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Thermal conductivity enhancement of copper–diamond composites by sintering with chromium additive

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Abstract The thermal diffusivity (TD) and thermal conductivity (TC) of Cu–Cr–diamond composite materials were examined in the temperature range from 50 to 300 °C for diamond volume fractions of 22, 40, 50, 55, and 60 %. The samples were fabricated by the plasma pulse sintering (PPS) method. TC does not increase proportionally with the diamond fraction in the particular composite materials. The highest TD was determined for 50 % diamond volume fraction, and the evaluated TC reached 658 W m^{-1} K^{-1} at 50 °C. This article complements earlier articles concerning synthesis and characterization of the diamond–copper composites produced by the PPS method.

Keywords Diamond · Composite · Thermal conductivity · Metal · Matrix

Introduction

Heat fluxes more often turn out to be a problem during the manufacturing of various products or during the usage (for example, electronics). Several active or passive methods are applied to act as the heat sink in such small structures and new devices. Thermal diffusivity (TD) and thermal conductivity (TC) enhancements lead to heat sink improvement from highly thermal loaded objects.

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Among materials studied for heat sink applications, diamond–metal composites are becoming more and more popular [1] because of their intriguingly high thermal conductivity. Many recent publications concern different physical parameters of such composites [2–8].

Potential applications for these materials can be seen in electronics for building heat sinks, heat spreaders, or simply heat conductors to transfer the heat from one point to another. Fast development of semiconductor technology (high-frequency transistors, high-power laser diodes) and devices, such as radars, amplifiers, or supercomputers, requires even more effective materials for heat flux removal than the commonly applied copper. Diamond powder can raise TC of pure copper theoretically even up to 200 %.

Pure copper and diamond do not bond in any way, but, in the presence of carbide-forming additives, i.e., zirconium, chromium, and boron, the bonding can be achieved [2, 3]. Chromium and boron considerably improve wettability and create a strong bond between the diamond and matrix. In case of chromium, during Cr_3C_2 sintering, an interface is created [9], which affects thermal conductivity by the appearance of interfacial thermal resistance. The Cr_3C_2 connection does not seem to form heterogeneous bonds depending on the Miller index as in Al–diamond compounds [10]. Large amounts of Cr bonds minimize thermal contact resistance within a composite structure.

The Maxwell equation [5], which assumes perfect bonds, shows that the theoretical value of the effective thermal conductivity of the copper–diamond material in proportion 1:1 reaches 842.1 W m^{-1} K^{-1} for $\lambda_{Cu} = 400$ W m^{-1} K^{-1} and $\lambda_D = 1{,}800$ W m^{-1} K^{-1}. This means that the thermal conductivity of 1:1 Cu–diamond composites will never reach that value, whatever be the size of diamond particles applied. Gaps between particles and matrix may also appear during the sintering process. This effect decreases TD and TC values

even further. The idea behind this research was achieving TC as close as possible to Maxwell's theoretical value.

In order to combine diamond powder with non-ferrous metals, several techniques are applied. Plasma pulse sintering (PPS) is one of the pulse current methods from which one of the best known is spark plasma sintering (SPS). A considerably higher single pulse energy of electrical current flowing through the material is the main advantage of PPS compared with SPS. Obtaining of the maximum possible value will require further understanding of the sintering technique development.

This article refers to [11] and is a complement of [3], where synthesis and interfacial characterization of Cu–Cr–diamond composites were investigated. The quality of the synthesis process will be evaluated by examination of thermal properties in a wide temperature range, above room temperature. Moreover, potential usability to above mentioned applications will be evaluated by a thermal characteristics analysis.

Experimental

Samples preparation

Samples were prepared by means of PPS method using powders of chromium–alloyed copper matrix with 0.8 % vol. content of Cr and FMD-80 diamond powder (60/80 mesh) in the following volumetric ratios of: 22, 40, 50, 55, and 60 % diamond to the matrix. Powder mixtures were consolidated in a graphite die using PPS method at the temperature of 930 °C and under the load of 80 MPa. The detailed PPS process description can be found in [12]. Thicknesses of the samples were measured using micrometer. The lowest sample had 3.55-mm height, and the time to reach maximum temperature stayed above 20 ms for all measurements. A trigger pulse for the laser causing TD error according to Schoderböck correlation amounted to less than 1 % [13]. The densities of samples were measured based on Archimedes principle.

Measurements

Thermal properties of fabricated composites were investigated. Samples' TD measurement was carried out by means of a laser flash technique [14–16] in the temperatures ranging from 50 to 300 °C using Netzsch LFA 457 Microflash equipment. The specific heat Cp of sintered composite was difficult to examine with precise diamond volume fractions. Cp of the composite was obtained by differential scanning calorimetry (Netzsch DSC 404 Pegasus F1) measuring copper, diamond, and chromium separately, Table 1. The densities of the specimens were also evaluated according to the formula [17]:

$$\rho_e = \rho_{Cu}(1 - v_d) + \rho_d v_d + v_{Cr}\rho_{Cr}v_d \quad (1)$$

where v_d and v_{Cr} are the diamond volume fraction and the chromium volume fraction; and ρ_{Cu}, ρ_d, and ρ_{Cr} are the densities of copper, diamond, and chromium, respectively. The thicknesses and densities of the specimens are given in Table 2. The heat capacity was determined from the relation [18]:

$$Cp(T) = \sum_i g_i Cp_i(T) \quad (2)$$

where g_i, and $Cp_i(T)$ are the mass fraction and temperature dependent heat capacity of each of the constituents, respectively. The TC was obtained from the formula:

$$\lambda(T) = a(T)\rho Cp(T) \quad (3)$$

where $\lambda(T)$ is calculated TC and $a(T)$is a measured TD.

Uncertainties of measurements for both TD and Cp were determined, which consist of systematic and random errors. Systematic error was assumed according to Netzsch instrument's accuracy ±3 %.

Results and Discussion

Five samples containing 22, 40, 50, 55, and 60 % of diamond powder in copper matrix with 0.8 %Cr addition were examined. Research was conducted in the temperatures

Table 1 Specific heat and density of the constituents of composites in a range of temperature 50–300 °C

T/°C	C_p/J g^{-1} K^{-1}			ρ/g cm^{-3}		
	Diamond	Cr	Cu [25]	Diamond	Cr	Cu [25]
50	0.609 ± 0.0193	0.427 ± 0.0134	0.392	3.52	7.15	8.9
100	0.768 ± 0.0270	0.468 ± 0.0138	0.397			
150	0.922 ± 0.0297	0.485 ± 0.0142	0.403			
200	1.067 ± 0.0320	0.491 ± 0.0144	0.407			
250	1.193 ± 0.0356	0.507 ± 0.0144	0.409			
300	1.300 ± 0.0369	0.515 ± 0.0146	0.411			

Table 2 Measured thickness and density of samples (calculated density differences)

Diamond content/ %	Sample thickness/ mm	Measured density/ρ/ g cm^{-3}	Density difference/ $\Delta\rho$/gcm^{-3}	Estimated porosity/ %
22	5.08	7.732	+0.027	0.3
40	6.33	6.610	+0.168	2.5
50	3.55	6.100	+0.133	2.1
55	4.65	5.480	+0.481	8.1
60	4.28	5.300	+0.388	6.8

ranging from 50 to 300 °C. This temperature range corresponds to typical electronics working conditions. Specific heat and density values for copper, diamond, and chromium, necessary for TC calculations are given in Table 3. On analyzing TD of specimens (Fig. 1), it can be noticed that 50 % of diamond volume fraction is characterized by the highest TD up to 238 mm^2 s^{-1} for 50 °C temperature. For these measurement conditions and diamond content, the TC reaches a value of 658 W m^{-1} K^{-1} (Fig. 2). The results from recent worldwide research did not exceed 620 W m^{-1} K^{-1} for sintering techniques with similar diamond content [2, 19, 20] except [20] where those authors report 654 W m^{-1} K^{-1} for 40 % SPS technique and 640 W m^{-1} K^{-1} for directly heated hot pressing technique [22]. Recently, values for copper–diamond sinter composite reached 750 W m^{-1} K^{-1} with the diamond content of 90 % and sintering pressure 6 GPa [23], and 900 W m^{-1} K^{-1} was reached with high temperature–high pressure technique [24]. At 300 °C, TD of 50 % diamond content specimen reached 133.1 mm^2 s^{-1}. For composites with higher diamond content, quick decreasing of TD with temperature is observed.

The lowest TD decrease with temperature occurs for pure copper (0 %) [25]. For higher TD value, this process accelerates. Comparing with copper, there is a slight TD change in temperature from 115.6 to 104 mm^2 s^{-1}.

Rapid TD drop is the characteristic for diamond. Thus, the higher diamond powder content causes higher TD drop

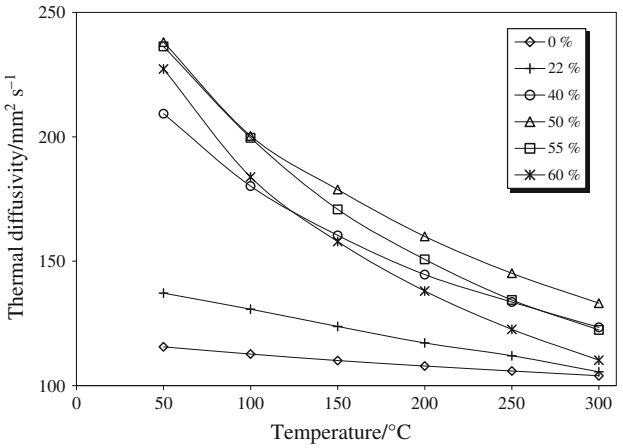

Fig. 1 Thermal diffusivity variation in function of temperature for copper–diamond composites for 0–60 % of diamond volume fraction

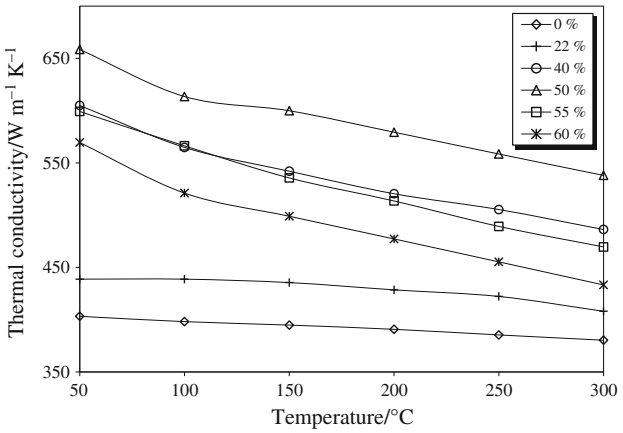

Fig. 2 Thermal conductivity of copper–diamond composites with diamond content form 0 to 60 % in function of temperature

in composite with the increasing temperature. Therefore, while analyzing TD at 300 °C, it has been noticed that very close values were achieved for 22, 60, and 0 % samples despite considerably varying diamond content. Unequal TD drop can be distinctly observed comparing two

Table 3 Thermal diffusivity a(T) of composites in a range of temperature 50–300 °C with measurement uncertainties

T/°C	a/mm^2 s^{-1}					
	0 % [25]	22 %	40 %	50 %	55 %	60 %
50	115	137 ± 5.01	209 ± 11.20	238 ± 10.54	236 ± 7.47	227 ± 8.47
100	112	130 ± 4.48	180 ± 7.55	200 ± 8.18	199 ± 7.13	183 ± 7.06
150	110	123 ± 4.16	160 ± 5.37	178 ± 5.38	170 ± 6.11	157 ± 6.10
200	107	117 ± 4.51	144 ± 4.79	160 ± 5.10	150 ± 4.88	138 ± 4.32
250	105	112 ± 4.40	133 ± 6.08	145 ± 4.44	134 ± 4.15	122 ± 4.12
300	104	105 ± 4.17	123 ± 5.21	133 ± 4.08	122 ± 3.96	110 ± 3.39

Table 4 Thermal conductivity $\lambda(T)$ of composites in a range of temperature 50–300 °C

T/°C	λ/W m^{-1} K^{-1}					
	0 %	22 %	40 %	50 %	55 %	60 %
50	403	438	605	658	599	569
100	398	438	565	613	566	521
150	394	435	542	600	535	499
200	390	428	520	579	513	477
250	385	422	505	558	589	455
300	380	408	486	538	469	433

samples: 40 and 60 % of diamond volume fractions. The first one features lower TD at 50 °C, but with rising temperature, the TD drop clearly proceeds slower.

In the range of 50–300 °C, density variation with temperature does not influence significantly on TC for Cu–Cr–diamond composite; thus, in this case it is negligible.

Estimated porosity level (Table 2) in fabricated composites below 55 % of diamond volume fraction is relatively small. Higher diamond contents intensify this porosity that effectively prohibits the transport of electron–phonon. Lower densification of samples with 55 and 60 % of diamond content should be attributed to difficulty with proper homogenization of initial copper/diamond powder mixture used for the pulse plasma sintering. The copper–diamond samples with 50 % diamond volume fraction characterize moderate, approximately linear TC drop. From 50 to 150 °C, this drop amounts to 9 % of the maximum value, and even then, the diamond composite is 155 % more capable of heat removal than pure copper. At this fraction, copper–diamond sinters seem to be perfectly applicable to heat sinks or heat spreaders because of high isotropic TC and relatively low TC drop within the temperature range of working electronics. It is also possible to apply this composites to work in higher temperatures with magnetrons, but the upper temperature limit of continuous operation was not determined (TC data are listed in Table 4).

An important issue which should be addressed in the future is graphitization of diamond caused by the sintering process. Based on the literature, we know that the allotropic transformation of diamond to graphite starts in vacuum at a temperature as low as 700 °C, and its rate increases with the increasing temperature [26]. Because the Gibbs free energy of Cr_3C_2 formation on diamond is lower than that on graphite [27], it is worth trying to fabricate copper–diamond composites at lower temperatures to minimize the graphitization of diamond. Moreover, because of a low thermal conductivity of graphite (especially in normal direction to graphene planes) [28], it may be also beneficial for the increase of the interfacial thermal conductance at the copper–diamond interface.

Conclusions

TC estimated by TD measurement of copper–diamond composites with chromium additives was investigated. Samples were prepared by a PPS technique. The highest TC that was observed for 50 % volume fraction diamond in matrix for samples ranged from 22 to 60 %. At 50 °C, TC reached 658 W m^{-1} K^{-1} which is the highest value for 50 % of diamond volume fraction according to the relevant literature. Decreasing TC with larger than 50 % diamond content seems to be connected mostly with the insufficiently homogenized Cu–Cr–diamond mixture, and thus with larger amount of pores in sinters volume (which is indicated by density differences $\Delta\rho$), but, at this stage of study, it cannot be concluded definitively. To confirm this assumption, further examinations concerning detailed matrix-diamond interfacial characterization are required.

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