2840.
[17] LANDAUER, R.: In: AIP Conf. Proc. 40. New York, AIP 1978, p. 2.
[18] BARTA, Š.—DIEŠKA, P.: Kovove Mater., *40*, 2002, p. 99.
[19] BARTA, Š.—DIEŠKA, P.: Kovove Mater., *41*, 2003, p. 223.

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