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Thermal Physical Properties of Al-coated Diamond/Cu Composites

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Abstract: To acquire a well bonded interface between the copper and the diamond particles in diamond-copper matrix composites, an available process to apply a vapor deposited aluminum (Al) coating onto diamond particles was used to solve this interfacial problem. The diamond-copper matrix composites were prepared by spark plasma sintering (SPS) process and the effect of Al-coated diamond particles was demonstrated. The experimental results showed that the densification, interfacial bonding and thermal conductivity of Al-coated composites were evidently improved compared to those of the uncoated composites. A maximum thermal conductivity (TC) of 565 W/(m・K) was obtained in the coated composite containing 50vol% diamond particles sintered at 1 163 K. Additionally, the experimental data of thermal conductivity and coefficient of thermal expansion (CTE) were compared with the predictions from several theoretical models.

Key words: diamond; Cu; thermal properties; microstructures; SPS

1 Introduction

Much attention has been focused on Cu/diamond composites due to their high thermal conductivity and low coefficient of thermal expansion, and they have been considered as candidate for thermal management materials in the electronic packaging industry. It is known to all that the major challenge in the development of Cu/diamond composites is to obtain a well bonded interface between the copper and the diamond materials because copper is known to be naturally non-wetting with diamond.

As a solution to overcome the interfacial problems, two processes are available, namely matrix alloying and diamond particle surface metallization (metal coating). For example, diamond/5wt%Si-Cu composite materials prepared by vacuum hot pressing yielded a thermal conductivity of 455 W/(m・K) at a volume fraction of 5% diamond particles[1]. Cu/diamond composites with high diamond volume fractions, which could be produced by infiltration of molten Cu alloys into a dense bed of diamond particles, had the thermal conductivity of up to 900 W/(m・K)[2]. Ke Chu *et al*[3] reported that diamond-Cu matrix composites, which were prepared by SPS with Cr-coated diamond particles, yielded a maximum thermal conductivity of 284 W/(m・K). Moreover, compared with the traditional packaging materials, such as Cu-Cr-Zr[4], W[5] or W-La_2O_3[6], diamond-copper matrix composites have higher thermal conductivity. Hence, development of diamond-copper matrix composites is very important from both scientific and practical points of view.

Many researches have demonstrated that the diamond particles have been strongly bonded with Al-matrix in the composites. For example, Ruch *et al*[7] reported that Al/diamond composites by gas-pressure infiltration yielded a thermal conductivity of 670 W/(m・K). Nevertheless, until now, no previous research was addressed to optimize the interfacial bonding of Cu/diamond composites by using Al-coated diamond particles. Therefore, it is very necessary to evaluate the effectiveness of Al coating method for the interfacial modification of Cu/diamond composites. In addition,

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SPS is a very effective technique to promote the densification of diamond-particle-filled composites[8]. With this method, the sintering temperature was well controlled below the melting point of Cu (1356K), which made the whole diamond-Cu matrix composites preparation process more energy-efficient with low cost.

In this study, SPS was used to prepare the Cu/diamond composites, and attention was focused on the effectiveness of Al coating applied onto the diamond particles for the improvements in densification, bonding strength and thermal conductivity of the composites. The effects of diamond volume fraction on the relative density, thermal conductivity and interfacial microstructure of both composites with coated and uncoated diamonds were investigated. The possible explanations for the various disadvantages inducing degradation in thermal conductivity of the composites were discussed.

2 Experimental

2.1 Composites preparation

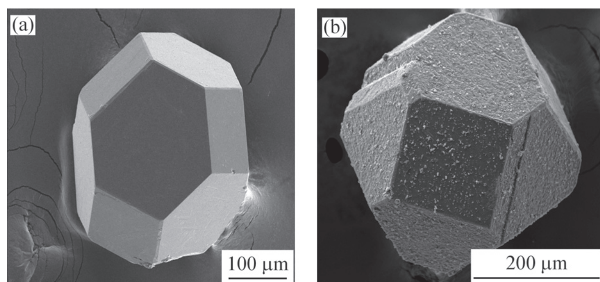

Fig.1 SEM images of reinforcements: (a) uncoated diamond; (b) Al-coated diamond

The copper powders (99.99% by weight) were used as matrix materials. The selected reinforcement diamond particles were synthetic MBD8 diamonds with an average particle diameter of 300 μm. A part of as-received diamonds were coated with aluminum by using vacuum evaporation technique. A coating thickness of about 0.5 μm was estimated from cross section by SEM. The morphologies of uncoated and Al-coated diamond particles are shown in Fig.1. The diamond volume fraction amounted to approximately 40% to 60%. The SPS system (Mod.1050, Sumitomo Coal Mining Co. Ltd., Japan) was used to synthesize disk-shaped Cu/diamond composites with 1-5 mm thick and 10-30 mm in diameter. The diamond and Cu powders were mixed in methanol using a magnetic stirrer. The mixing time was 50 hours so as to obtain uniform mixture of diamond and copper matrix powders. After mixing, methanol was removed by evaporation. The mixture of diamond and Cu powders was sintered at 1 163 K for 3min. Before sintering, the chamber was pumped to low vacuum (<10 Pa). The heating rate was 50 K/min and a pressure of 50 MPa was applied throughout the sintering process.

2.2 Characterization

Field emission scanning electron microscope (FE-SEM, Sirion 200, FEI, Holland) was used to examine the microstructure of samples and energy dispersive X-ray (EDX) was used to analyze the elements of the samples. X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V, Holland) with monochromatic radiation source was used to get the diffraction patterns of the samples, which identified the phases present. Thermal conductivity of the samples was measured at room temperature by a laser flash apparatus (LFA427/3/G, Netzsch, Germany) with an international standard[9]. This system directly measured the thermal diffusivity (α) and specific heat capacity (Cp). The density (ρ) of the samples was measured by Archimedes method. The thermal conductivity could be derived from the equation: Thermal conductivity (λ) = $\alpha \times Cp \times \rho$. The coefficient of thermal expansion was measured from room temperature to 473 K at a rate of 5 K/min for both heating and cooling in an argon atmosphere by using a dilatometer (DIL 403PC, NETZSCH, Germany), with an international standard[10].

3 Results and discussion

3.1 Effect of diamond volume fraction

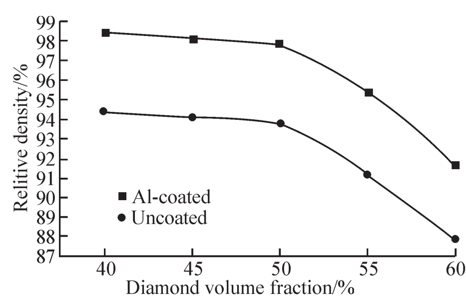

Fig.2 Effect of diamond volume fraction on the relative density of the composites sintered at 1 163 K

Fig.2 shows the effect of diamond volume fraction on the relative density of the composites sintered at 1 163 K. It is clear that the coated diamond composites exhibit a better densification than the uncoated ones, in which an average 4% improvement in relative density is obtained after using coated diamonds. Additionally, the increase of diamond particles content in samples decreases the relative packing density obviously. This is mainly because of the fact that there is no sufficient matrix that can fill up the gaps left by the adjacent diamond particles.

The effect of diamond particles volume fraction on the thermal conductivity of composites sintered at

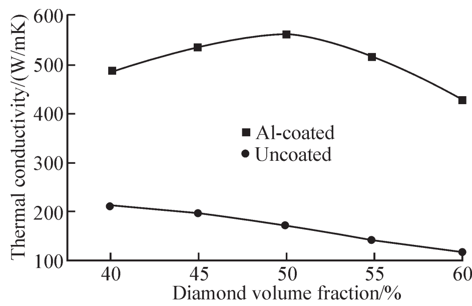

Fig.3 Effect of diamond particles volume fraction on the thermal conductivity of composites sintered at 1 163 K

1 163 K is plotted in Fig.3. As can be seen, the Al-coated diamond/Cu composites show a much higher thermal conductivity compared to the uncoated ones. The composites with 50vol% Al-coated diamond particles, for instance, show the highest thermal conductivity of 565 W/(m · K), which corresponds to 390 W/(m · K) increase in comparison with that of uncoated composites. It can be deduced that such remarkable thermal conductivity enhancement is originated from the good interfacial bonding at Cu/Al-coated diamond particles interface.

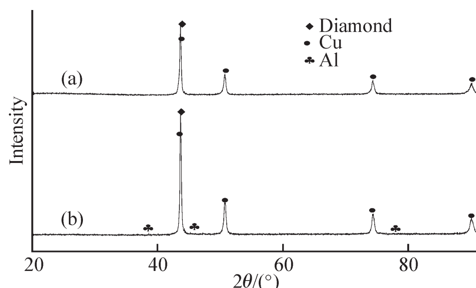

Fig.4 XRD patterns: (a) Cu-50vol% diamond (uncoated) composites sintered at 1 163 K; (b) Cu-50vol% diamond (Al-coated) composites sintered at 1 163 K

3.2 XRD results

The X-ray diffraction patterns of sintered samples are shown in Fig.4. We can find out peaks that correspond to Cu, Al and diamond(C) in the patterns of samples with Al-coated diamond particles. In the pattern of samples with uncoated ones, the peaks corresponding to Cu and diamond(C) are identified. Micron-grade diamond particles are susceptible to allotropic reconversion to graphitic sp^2 or amorphous carbon during isothermal exposure in non-oxidizing atmospheres at temperature as low as 750 ℃[11]. It is noteworthy that there is not any peak corresponding to graphite from X-ray diffraction patterns.

3.3 Microscopic analysis

Fig.5 presents the microstructure of fracture surfaces of coated and uncoated diamond/Cu composites. In the typical case of uncoated composites, as illustrated in Fig.5(a), large cracks appear at the interfaces and most of the diamond particles are bared on the fracture surfaces, indicating weak interfacial bonding between the copper and the diamond particles. A good interfacial adhesion, by contrast, can be observed for Al-coated composites in which the diamond particles are tightly embedded into the copper matrix (Fig.5(b)). No clear pores and cracks can be found in this case. These findings suggest that the application of Al-coating can effectively improve the interfacial bonding between the particles and the copper matrix, and in turn facilitate the densification of overall composites. The enhancement of thermal conductivity in Cu/Al-coated diamond composites can be explained as follows. The interface and relative density play critical roles in determining both microstructure and thermal conducting behavior of the composites. The interfacial Al acts as a bridge between diamond reinforcements and Cu matrix. And interfacial Al has a high thermal conductivity, which is useful for heat transfer to occur across the Cu-diamond interfaces.

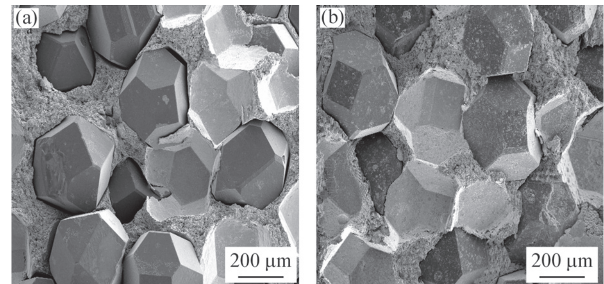

Fig.5 Microstructures of fracture surfaces of the composites: (a) Cu-50vol% diamond (uncoated) composites sintered at 1 643 K; (b)Cu-50vol% diamond (Al-coated) composites sintered at 1 163 K

3.4 Thermal conductivity

In order to profoundly understand the thermal conductivity behavior of diamond-Cu matrix composites, it is important to compare the experimental results with the theoretical predictions. Hasselman and Johnson (H-J) model[12] is frequently applied to estimating the thermal conductivity of isotropic composites reinforced with spherical inclusions in which the interfacial thermal resistance (ITR) effect and particle size are included:

$$\lambda = \lambda_m \left[\frac{2\left(\frac{\lambda_d}{\lambda_m} - \frac{\lambda_d}{\alpha h} - 1\right)V_d + \frac{\lambda_d}{\lambda_m} + \frac{2\lambda_d}{\alpha h} + 2}{\left(1 - \frac{\lambda_d}{\lambda_m} + \frac{\lambda_d}{\alpha h}\right)V_d + \frac{\lambda_d}{\lambda_m} + \frac{2\lambda_d}{\alpha h} + 2} \right] \quad (1)$$

where, λ_m, λ_d and λ are the thermal conductivities of the matrix (in this case copper, λ_m=400 W/(m · K), reinforced particles (in this case diamond, λ_d= 2 000 W/(m · K)) and composites, respectively; V_d and α represent the volume fraction and radius of the reinforcement particles. The thermal boundary conductance h will be used to quantitatively assess

the efficiency of heat transfer in composites. h is the inverse of interfacial thermal resistance (ITR). ITR can be explained as the discontinuity in the temperature when heat flows between two dissimilar elements. Using the values measured for TCs in this study, ITR can be back-calculated for composites using the equation of H-J model. ITR for the composites fabricated in our present work was calculated using H-J model and the values of ITR obtained were 1.167-2.629×10^{-7} m^2 K/W in a volume fraction range of Al-coated diamond between 40% and 60%. Assuming the perfect bonding between the diamond particle and the Cu-matrix in the composite, the value of ITR becomes 0 and H-J model is simplified to Maxwell-Eucken (M-E) model proposed by Eucken[13]:

$$\lambda = \lambda_m \times \frac{2(\lambda_d/\lambda_m - 1)V_d + \lambda_d/\lambda_m + 2}{(1-\lambda_d/\lambda_m)V_d + \lambda_d/\lambda_m + 2} \tag{2}$$

In the present study, M-E model was also utilized to evaluate the effect of consolidation for Cu-matrix composite containing diamond particles made by SPS process. Fig.6 also depicts theoretically calculated values of thermal conductivity for the diamond-Cu matrix composite using the Maxwell-Eucken equation for cases with various percentages of conductivity as opposed to the theoretical values.

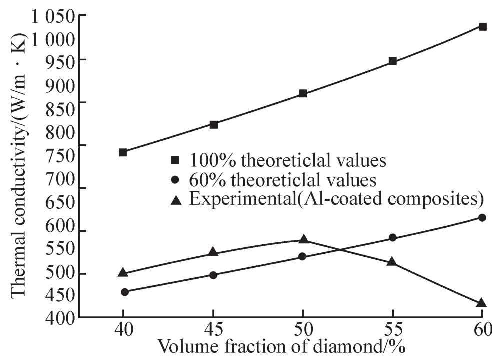

Fig.6 Experimental data and theoretical predictions of thermal conductivity for Cu/Al-coated diamond composites with various volume fractions of diamond

As shown in Fig.6, experimental values of composites including 40vol%-50vol% Al-coated diamond particles are much higher than 60% the theoretical value calculated using Maxwell-Eucken equation. It should be emphasized that this result indicates that the bonding between the Al-coated diamond particles and the Cu-matrix is strong. As shown in Fig.6, the thermal conductivity values of Cu/Al-coated diamond composites, which was prepared by spark plasma sintering, can not be compared with those fabricated by high pressure high temperature sintering[2]. This is mainly because of the reason of two respects. First of all, the high volume fraction of diamond (80vol%) has remarkable influence that can not be ignored in improving the thermal conductivity of samples. Secondly, the actual ideal thermal boundary conductance of Cu-diamond composites may be achieved by the formation of partial grain-to-grain diamond contacts at higher pressure.

3.5 Thermal expansion

Kerner model[14] and Rose-Hashin Bounds model (R-H model)[15] have been used widely to predict the theoretical coefficients of thermal expansion of composites. They take shear effects into account at the boundaries between particles and the matrix. Hence, we utilized Kerner model and Rose-Hashin Bounds model to evaluate CTEs of the samples in the present study. Kerner model can be expressed by the following equation:

$$\alpha_c = \alpha_m V_m + \alpha_d V_d + V_d V_m(\alpha_d - \alpha_m) \times \frac{K_d - K_m}{V_m K_m + V_d K_d + (3K_d K_m / 4G_m)} \tag{3}$$

And Rose-Hashin Bounds model can be expressed by the following equation:

$$\begin{cases} a_c^u = \dfrac{4V_m V_d G_d (K_m - K_d)(a_m - a_d)}{3K_m K_d + (4G_d(K_m + K_d)/2)(a_m V_m + a_d V_d)} + \\ a_c^l = \dfrac{4V_m V_d G_m (K_m - K_d)(a_m - a_d)}{3K_m K_d + (4G_m(K_m + K_d)/2)(a_m V_m + a_d V_d)} + \end{cases} \tag{4}$$

where, α_c is the coefficient of thermal expansion of the composite, α_d is the coefficient of thermal expansion of the dispersions, α_m is the coefficient of thermal expansion of the matrix, V_d is the volume fraction of the dispersions in the composites, V_m is the volume fraction of the matrix in the composites, K_d is the bulk modulus of the dispersions, K_m is the bulk modulus of the matrix, G_m is the shear modulus of the matrix, G_d is the shear modulus of the dispersions, the superscript u represents upper bound and l signifies lower bound.

Table 1 Properties of diamond and Cu assumed for calculation of thermal expansion and thermal conductivity

Material	λ/(W/mK)	α/(10^{-6}/K)	K^c/(10^9Pa)	G^d/(10^9Pa)
Cu (matrix)	400^a	17.6^a	110^b	40^b
Diamond	2000^b	1.1^b	440^b	550^b

[a]Measured; [b]Provided by the manufacturer;
[c] Bulk modulus; [d] Shear modulus

Properties of diamond and Cu assumed for calculation of thermal expansion are shown in Table 1. A comparison between the theoretically predicted

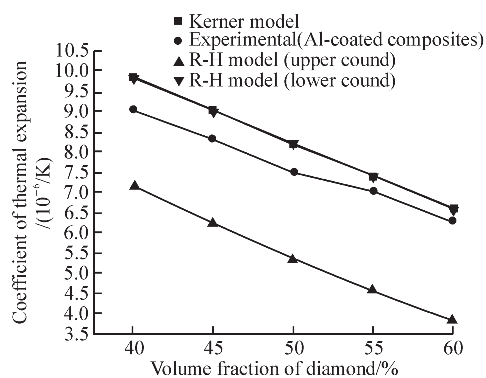

Fig.7 Experimental data and theoretical predictions of coefficients of thermal expansion for Cu/Al-coated diamond composites with various volume fractions of diamond

and experimentally obtained CTEs for Cu/diamond composites is shown in Fig.7. As shown, CTEs of the Al-coated composites obtained experimentally are lower than the values of theoretical models (Kerner model and R-H model lower bound). This is a good indication in that the Al-coated diamond particles have strongly bonded with the Cu-matrix in the composite fabricated by SPS. The thermal expansion values for samples obtained in the present study are found to be in the range of 6.31×10^{-6}-9.06×10^{-6}/K in a volume fraction range of Al-coated diamond between 40% and 60%. On the other hand, some packaging base materials currently in use are Cu-W and SiC/Al, and their CTEs are 6.2×10^{-6}-7.3×10^{-6}/K[16-18]. To apply Cu-diamond composites as thermal management materials, it is necessary to add more diamond powders to such composites. That is, Cu-matrix composites containing diamond higher than 50vol% would be more preferable in application.

4 Conclusions

The interfacial microstructures and thermal conductivities of Cu/diamond composites fabricated by spark plasma sintering process were examined. The results show that Al-coated diamond particle is an effective approach to promoting the relative packing density and improving the thermal conductivity of samples sintered.

The thermal conductivity of Al-coated diamond particles dispersed Cu-matrix composites containing 40vol%-50vol% diamond reached 491-565 W/(m · K), higher than 60% the theoretical thermal conductivity estimated by Maxwell-Eucken's equation.

The coefficient of thermal expansion of the Al-coated diamond/Cu composites falls in the lines of Kerner model and R-H model lower bound, indicating strong bonding between the Al-coated diamond particles and the Cu-matrix in the composite.

On the basis of the present work, the following research activities are necessary to further improve the thermal conductivity of diamond/copper composites, which includes: to optimize the sintering process parameters, especially combine the heating rate and holding time to improve the relative density of composites sintered; to optimize the quality and thickness of Al-coating layers;to optimize the interface design, for example, the addition of Ti or Si (with different contents) to Al coating layer.

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