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Effect of tungsten based coating characteristics on microstructure and thermal conductivity of diamond/Cu composites prepared by pressueless infiltration

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Abstract: Tungsten coatings were deposited on diamond particles by vacuum magnetron sputtering. The coated diamond particles were firstly heat treated at different temperatures, and diamond/copper (Cu) composites were fabricated by using a pressureless infiltration method afterwards. The influences of heat treatment on the microstructure and composition of tungsten based coating surface and diamond/copper composites were analyzed. Notable differences were found in the microstructure with heating temperatures. Moreover, the tungsten based coating surface contained large quantities of oxidized tungsten, and the phase composition of the coatings varied within the range of tungsten–W_2C–WC as the heat treatment temperature increased. The fracture surface morphologies in the copper matrix composites reinforced with diamond particles with coatings were identically characterized with the presence of ductile fracture of matrix accompanied by dissociation of diamond particles from the matrix. The thermal conductivity (TC) and gas tightness behaviors of the diamond/copper composites were also explored. A maximum TC of 768 $W \cdot m^{-1} \cdot K^{-1}$ and a fine gas tightness of 2.5×10-10 $Pa \cdot m^3/s$ were obtained with reinforcement of tungsten-coated diamond particles treated at 800 ℃. The value of the interface thermal resistance between copper and diamond particles was also estimated and specifically discussed.

Keywords: Diamond/Cu composites, Tungsten coating, Heat treatment, Thermal conductivity

1 Introduction

Advances in thermal management technology require both reliable design of electronic packaging and new materials with desirable performances [1]. The combined advantages of high thermal conductivity (TC) metal and nonmetal materials provide outstanding performances. For instance, copper/silicon carbide, copper/carbon nanofibres, aluminium/diamond, aluminium/graphite and aluminium/silicon carbide composites have been used as heat sink materials [2–7]. Diamond/copper composites offer an ideal property, with both the filler and the binder being substances with high TC [5]. Copper with a TC of 400 $W \cdot m^{-1} \cdot K^{-1}$ is used as the binder for composites and diamond with the highest TC ~2200 $W \cdot m^{-1} \cdot K^{-1}$, and an appropriate coefficient of thermal expansion (CTE) of 2.3×10^{-6}/℃ can be used as an ideal reinforcement for composites. Thus, diamond/copper composites that have relatively low and adjustable CTE in combination with a high TC meet the ever-increasing demand for heat sinks and thermal conductors in high-heat-flux systems [8,9]. Hence, fabricating high-performance diamond/copper composites ~~from~~ benefits both scientific research and practical applications.

Unfortunately, the TC of composites that combine diamond particles and copper directly without the application of high pressures ≥1 GPa is lower than that of substances [10–13]. The reason for this condition is that copper does not naturally spread on diamond surfaces because the solid solubility of carbon is near zero in copper and copper is a non-carbide-forming material [14]. Therefore, achieving a well-bonded interface and low thermal resistance between the diamond and copper matrix is difficult. At present, minimising interfacial thermal resistance without affecting the intrinsic properties of the diamond particles and the copper matrix widely explored. Some research results pertaining to the improvement of interfacial bonding strength with metal matrix alloying have already been presented [12,15,16]. However, methods of reducing interfacial thermal resistance cannot realise the maximisation of thermophysical characteristics, because most additives remain in the copper matrix and form interfacial chemical reaction products between the diamond and copper matrix, thereby deteriorating the thermal properties of diamond/copper composites. To improve the wetting ability between liquid copper and diamond, diamond particles with coating such as Ti, Cr, Mo, B and W are modified by applying a molten salt route or diffusion method [17-23]. The intrinsic TC of the interfacial layer is another important factor in choosing carbide-forming elements. Among various carbide-forming elements, tungsten is the most suitable as diamond coating because it ensures higher TC and lower wetting angle without sacrificing the thermal property of the copper matrix [9]. However, few studies have been conducted on the use of tungsten coating deposited by magnetron sputtering method as a modified layer on the surface of diamond particles.

In this study, tungsten coating was deposited on the surface of diamond particles by DC magnetron sputtering, followed by additional heat treatment of the coated diamond in vacuum. Thereafter, diamond/copper composites were fabricated by using the spontaneous infiltration technique. Our purpose is to investigate the effect of heat treatment on the phase composition and heterogeneity of the tungsten coating. The tungsten based coating surface characteristics were evaluated by conducting a morphological study and chemical composition analysis. The microstructures of diamond/copper composites were also investigated to clarify the influence of various factors on the TC of diamond/copper composites.

2 Experimental

Diamond/copper composites were made by vacuum pressureless infiltration. High purity oxygen-free copper (>99.99 wt.%) was used as the matrix. Synthetic diamond particle of HWD40 type, estimated its thermal conductivity up to 1500 $W\cdot m^{-1}\cdot K^{-1}$, with hexagonal or octahedral shapes and diameters around 150～180um was used.

2.1. Preparation of tungsten coated diamond particles

Thin tungsten coatings were deposited on diamond particles by DC magnetron sputtering system with a rotary sample holder. The distance between sample holder and tungsten metal target with 99.99% purity was 145mm. The diamond particles were cleaned in a standard solution (dilute nitric acid hydrochloric acid mix) by ultrasonic treatment with the frequency time and power of 40 kHz, 30min and 1 kW, respectively. The base pressure in the vacuum chamber was lower than 4.0×10^{-4} pa before deposition. A 10 min presputtering was excuted in order to clean the target. During deposition, the sputtering power and gas working pressure were kept at 300 W and 1.5Pa, respectively. Then, tungsten coated diamond particles were treated for 90 min in a vacuum induction furnace at different temperatures.

2.2. Preparation of the diamond/Cu composites

Diamond/copper composites with 65 vol.% of coated diamond particles were fabricated by vacuum pressureless infiltration. Before the spontaneous infiltration experiment, 1.25 g the coated diamond particles were delicately packed into graphite and compacted by means of vibration. This method ensures high-density compaction and prevents diamond particles from floating during the process of pressureless infiltration. Subsequently, a copper cylinder was placed inside each graphite crucible on top of the packed coated diamond particles. To shorten the infiltration time and explore the process of fabricating large products, graphite die that contains diamond particles and copper was heated to a maximum temperature of 1350 ℃ within 50 min and stored for 45 min at 1350 ℃ in a vacuum furnace. Thereafter, the graphite die was naturally cooled by switching off the radiation heating power. The schematic representation of the pressureless infiltration unit used for the production of diamond/copper composites is shown in Fig. 1.

2.3. Characterization

Samples (12.7 mm in diameter and 3mm in height) were obtained to investigate the thermal conductivity by Netzsch LFA427 Laser Flash machine. The helium mass spectrometry leak detector ZQJ−542 was used to measure gas tightness. The morphology and microstructures of composites and interior structural information were investigated using a S4800 scanning electron microscope (SEM) and NDT/analyzer high energy X-rays non-destructive detection system. The XPS spectrum was obtained from Krators AXIS UItra DLD by X-ray radiation of Mg Ka of 1253.6 eV to analyze the chemical state of the coatings. The phase constitutions were examined by a D/maX 2550 VB^+ X-ray diffraction.

3. Test results and discussions

3.1. Microstructure of the tungsten based coatings on diamond particles

3.1.1 AFM and SEM analyses of coatings on diamond particles

The thickness of tungsten coatings is a crucial parameter for thermophysical characteristics and ~~the~~ carbonisation reaction. To perform the measurements, the coating was stripped from the diamond particle surface by thermal shock, exposing the cross section of the coatings and the diamond interface. Coating with a thickness of approximately 300 nm is shown in Fig. 2.

As shown in Fig. 3, the tungsten coating surface has a lumpy characteristic, and the tapered grains are nonuniformly distributed. This morphology can be explained by the fact that a collision occurs between the diamond particles and the holder before a target atom reaches the diamond particle surface, and the magnetron sputtering experiments were performed at room temperature. Therefore, the deposited atoms were inclined to fall out, and the coating's thickness is fluctuant. Typical SEM pictures of a diamond surface deposited with tungsten coatings are presented in Figs. 4a and 4b. Evidently, the as-deposited coatings adhere well to the diamond particle surfaces; meanwhile, the original diamond surface is densely covered by submicron particles. With appropriate heat treatment in ~~a~~ vacuum, the coating quality will improve, that is, the surface chemical composition and roughness are altered with reduced defects [24,25].

Fig. 4 (c–h) reveal the morphology of the tungsten-coated diamond particles after heat treatment at various temperatures for 90 min. Tungsten-coated diamond particles after 800 ℃ heat treatment are shown in Fig. 4 (c,d). Low-magnification images show that the particles exhibit uniformity with initial morphology and maintain a stable macromorphology. However, Fig. 4d shows that the surface microstructures of coatings subjected to heat treatment are different. The heat-treated coating is in a more densely crystallite compact state than the unheated coating, but the grain boundary is less evident. This finding means that coating grain is grown in ~~a~~ vacuum heated at 800 ℃, and the continuity and densification were improved as well. Since the surface morphology of coating is obviously related to the crystallinity degree, in the case where the coated diamonds were heat treated at 900 ℃, the tungsten based coating grain size increased as the temperature increased, as shown by a closeup view of Fig. 4e. Moreover, as shown in Fig. 4f, the coating is composed of a relatively distinct grain boundary and some small grains separated by voids, which is a porous nature of films grown at low temperature. This defect (porous) microstructure will disrupt phonon and electron flow, ~~thus~~ leading to a much higher thermal resistance. Disruption of phonon and electron flow is a result of dimensional expansion and/or contraction that would normally occur at the interface before cooling to room temperature inside the furnace. When the heat treatment temperature reached 1050 ℃, the surface of the partially coated regions ruptured and the microstructure shifted to a discontinuous morphology, especially on diamond (111) surfaces, as shown in Fig. 4g. This result is also attributed to residual stress, which weakens the adhesive strength between tungsten based coating and diamond particles because of their discrepant coefficient. Moreover, in accordance with SEM combined with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses, a carbonisation layer formed on the coated diamond particle subsurface was found. .

3.1.2. XPS analysis

XPS analyses were conducted to investigate the chemical state of coating surfaces. C1s core-level spectra and W4f peak fitting curve are shown in Figs. 5 and 6, respectively. W4f exists as four major symmetry peaks with binding energies of 35.7 and 37.8 eV and two weak peaks at 31.1 and 33.2 eV. compare binding energy values with the W and W-O, the W4f spectrum is composed of two sets. The binding energy values at 35.7 and 37.8 eV are consistent with the chemical state of tungsten in W-O and the matched hexavalent state (W^{6+}) in WO_3. The other W4f doublet peaks located at 31.1 and 33.2 eV are in good agreement with metallic W^0 based on the NIST XPS Database [26,27].

C1s core-level spectrum (Fig. 5a, b and d) shows a sharp peak at 284.6 eV, which is consistent with the standard results. Fig. 5c reveals a pronounced difference in the C1s peak location; the C1s peak is located at 284.3 eV, and similar shifts are observed in the case of Fig. 6c. Fig. 5d shows the presence of W-C (283.1eV) and C-C [27-29]. Results obtained by XRD (Fig. 7) and XPS analyses also are in good agreement with each other, confirming this type of coating composition consists of WC.

Figs. 6a and b display a higher peak at 35.7 and 37.8 eV compared with peaks at 31.1 and 33.2 eV. As for W4f, hexavalent tungsten is enriched at a shallow depth (less than 10 nm) below the surface because the tungsten coating surface oxidised easily with residual oxygen in the magnetron sputtering chamber. As indicated by the XPS results (Fig. 6a, b, c), the W^{6+} peak areas decrease with the heat treatment temperature, indicating that the relative amount of metallic W^0 increases on the surface of tungsten based coating. This result occurred because the sublimation of some WO_3 leads to ~~the~~ a weight loss of the mixture at 800 ℃–1050 ℃ and lattice oxygen in metal oxide has a stronger tendency to move than metal atoms. In contrast to the above mentioned results, the tungsten-coated diamond heated at 1050 ℃ for 90 min, shown in Fig. 6d, indicates that the high abundance of zero-valent tungsten is enriched in the surface, thereby also proving the reduction of hexavalent state (W^{6+}) with heat treatment.

3.1.3. XRD analysis

The X-ray diffractogram patterns of the four types of coatings on diamond are displayed in Fig. 7. In curves (a) and (b), the attained phase is diamond and tungsten. None of the peaks could be indexed as WO_3 phase possibly because the WO_3 content is too limited to be observed. The Gibbs free energy (ΔG) of the formation for WC, W_2C and WO_3 was calculated using thermodynamic data from previous investigations. All calculated ΔG values were negative [30,31]. The heat treatment of the tungsten-coated diamond particles will be likely to lead to the carbidisation of the coating. Temperature has no evident effect on the phase of the coatings at 800 ℃ for 90 min due to the diffusion process, which leads to the minimal growth of the carbide layer, and no significant carbonisation occurred at $T \leqq 800$ °C for this dwell time. When the heat treatment temperature increased to 900 ℃, additional peaks were detected. Curve (C) identifies the existence of WC, and the W_2C phase. A part of the tungsten simple substance remained in the surface of coating without being converted to W_xC. Evidently, the carbon of diamond interacts with the tungsten coatings to form tungsten semicarbide and monocarbide at temperatures ranging from 800 °C to 900 °C in the presence of vacuum of 10^{-2} Pa for 90 min. This result is in line with the data from other literature [19].

When the temperature increased to 1050 °C, WC became the major phase of coatings. No reflections that correspond to W_2C were observed. This phenomenon could be explained by the fact that the W_2C is thermodynamically less stable than WC. As temperature increases to 1050 ℃, W_2C is converted to WC, and accordingly, the phase of coating overwhelmingly consists of WC, that is, the diamond carbon interacts with semicarbide to form monocarbide through the following reaction:

$$W_2C + C_{Diamond} = 2WC$$

The reaction of W_2C and diamond is diffusion-controlled. Gibb's free energy (ΔG) transformation from W_2C to WC is expressed as:

$$\Delta G_{W_2C \to WC} = -50924.901 - 67.501T + 3.430 \times 10^{-3} T^2 + 0.334 \times 10^{-6} T^3 - 1.088T^{-1} + 12.176T \ln T$$

At 800, 900 and 1050 ℃, the calculated ΔG values are -27124.305, -23039.39 and -16724.283 J, respectively. Therefore, WC can be generated by the reaction between W_2C and $C_{Diamond}$. The phase from W_2C to WC can be considered as a shift from a metastable state to a stable state.

The microstructures and XRD patterns of coatings indicate that the interface between the diamond surface and coatings have strong chemical adherence. In addition, after heat treatment (800, 900 and 1050 ℃, 90 min) of the tungsten-coated diamond particles, the dominant coating phase changes from tungsten phase to W_2C and WC. Moreover, a high temperature corresponds to a high carbide content.

3.2. Microstructure of diamond/Cu composites

The SEM images of the fracture morphology of the four types of composites are shown in Fig. 9. The main fracture mode of the composites is ductile fracture of matrix accompanied by dissociation of diamond particles from the matrix, and the destruction of composites occurs at the filler/matrix interface.

Fig. 9a displays the microstructures of diamond/copper composite prepared with initial tungsten-coated diamond particles as reinforcements. The coated diamond particles are tightly embedded in the copper matrix. The results shown in Fig. 9b are consistent with those in Fig. 9a. Fig. 10a shows the EDS line scan between two diamond particles (pretreated at 800 ℃ for 90 min) and the copper matrix that crosses them. The composites have a continuous interface, thereby showing that the coatings can enhance the interfacial bonding and is useful in assisting heat transfer across the interface of the matrix and reinforcements. In addition, when entering the interfacial coating from the copper zone, the intensity of the tungsten signal presents a sharp cutoff, indicating a low diffusion of tungsten atoms into the copper matrix during the infiltration. Therefore, the TC of the copper matrix will not be degraded by the present coatings.

X-ray CT was also conducted on the diamond/copper composite samples to demonstrate the diamond particle distribution. Fig. 11a shows the top view of the X-ray CT scan image on the composite sample. Strong bonding between copper and coated diamond is observed together with a reasonably uniform distribution of particles within the matrix alloy. When testing result obtained from the bottom view of samples, a Cu-rich zone is observed, as presented in Fig. 11b, which was induced by the greater difference in density of copper and diamond, thereby rearranging the diamond particles. The above findings show that obtaining a nearly uniform distribution of particles in diamond/copper composites is possible. However, various parameters need to be controlled and optimised during the process of packing diamond particles.

Apparently, the thermal effect induces the carbidisation of the tungsten coating on the diamond during the infiltration process. The XRD (Fig. 8) result reveals that WC phases were identified in coated diamond particles underwent the infiltration process. The W_2C phases were not observed, implying the WC coatings formed already after infiltrating and during subsequent solidification process. These findings indicate that diamond particles and Cu liquid wetting with the aid of W layer and coalesce together with WC at the cross-section are well controlled by optimised ~~and the processing control of~~ pressureless infiltration process.

Deterioration of the microstructure caused by residual porosity can be observed in Fig. 9(c, d). Furthermore, ~~in~~ Fig. 10b, pretreated at 1050 ℃ for 90 min, some areas of the diamond surface are exposed because of the shrinkage and rupture of coatings, thereby suggesting that these areas are the weakest interface region. However, the interface bonding in diamond/copper composites is satisfactory in the intact tungsten based coating interface areas, which is expected because of the good wettability of copper with coated diamond during cooling and solidification in the interface areas, as shown in Fig. 10c. We also performed infiltration using coated diamond particles pretreated at 1050 ℃ for 360 min as filler. This kind of coated diamond particles is unsuitable for spontaneous infiltration under such conditions. Compare with the results of other studies, the composite’s interfacial bonding is stronger with the use of WC coating than with the use of the initial tungsten coating [17,39]. However, the coating surface with carbide is averse to pressureless infiltration at 1350℃.

The results in Table 1 show that gas tightness exhibits optimum performance when the coatings are heat treated at 800 ℃ since interface is in a good bonding state. The gas tightness of the diamond/copper composites is decreased by increasing the pretreatment temperature for the coated diamond particles. When the prior heat treatment temperature reaches up to 1050 ℃, the porosity is the highest in the composites. With respect to porosity, no visible pores can be found considering that the wetting angle of copper on metal tungsten at 1350 ℃ is 0° . However, this is not the case when using coated diamond particles that underwent prior higher heat treatment, which was accompanied by coating carbidisation and a loss of continuity. During the infiltration process, the copper liquid flowed into the poor wettability surface region, thereby worsening the pores. Taking the above conditions into consideration, when pretreatment time is extended to 4 h at 1050 ℃, the pressureless infiltration experiment shows that the coating and uncovered diamond is no longer wetted by the copper. Thus, filtration cannot take place. These findings indicate that the unbroken coatings with tungsten surface shell facilitate the densification of overall composites.

A transformation model of the coatings is proposed. During the heating and infiltration, the coating consists of an external tungsten shell, which favours wetting and infiltration. Carbide formation in the subsurface area simultaneously accelerates. Thus, the diamond/copper infiltration process becomes copper/tungsten infiltration, and the outer tungsten layer induces the composites to form the copper/tungsten pseudo alloy layer and favours the fabrication of diamond/copper composites. During the cooling process, as a result of continuous high temperature, the carbonisation of tungsten, the formation of WC from the internal layer to the surface reaches a stable interface [32]. Given that the wetting angle on metal tungsten is lower than that on WC at a relatively high temperature (1350 ℃), the surface will be carbonised completely during the heating process when fillers treated at 1050 ℃ and 90 min are used. This condition explains why the microstructure of this type of diamond/copper composites is so much worse than expected.

3.3. Thermal properties of the diamond/Cu composites

Experimentally determined values (from the measurements of three samples) for the four types of composites are shown in Table 1. For the composite obtained from coated diamond with a copper matrix, the dependence of TC on the prior heat treatment of tungsten coatings was investigated. Obviously, a maximum TC of 768 $W\cdot m^{-1}\cdot K^{-1}$ can be achieved, which is approximately 12.1% better than composites ~~that~~ which use untreated particles as filler. This difference is due to the fact that the coatings possess a denser microstructure when the thin film underwent annealing [24-26]. Thus, the TC of composites is associated with the coating state before infiltration. When a coating is heat treated up to 900 ℃, the TC falls to about 670 $W\cdot m^{-1}\cdot K^{-1}$. The microstructures of the diamond/copper composites (Fig. 9) are compared. According to Fig. 9c, diamond particles are segregated from the matrix by micropores, differs from Fig. 9b, ~~thereby~~ indicating that contact among some diamond particles is inhibited. The thermophysical properties of the composite of the diamond particle that had previously undergone heat treatment (1050 ℃) are unexpectedly low, because the interface layer ruptures and microporosity critically degraded the TC of the composites. These results indicate that additional heat treatment above 800 ℃ for 90 min will weaken the thermophysical property of the composite. The gas tightness data (Table 1) corresponding to the diamond/copper system are consistent with the TC mentioned above. This finding confirms that the heat treatment of coated diamond particles at 800 ℃ positively affects the properties of the diamond/copper composites unlike the others. The interface thermal resistance is a basic factor that affects the TC of the overall composites so it worths being quantitatively analysed. On the basis of effective medium approximation theory and Maxwell theory, Hasselman and Johnson proposed a model (Hasselman–Johnson model) that considers the influence of interface thermal resistance [35]. It is expressed as:

$$\lambda_c = \lambda_m \times \left[\frac{2V_p \times (\frac{\lambda_p}{\lambda_m} - \frac{R_C\lambda_p}{a} - 1) + \frac{\lambda_p}{\lambda_m} + \frac{2R_C\lambda_p}{a} + 2}{V_p \times (1 - \frac{\lambda_p}{\lambda_m} + \frac{R_C\lambda_p}{a}) + \frac{\lambda_p}{\lambda_m} + \frac{2R_C\lambda_p}{a} + 2}\right] \quad (1)$$

where a is the radius of spherical dispersions, Rc is the interface thermal resistance, λ is the TC and Vp is the volume fraction of dispersions. The subscripts c, m and p refer to composite, substrate and reinforced particles, respectively. Using the Hasselman–Johnson model and experimentally determined values of TC, this paper deduced the interfacial thermal resistance of diamond/copper composites presented in Table 1. Given that the relatively high porosity, composites with coated diamond particles treated at 1050 ℃ were not considered in the calculations. The calculation results clearly show that the coating state before infiltration plays a vital important role in determining the interfacial thermal resistance.

An approximate theoretical calculation of the minimum interface thermal resistance of composites was conducted according to the thermal series circuit analogy [36]. The total interfacial thermal resistance that accounts for diamond/copper composites consists of three terms, namely, WC/Cu ($R_{WC/Cu}$), WC interphase (R_{WC}) and diamond/WC ($R_{diamond/WC}$). The thermal resistance of the interface is given by Eq. (2):

$$R_c = R_{WC/Cu} + R_{Diamond/WC} + R_{WC} \tag{2}$$

To describe $R_{Diamond/WC}$ and $R_{Cu/WC}$, we ~~can~~ assume that the majority is the matrix and WC is the reinforcement. R_{WC} can be estimated using R_{WC}=L/λ, where L is the thickness and λ is the TC of the WC coatings. The interface thermal resistance $R_{WC/Cu}$ and $R_{Diamond/WC}$ were calculated based on the acoustic mismatch model and the Debye model, which assumes that the interfacial bonding is excellent and the propagation of phonons through the interface occurs in an elastic manner, which can be calculated by references [34,37,38].

$$R_c = \frac{2(\rho_m v_m + \rho_p v_p)^2}{C_m \cdot \rho_m^2 \cdot v_m^2 \cdot \rho_p \cdot v_p}\left(\frac{v_p}{v_m}\right)^2 \tag{3}$$

Where R_c is the interfacial thermal resistance, ρ is the density, C is the specific heat and v is the Debye velocity of the matrix (longitudinal or transverse). R_{WC} can be estimated by using $R_{WC}=L/\lambda$, where L is the thickness and λ is the TC of the WC.

Substituting table 2 shown all values of parameters into model Eq. (3), $R_{Diamond/WC}=3.733\times10^{-10}$ $m^2 \cdot KW^{-1}$, $R_{Cu/WC}=1.375\times10^{-10}$ $m^2 \cdot KW^{-1}$ and $R_{WC}=1.734\times10^{-9}$ $m^2 \cdot KW^{-1}$. Thus, the theoretical interfacial thermal resistance of the composites can be ultimately determined as 2.248×10^{-9} $m^2\cdot KW^{-1}$.The lowest value obtained from Hasselman-Johnson model increases by one order of magnitude, which indicate that the Hasselman-Johnson calculation model is reasonable. These results are in good agreement with previously reported data by Chun Zhang et al[19].

The above analysis shows that the interfacial thermal resistance is associated not only with interface bonding but also with the coating state before infiltration [39]. These results confirm that a suitable coating pretreatment parameter can improve the coating quality state and greatly decrease interfacial heat obstacle between electronic and phononic heat conductions. The composites with coated diamond particles and underwent heat treatment at 800 ℃ exhibit the lowest interfacial thermal resistance.

4. Conclusion

Tungsten coatings were deposited onto diamond particles, and the effect of heat treatment on its phase and chemical state composition was investigated. Results show that metal tungsten is the dominant phase, and metallic (W^0) and hexavalent (W^{6+}) were identified in the surface of as-deposited and heat treated at 800 ℃ coatings. The phase of the tungsten based coating changes from tungsten phase to W_2C and WC phase ~~while~~ when the heat treatment temperature exceeds 800 ℃. The relative amount of metallic (W^0) presents increases with the heat treatment temperature on the coating surface.

Diamond/copper composites exhibit optimal performance, which can be attributed to appropriate pretreatment, that is, the continuous coating surface with tungsten that facilitates infiltration. The tungsten based coating surface with carbide is averse to pressureless infiltration, which was conducted at a high temperature (1350 ℃), However, WC plays a vital important role in the interface of diamond/copper composites.

This study obtained diamond/copper composites with a thermal conductivity as high as 768 $W\cdot m^{-1}\cdot K^{-1}$ and an acceptable gas tightness 2.5×10^{-10} $Pa\cdot m^3\cdot s^{-1}$ when raw materials use coated diamond particles heat treated at 800 ℃ for 90 min as filler. Thus, the materials meet the requirements of advances in thermal management.

Conflict of interest

All authors declare no conflict of interest.

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Fig.1. Schematic representation of infiltration unit used for the production of diamond/copper

Fig.2. Typical cross-section cross-sectional view image

Fig.3. AFM images of the surface of as-deposited tungsten on diamond particles surface

Fig.4. SEM images of coated diamond used in the present study : (a, b) virgin W-coated diamond particles, (c,d) diamond (W-coated) particles treated at 800℃, (e,f) diamond (W-coated) particles treated at 900℃, (g, h) diamond (W-coated) particles treated at 1050℃

Figure.5. C1s XPS peaks of the coated diamond particle (a) before heat treatment , and after heat treatment for at (b) 800℃, (c) 900℃ and (d)1050 for 90min.

Fig.6. Core level XPS spectra of coated diamond particles surfaces: (a) initial, (b) , (c), (d) with a coating after heat treatment at temperature of 800℃, 900℃, 1050℃

Fig.7. X-ray diffractogram of the coated diamond particle: (a) with an initial tungsten coating, (b), (c), (d) annealed at 800℃, 900℃, 1050℃

Fig.8. XRD pattern of tungsten coated diamond particles underwent infiltration process

Fig.9. Microstructures of the diamond/Cu composites using different coated diamonds as initial filler: (a) initial, (b, c, d) diamond particles with a W coating subjected to heat treatment at 800℃, 900℃, 1050℃

Fig.10. SEM images of composites with WC coating on diamond particles (a) EDS line-scanning analysis across the matrix and filler (treated at 800℃) (b) EDS line scan along fracture surfaces between coating and diamond (treated at 1050℃) (c) SEM images in back-scattered and secondary electrons of the diamond/Cu composite interface (heat treated at 1050℃)

Fig.11. X-ray imaging of diamond/Cu composites (a) the top view of sample (b) The bottom view of sample

Table 1

Experimentally measured values of thermal conductivity for the four copper–diamond composite

Table 2

Parameters of materials for interfacial thermal resistance calculation[33, 34].