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Effect of coating on the microstructure and thermal conductivities of diamond–Cu composites prepared by powder metallurgy

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ABSTRACT

Diamond–Cu composites from the direct combination of diamond and Cu show low thermal conductivities due to weak interface and high thermal resistance as a result of chemical incompatibility. In this paper, a new method is proposed to strengthen interfacial binding between diamond and Cu by coating strong carbide-forming elements, e.g., Ti or Cr on the surface of the diamond through vacuum micro-deposition. Interfacial thermal resistance of diamond–Cu composites is greatly decreased when diamond particles are coated by a Cr or Ti layer of a certain thickness before combining with Cu. Thermal conductivity is also increased several times. Cr coating can reduce more effectively interface thermal resistance between diamond and Cu than Ti coating. Moreover, it has a smaller negative impact on the thermal conductivity of the Cu matrix, resulting in higher thermal conductivity of Cr-coated diamond–Cu composites. Through the vacuum micro-deposition technology, Cr on the diamond particle surface is present in the form Cr_7C_3 near diamond and a pure Cr outer layer at 2:1. The optimum thickness is within 0.6–0.9 μm; at this depth, the thermal conductivities of 70 vol% diamond–Cu composites can be increased four times and reach as high as 657 W/m K. In this work, an original theoretical model is proposed to estimate the thermal conductivities of composite materials with an interlayer of a certain thickness. The predicted values from this model are in good agreement with the experimental values.

1. Introduction

Diamond–Cu composites have drawn much attention as new generation heat sink materials in the field of electronic packing because of their potential thermal conductivity higher than 500 W/m K, which is more than twice the value of current SiCp–Al composites or W–Cu alloys, and has lower CTE matching that of the chip [1–3]. Diamond–Cu composites can be prepared by powder metallurgy or metal infiltration; both have been widely used in the production of other heat sink materials, such as SiCp–Al or SiCp–Cu composites [4,5]. However, regardless of preparation techniques, the thermal conductivity of diamond–Cu composites is much lower than that of Cu itself if diamond particles compound directly with Cu. The reason for this is that diamond and Cu are chemically incompatible and their interface shows weak mechanical bonding; as a result, their interface thermal resistance is so high that the composites show low thermal conductivities. In order to reduce the interface thermal resistance between diamond and Cu, some methods must be used to turn their mechanical and physical bonding state into a chemical and metallurgical bonding. Based on a previous study, alloying Cu with minor amounts of carbide formers, e.g., Cr or B can improve bonding strength and thermo-physical characteristics by forming a thin nano-sized chromium carbide layer at the interface between diamond and Cu [1].

In this work, a new method is proposed to solve poor interface binding between diamond and Cu. In the proposed method, the diamond surface is coated with strong carbide-forming elements, e.g., Ti, Cr, Mo or W. These metal elements can act as middle layers that strengthen the interface; in addition, they can also protect the diamond powder from the atmosphere and reduce the degree of graphitization at high temperatures.

In this paper, both Ti and Cr metals are selected as the surface coating elements of diamond particles for two reasons: (1) the bonding force between Cu and Mo or W are much smaller than that between Cu and Ti or Cr because the solid solution degree of Mo or W in copper is zero; and (2) the process of coating Ti or Cr on the surface of the diamond particle can be carried out by vacuum micro-deposition technology, a method widely used in the manufacture of diamond tools. Although sputtering can be used to coat Ti or Cr metal on the surface of diamond particles, Wang [6] found that the resulting bonding state between diamond and Cr or Ti coating is still physical, and the interface bonding between diamond and Ti or Cr is so weak that Ti or Cr metal layer can be separated from the surface of diamond in the course of the collision with milling balls in the subsequent process of mixing with Cu powder. In this

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case, a second heat treatment must therefore be adopted to strengthen the interface binding by the formation of carbides between diamond and pure Ti or Cr. Magnetron sputtering is believed to be more suitable for W or Mo coating on the surface of the diamond. In comparing the two methods mentioned above, the method to coat Ti or Cr on the surface of the diamond is easier, cheaper, and more suitable for industrial production than that in which W or Mo is used. In this paper, both Ti and Cr are therefore chosen as the coating elements, with which to study the effect of surface metal-coating of diamond particles on the microstructure and thermal conductivities of diamond–Cu composites.

2. Experimental procedures

2.1. Preparation of composite

The diamond particle used in this work is an MBD4 grade diamond with a nitrogen content of 250 ppm, purchased from Yanshan University, Hebei, China. And its thermal conductivity is estimated to be about 1450 W/m K according to the level of nitrogen content. To obtain a volume fraction of diamond particle in the range of 55–70 vol% in diamond–Cu composites, two kinds of diamonds with designated size, 125–106 μm (mesh 120/140) and 45–38 μm (mesh 325/400) were mixed at a weight ratio of 3 to 1, at which the mean size was about 100 μm and the maximum fraction of diamond can reach as high as 70 vol% of the powder bed. The surface of diamond particle was coated with chromium or titanium of a certain thickness through vacuum micro-deposition technology. And the thickness of Ti or Cr coating can range from several nanometers to ten microns by adjusting the deposition temperature and time, as well as the weight ratio of diamond to coating raw materials such as $TiCl_3$ and TiH_2 powders (for Ti coating) or $CrCl_3$ and CrH_3 powders (for Cr coating). In this work, the coating process is performed at the Yanshan University, China, the developer of vacuum micro-deposition technology. Electrolytic copper powders with d_{50} of 80–90 μm and a purity >99.9% (purchased from General Research Institute for Nonferrous Metals, Beijing, China) were mixed by ball milling with surface-pretreatment diamond powder at a designed volume fraction. This was then synthesized through the spark plasma sintering (SPS) using a sintering pressure of 37–43 MPa and a sintering temperature of 930–950 °C for 15–22 min. Given that the sintering process parameters have been optimized in our previous work, the detailed process about SPS are no longer discussed in this paper.

2.2. Property testing

Cylindrical disk specimens with a diameter of 10 mm and a thickness of 3 mm were produced for the testing of thermal diffusivity and specific heat. Thermal conductivity is specifically calculated as the product of density, thermal diffusivity, and specific heat. In this work, thermal diffusivity and specific heat were measured by Xenon pyrometry with LFA 447 Nanoflash from Netzsch, Germany using the laser flash method and calorimetric techniques, respectively. The bulk density of the composites was measured using a method based on Archimedes' law and compared with the theoretical density. Microstructure of the composite was observed on the LEO1450 Scanning Electron Microscope (SEM). XRD analysis was carried out on a Siemens D 5000 X-ray Diffractometer using Cu radiation.

3. Results and discussion

Fig. 1 shows surface morphology of (a) raw diamond particles, (b) Cr-coated diamond particles, and (c) Ti-coated diamond particles; it also shows that the surface of diamond particles are evenly coated by Cr or Ti. The designed thickness of Cr or Ti coating layer through vacuum micro-deposition is ~1.5 μm.

Thermal conductivities and relative densities of diamond–Cu composites made from three kinds of diamond powder by SPS are shown in Fig. 2. The thermal conductivity of the uncoated diamond (55 vol%)–Cu composite is 178 W/m K, which is much lower than that of Cu itself (378 W/m K). Coating the diamond with a 1.5 μm thick Ti layer increased the thermal conductivities of the prepared composites to 349 W/m K. When the Ti layer was replaced by a Cr layer, the thermal conductivities of the corresponding composites reached as high as 528 W/m K. The change of relative density of prepared composites in Fig. 2 shows that surface pretreatment of the diamond particle by Ti or Cr raised the density of diamond–Cu composites from 98.2% to 99.5% or higher.

The thermal conductivities of composites are directly related to the thermal conductivities of both matrix and reinforcement, as well as the microstructure of the composites, especially the interface structure. In this experiment, the three kinds of composites demonstrated a marked difference in interface structure (Fig. 3).

Fig. 3 shows the interfacial microstructures of the composites made from the compositions corresponding to Fig. 1. The interface gap (shown by the arrow) is obvious between the diamond particles and the Cu matrix; the surface of the diamond is intact, indicating that binding between diamond and Cu is very weak (Fig. 3a). The separation between diamond and copper (Fig. 3a), is generated during the cooling process due to their chemical incompatibility and the different thermal expansion coefficients. Assuming all pores in the composites are considered as gaps between diamond and Cu, and that the shape of the diamond particle is spherical, the thickness of the gap (x) could be estimated from the porosity of composites according to the following equation:

$$\left(\frac{a}{a+x}\right)^3 = \frac{(100 - V_2)\cdot V_1}{(100 - V_2)\cdot V_1 + V_2}, \tag{1}$$

where a and V_1 are the size and volume fraction of diamond particle, respectively, and V_2 is the porosity of corresponding composites. Thus, a density of 98.2% means that the thickness of the gap is about 1 μm, which is close to the observed value by SEM. The diamond–Cu interface became denser when coated by a Ti or Cr layer; at the interface, C and Cu elements diffused into the Ti or Cr interlayer, the Ti or Cr in the interlayer also diffused into the Cu matrix (Fig. 3b and c). To further determine phase composition of these composites, Fig. 4 gives X-ray diffraction patterns of Cr-coated diamond and the corresponding diamond–Cu composites. Given the identical phase change of Cr-coated and Ti-coated diamond, X-ray diffraction patterns of Ti-coated diamond and the corresponding composites are not given in this paper. Cr_7C_3 and Cr phases both appeared in Cr-coated diamond particles; however, the Cr phase disappeared after the formation of composite materials. The same phase variation also appeared in Ti-coated diamond particles and the corresponding composite materials: both TiC and Ti appeared in the Ti-coated diamond particles, and the Ti phase also disappeared in the formed diamond–Cu composites.

It should be mentioned that although the surface of the diamond particle was coated by a pure Ti or Cr layer, the carbides coexisted in the coating. This special structure is directly related with the chosen plating process. The mechanism of vacuum micro-deposition process can be described in the following reaction equations:

$$\begin{aligned} &2\mathrm{TiCl_3(g)} + 3\mathrm{TiH_2(s)} \rightarrow 5\mathrm{Ti(s)} + 6\mathrm{HCl(g)} \\ &\mathrm{Ti(s)} + \mathrm{C}(\mathit{diamond}) \rightarrow \mathrm{TiC(s)} \end{aligned} \tag{2}$$

and

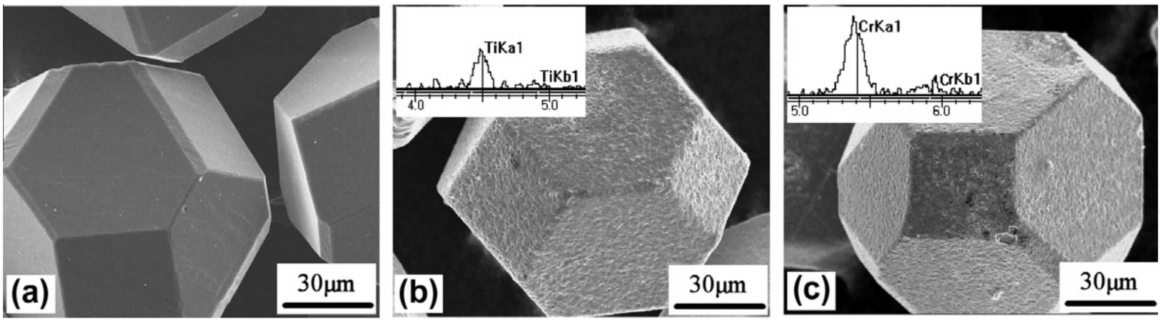

Fig. 1. Surface morphology of diamond particles (a: raw, b: Ti-coated, c: Cr-coated).

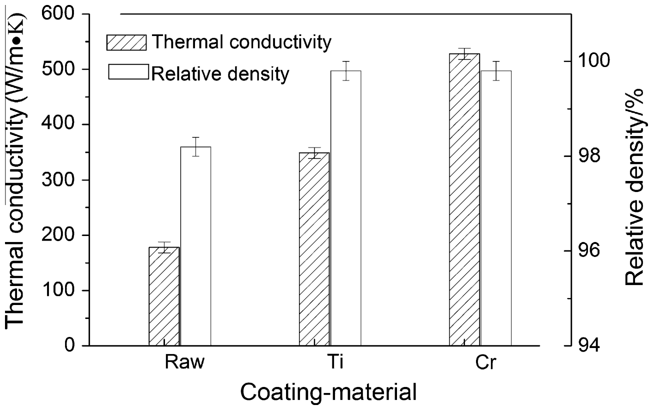

Fig. 2. Thermal conductivity and relative density of diamond (55 vol%)–Cu composites from diamonds with different coating materials.

$$CrCl_3(g) + CrH_3(s) \rightarrow Cr(s) + 3HCl(g)$$
$$7Cr(s) + 3C(\mathit{diamond}) \rightarrow Cr_7C_3(s). \qquad (3)$$

To coat Ti on the surface of the diamond powder, diamond particles were mixed with $TiCl_3$ and TiH_2 powders at a certain proportion; with the increase of temperature, $TiCl_3$ gasified and reduced to Ti atoms by reacting with TiH_2. These generated reactive gaseous Ti atoms deposited on the surface of the diamond particles and then reacted with diamond to form the TiC layer at a plating temperature higher than the forming temperature of TiC. With the increase of plating time, the C atom at the surface of the diamond particle diffused into the TiC layer and continued to react with the Ti atoms through Eq. (2). In the process, diffusion of C atoms and deposition of Ti atoms occurred simultaneously; because the former was slower than the latter, a pure Ti layer remained on the TiC layer. The Ti-coated layer on the surface of diamond actually consisted of a TiC layer and an outer layer of pure Ti. Wang [6] and Li [7] studied the thickness ratio of two layer and lattice relationship by small angle X-ray diffraction and TEM, respectively; they found that the thickness ratio of the TiC layer and the Ti layer was about 2:1 and a coherent interface of (1 0 0 0)Ti//(1 1 1)TiC existed between Ti layer and TiC layer. Cr coating has a similar layer structure: the layer is made up of a Cr_7C_3 layer close to the diamond surface and a pure Cr outer layer. Based on these results, the thickness of carbide layer was 1 μm, and the pure Ti or Cr layer was 0.5 μm thick in this experiment.

A middle layer with a strong binding force with the diamond and copper caused the interface structure of diamond–Cu composites to change from mechanical bonding into chemical, metallurgical bonding; at the same time, the composites also reached full density. The interface layer of prepared diamond–Cu composites can be described by the following forms (according to the different surface states of diamond):

diamond|air gap|Cu (for raw diamond);
diamond|TiC|copper solid solution containing titanium (for Ti-coated diamond); and
diamond|Cr_7C_3| copper solid solution containing chrome (for Cr-coated diamond).

It should be noted that pure Ti or Cr was not added to the interface structure. The composition of Cu matrix was analyzed using energy scattering spectroscopy, and the matrix contained 1.8 wt% Ti or 2.2 wt% Cr. These values are close to the theoretical estimates of 1.9 wt% Ti or 2.6 wt% Cr in the Cu matrix if a pure 0.5 μm thick Ti or Cr layer on the surface of the diamond particle completely dissolves in copper. Moreover, the XRD result in Fig. 4 also shows that no pure metal coating existed in the composites. Based on both facts, we did not add pure Ti or Cr onto the interface structure.

The resulting layer structure is what the authors aim for; it is also the reason for using the vacuum micro-deposition process instead of sputtering and other processes. The Cr or Ti layer formed by vacuum micro-deposition as an interlayer could enable the formation of

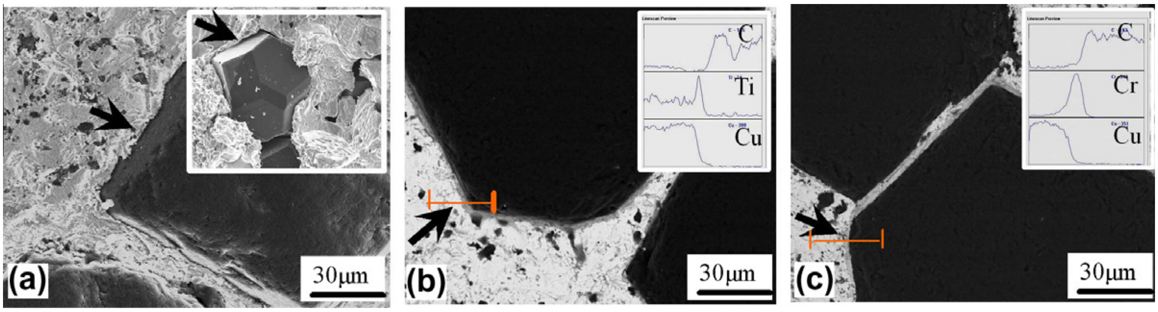

Fig. 3. SEM of diamond–Cu composites made from diamond with different surface treatments (a: raw diamond, b: Ti-coated, c: Cr-coated).

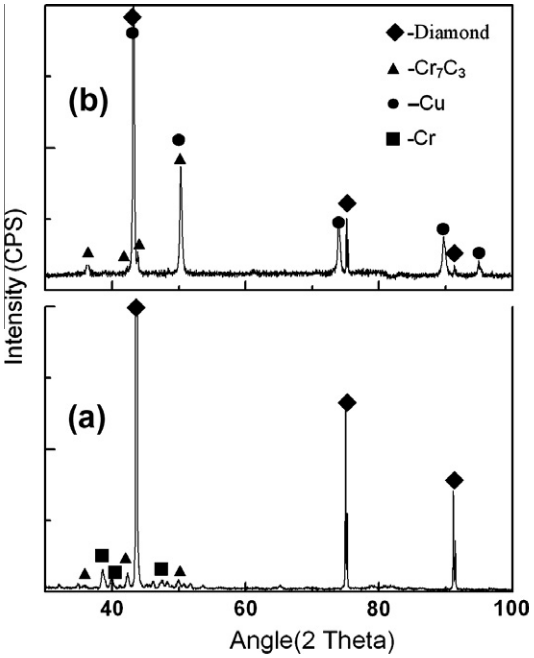

Fig. 4. XRD of Cr-coated diamond (a) and corresponding composites (b).

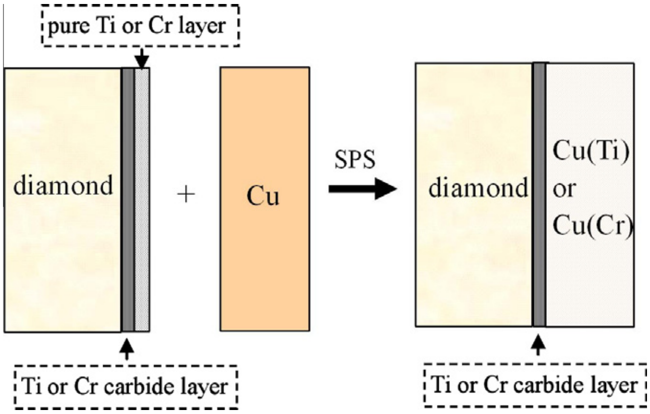

Fig. 5. Composite schematic diagram of Ti-coated or Cr-coated diamond and Cu.

metallurgical bonding between diamond and Cu in two ways: by the solution of pure Ti or Cr in the Cu matrix and by the formation of a metal carbide layer, (Fig. 5). Wang [6] has researched on the interface between diamond and coated-Ti or Cr by Magnetron sputtering, and found that if sputtering is used to coat Ti or Cr on the diamond, the surface is going to be coated by pure Ti or Cr layer with no carbide layer; a second heat treatment must therefore be adopted to form carbides between diamond and pure Ti or Cr, making the coating process complex and difficult to control.

After analyzing the interface structure, we present in the following section a theoretical argument on the change of thermal conductivities of diamond–Cu composites with the surface state of diamond.

Table 1
The values of the parameters and calculated thermal resistance.

Material	ρ (g/cm^3)	G (GPa)	C (J/kg K)	λ (W/m K)	$R \times 10^{-8}$ m^2 K W^{-1}
Diamond[12]	3.52	504.4	515	1450	$R_{\text{diamond}\|\text{TiC}} = 0.15$
Cu[a]	8.96	42.9	381.5	381	$R_{\text{TiC}(1\,\mu\text{m})} = 5.98$
TiC[12]	4.93	208.9	564	16.7	$R_{\text{TiC}\|\text{Cu–1.8wt\%Ti}} = 0.92$
Cr_7C_3[12]	6.92	148.4	543	19.11	$R_{\text{diamond}\|\text{Cr7C3}} = 0.31$
Cu–1.8 wt%Ti[a]	8.84	45.2	382	189	$R_{\text{Cr7C3}(1\,\mu\text{m})} = 5.23$
Cu–2.2 wt%Cr[a]	8.91	52.7	381.7	370	$R_{\text{Cr7C3}\|\text{Cu–2.2wt\%Cr}} = 0.36$

[a] Experimental values.

The thermal conductivities of the composites depend on the thermal conductivity of each component: volume fraction, distribution and size of the reinforcement, density, and bonding between matrix and reinforcement. Many researchers have constructed theoretical models to describe the impact of these factors on the thermal conductivities of composites. Of these, the H–J model is believed to be most accurate because it takes into account the combined effects of particle size, volume fraction, and interfacial thermal resistance; the model [8] is as follows:

$$\lambda_c = \lambda_m \left[\frac{2(\lambda_p/\lambda_m - \lambda_p R_c/a - 1)V_p + \lambda_p/\lambda_m + 2\lambda_p R_c/a + 2}{(1 - \lambda_p/\lambda_m + \lambda_p R_c/a)V_p + \lambda_p/\lambda_m + 2\lambda_p R_c/a + 2} \right], \tag{4}$$

where λ_c refers to the thermal conductivities of the composites, W m^{-1} K^{-1}; λ_m is the thermal conductivity of the matrix, W m^{-1} K^{-1}; λ_p is the thermal conductivity of the reinforcement, W m^{-1} K^{-1}; V_p is the volume fraction of the reinforcement (vol%); a is the size of the reinforcement particle (m); and Rc is interfacial thermal resistance (m^2 K W^{-1}). For the three kinds of diamond–Cu composites in this experiment, the values of their λ_p, V_p, and a are the same, but λ_m and hc are different. If the diamond particles are directly composited with copper, λ_m value in the prepared composites becomes the thermal conductivity of pure copper, 381 W m^{-1} K^{-1}. If the diamond particle is coated with a chromium or titanium layer with a thickness of 1.5 μm using vacuum micro-deposition, a pure, 0.5 μm thick layer on the outer surface of diamond becomes completely soluble in the copper matrix, and the λ_m value for the Ti-coated diamond–Cu composites becomes the thermal conductivity of Cu–1.8 wt%Ti alloys, which is 189 W m^{-1} K^{-1} by experimental measurement. The λ_m value of Cr-coated diamond–Cu composites is the thermal conductivity of Cu–2.2 wt%Cr alloys, which is 370 W m^{-1} K^{-1} by experimental measurement. Rc cannot be measured from the experiment. In terms of the Acoustic Mismatch Theory, the interfacial thermal resistance Rc can be estimated by a simple Debye model [9,10] expressed by:

$$Rc = \frac{4}{\rho_m \cdot C_m \cdot v_m \cdot \eta}, \tag{5}$$

where ρ_m is the density, C_m the specific heat, v_m the Debye velocity of the matrix, and η is the average probability for the transmission of phonons across the interface into the particles. With the assumption that transverse phonons carry most of the heat, the value of v_m can be estimated by [11]:

$$v_m = \sqrt{G_m/\rho_m}, \tag{6}$$

where G_m is the shear modulus of the matrix. The value of η can be estimated by [9,10] using:

$$\eta = p \cdot q, \tag{7}$$

where p is the transmitted probability of a phonon incident within the critical angle θ_c, which can then be calculated by [9,10] using:

$$p = \frac{4Z_m \cdot Z_p}{(Z_m + Z_p)^2}. \tag{8}$$

In the above, Z_m, Z_p is the acoustic impedance of the matrix and reinforcement, which can be calculated by $Z = \rho \cdot v$.

In Eq. (7), q is the fraction of the phonons incident on the interface within the critical angle θ_c from the matrix side, because only these phonons have the opportunity of being transmitted:

$$q = \frac{1}{2}\sin^2\theta_c = \frac{1}{2}\left(\frac{v_m}{v_p}\right)^2. \tag{9}$$

Table 2
Measured values of thermal diffusivity, specific heat, density, relative density of all prepared diamond–Cu composites, as well as the preparation conditions.

Raw materials	Thickness of Cr_7C_3 layer (μm)	V_p (vol%)	Sintering pressure (MPa)/ temperature (°C)/time (min)	Density (g/cm^3)	Relative density (%)	Specific heat (J/g K)	Thermal diffusivity (mm^2/s)	Thermal conductivity (W/m K)
Diamond (D1:126–106 μm; D2:45–38 μm) D1:D2 = 3:1 + Cu powder 80–90 μm	0	55	37/930/15	5.861	98.2	0.440	69.02	178
	0.2	55	37/930/15	5.868	98.4	0.440	87.14	225
		60	37/940/15	5.606	98.5	0.445	96.61	241
		70	37/950/15	5.067	98.4	0.452	116.58	267
	0.5	55	37/930/17	5.947	99.8	0.441	224.20	588
		60	37/940/17	5.640	99.5	0.445	242.25	608
		70	37/950/17	5.121	99.5	0.452	283.84	657
	1.0	55	40/930/20	5.916	99.5	0.442	201.92	528
		60	40/940/20	5.653	99.6	0.446	216.16	545
		70	40/950/20	5.116	99.6	0.451	256.14	591
	1.5	55	43/940/22	5.913	99.6	0.440	180.65	470
		60	43/940/22	5.640	99.5	0.445	192.04	482
		70	43/950/22	5.105	99.5	0.453	219.67	508
	2.0	55	43/950/22	5.904	99.6	0.441	165.15	430
		60	43/950/22	5.637	99.6	0.445	173.41	435
		70	43/950/22	5.105	99.6	0.453	190.26	440

Thus, Eqs. (5)–(9) can be integrated into Eq. (10) as expressed by:

$$Rc = \frac{2\left(\rho_m v_m + \rho_p v_p\right)^2}{C_m \cdot \rho_m^2 \cdot v_m^2 \cdot \rho_p \cdot v_p}\left(\frac{v_p}{v_m}\right)^2. \tag{10}$$

In this experiment, two interfaces and a middle layer in the prepared diamond–Cu composites have been found to exist. Therefore, Rc is the sum of three thermal resistances in series, that is, for Ti-coated diamond–Cu composites, Rc is signed by $R_{\text{d-T-C}}$, $R_{\text{d-T-C}} = R_{\text{diamond|TiC}} + R_{\text{TiC}} + R_{\text{TiC|Cu-1.8wt\%Ti}}$, and for Cr-coated diamond–Cu composites, Rc is signed by $R_{\text{d-C-C}}$, $R_{\text{d-C-C}} = R_{\text{diamond|Cr7C3}} + R_{\text{Cr7C3}} + R_{\text{Cr7C3|Cu-2.2wt\%Cr}}$. When $R_{\text{diamond|TiC}}$ or $R_{\text{diamond|Cr7C3}}$ is calculated, we can assume that the carbide is the matrix and diamond is the reinforcement. Moreover, when $R_{\text{TiC|Cu-1.8wt\%Ti}}$ or $R_{\text{Cr7C3|Cu-2.2wt\%Cr}}$ is calculated, TiC or Cr_7C_3 is the reinforcement, and the Cu alloy is the matrix. Values for R_{TiC} or R_{Cr7C3} are from the following equation:

$$R = b/\lambda, \tag{11}$$

where b is the thickness of the carbide layer, and λ is thermal conductivity of the carbide.Table 1 lists all values of parameters in Eq. (10). And the thickness value (b) of both Cr_7C_3 and TiC layer is 1 μm. By substituting these parameters into Eq. (10) and (11), $R_{\text{diamond|TiC}}$, R_{TiC}, $R_{\text{TiC|Cu-1.8wt\%Ti}}$, $R_{\text{diamond|Cr7C3}}$, R_{Cr7C3}, and $R_{\text{Cr7C3|Cu-2.2wt\%Cr}}$ can all be obtained (Table 1). Thus, for Ti-coated diamond–Cu composites, $R_{\text{d-T-C}} = 7.05 \times 10^{-8}\ m^2\ K\ W^{-1}$; for Cr-coated diamond–Cu composites, $R_{\text{d-C-C}} = 5.9 \times 10^{-8}\ m^2\ K\ W^{-1}$. Given that the bonding between raw diamond and Cu is mechanical, Eq. (10) is not suitable for theoretical calculations of Rc of the composites. We can approximate the thermal resistance of air layer (1 μm in thickness) as the interface thermal resistance Rc, signed by $R_{\text{d-A-C}}$. Eq. (11) can be used to calculate $R_{\text{d-A-C}}$, where b = 1 μm and λ is the thermal conductivity of air (0.023 W/m K); $R_{\text{d-A-C}} = 4.3 \times 10^{-5}\ m^2\ K\ W^{-1}$. Thus, by substituting every interface thermal resistance into Eq. (4), theoretical values of the thermal conductivities of the composites can be obtained. Fig. 6 shows the theoretical curve based on Eqs. (4) and (10) of the thermal conductivities of the composites as well as the experimental values. The experimental value is close to the theoretical one, indicating that the calculation models are reasonable.

As proven by analysis, Cr coating on the diamond surface can reduce more effectively the interface thermal resistance between diamond and Cu than Ti coating; it also has a smaller negative impact on the thermal conductivity of the Cu matrix. The Cr-coated diamond–Cu composites exhibit higher thermal conductivities. In addition, we have also shown the effect of the carbide layer thickness on the surface of diamond on the thermal conductivity of the

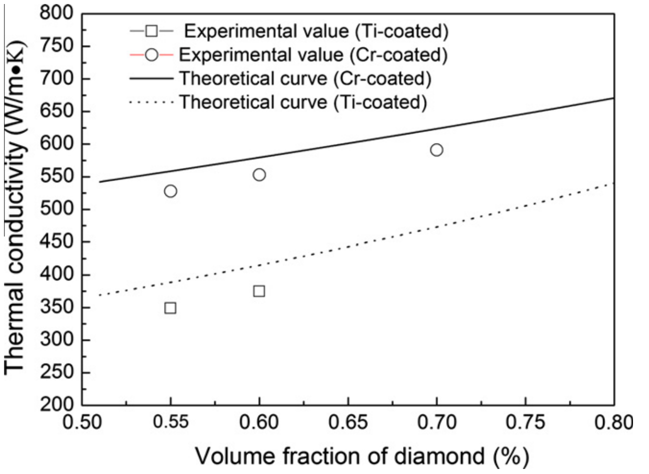

Fig. 6. Theoretical curves and experimental values of the thermal conductivities of the composites from diamonds coated by 1 μm Cr_7C_3 or 1 μm TiC layer.

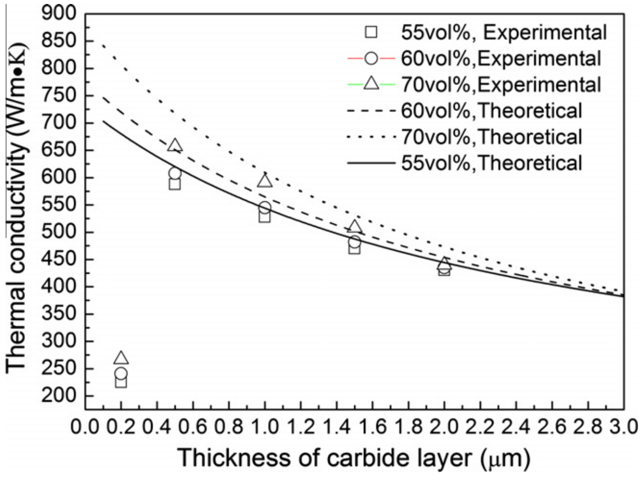

Fig. 7. The change of theoretical and experimental values of the thermal conductivities of Cr-coated diamond–Cu composites with different volume fractions of diamond with the thickness of Cr_7C_3 layer on the surface of the diamond particle.

Table 3
Interfacial thermal resistance of diamond/Cu composites prepared by different methods.

Raw material	Preparation method	Interfacial thermal resistance ($m^2 K W^{-1}$)	References
Cu/diamond	P/M(SPS, 37 MPa /930 °C/15 min)	190×10^{-8}	In this work
Cu/diamond	P/M(conventional hot pressing, 950 °C, 60 min)	200×10^{-8}	[1]
Cu/diamond	P/M (ultra-high pressure, 4.5 GPa, 1180 °C, 15 min)	3.36×10^{-8}	[13]
Cu/Cr-coated diamond	P/M(SPS, 37 MPa, 950 °C, 17 min)	4.957×10^{-8}	In this work
CuCr/diamond	P/M(directly heated hot pressing with heating/cooling rates of 100–150 K/min, 950 °C, 30 min)	1×10^{-8}	[1]

diamond–Cu composite. In this work, the thickness of Cr_7C_3 layer on the surface of diamond can be accurately controlled by comprehensive adjustments of coating temperature, time and the weight ratio of diamond to $CrCl_3$ and CrH_3 powders. Table 2 summarizes all experimental values of thermal diffusivity, specific heat, density of all prepared Cr-coated diamond–Cu composites samples.

Fig. 7 shows the change and comparison of theoretical and experimental values, based on Eqs. (4), (10), and (11), of the thermal conductivities of Cr-coated diamond–Cu composites with the thickness of the Cr_7C_3 layer. Change of the theoretical curve means that the decrease of Cr_7C_3 layer thickness helped increase the thermal conductivities of the composites. However, observing the experimental value, it is close to the theoretical one except that the thickness of Cr_7C_3 layer is 0.2 μm. When the thickness of Cr_7C_3 layer became less than 0.5 μm, the thermal conductivity of the composite dropped greatly due to the fact that Cr_7C_3 became too small to effectively combine diamond with Cu. The interface binding also became weak so the interface thermal resistance remained high, resulting in a composite with a very low thermal conductivity. In addition, with a high thickness of the Cr_7C_3 layer, the thermal conductivity of the composite became low because Cr_7C_3 itself had a low thermal conductivity that became detrimental to interfacial heat transfer. Under the premise of ensuring the ability to form a chemical combination between diamond and Cu, the thickness of the Cr_7C_3 layer should be as small as possible. From the shadow region in Fig. 6, the optimum thickness for the Cr_7C_3 layer ranged from 0.4 to 0.6 μm, indicating that the thickness of the chromium compound layer (composed of Cr_7C_3 and Cr at 2:1 on the diamond surface by vacuum micro-deposition technology) should be controlled within 0.6–0.9 μm, where the thermal conductivity of the diamond–Cu composites with 70 vol% diamond can reach as high as 657 W/m K, and the interface thermal resistance can be estimated to be about 4.957×10^{-8} $m^2 K W^{-1}$. Table 3 summarizes interfacial thermal resistance of diamond–Cu composites prepared by various methods, reported in the recent literatures, as well as our work. Observed from Table 3, it is obvious that thermal resistance between diamond and Cu relies heavily on raw material and/or preparation methods. Although Cr metal layer (actual as chromium carbide) is adopted as the transition layer between diamond and Cu in [1] and our work, the thermal resistance in our work is higher than that in [1]. As a result of lower thermal resistance, the thermal conductivity in [1] is near to that in this work although the volume fraction of diamond is only 42 vol%, much lower than 70 vol% in our work. This may be attributed to the different formation ways of chromium carbide between diamond and Cu. The in situ formation of carbide can result in thinner layers with lower interfacial thermal resistances so that CuCr/diamond composites in [1] exhibited higher thermal conductivity.

4. Conclusion

(1) Diamond–Cu composites from direct combinations of diamond and Cu showed low thermal conductivities due to a weak interface and high thermal resistance resulting from chemical incompatibility. The diamond–Cu interface was strengthened when the surface of the diamond particle was coated by Cr or Ti through vacuum micro-deposition technology before forming the compound with Cu. As a result, interfacial thermal resistance in prepared diamond–Cu composites became greatly reduced and their thermal conductivities increased several times.

(2) Cr-coating on the surface of the diamond reduced more effectively the interface thermal resistance between diamond and Cu than Ti coating; moreover, it had a smaller negative impact on the thermal conductivity of the Cu matrix. Therefore, Cr-coated diamond–Cu composites exhibited higher thermal conductivities than Ti-coated diamond–Cu composites.

(3) Cr-coating on the diamond particle by vacuum micro-deposition technology was present in the form of Cr_7C_3 near diamond and a pure Cr outer layer, whose ratio in thickness was 2:1. The optimum thickness of the Cr layer fell within 0.6–0.9 μm, at which the thermal conductivities of 70 vol% diamond–Cu composites reached as high as 657 W/m K, making them very interesting materials for electronic substrate materials.

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