Effect of diamond particle type on the thermal properties of diamond/copper composites

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Abstract

The molten salt method was used to plate chromium on the surfaces of MBD (Diamond grains for the Metal Bond tool) and RVD (Diamond grains for Resinoid and Vitrified bond) diamond particles, respectively, to metalize their surfaces. The Cr-coated diamond/copper composites were obtained by vacuum hot pressing method, and the thermal conductivity and coefficient of thermal expansion of the two composites were compared. The results indicate that the thermal conductivity of both composites prepared by Cr-coated diamond particles and copper matrix was greatly improved. The thermal conductivity showed a trend of increasing and then decreasing with the increase of chromium content. The thermal conductivity of RVD diamond/copper composites was up to 483 W m^{-1} K^{-1}, and MBD diamond/copper composites was up to 450 W m^{-1} K^{-1}, and the thermal conductivity of RVD diamond/copper composites was generally higher than that of MBD diamond/copper composites, the CTE of the composites prepared by Cr-coated diamond particles and copper matrix decreased significantly.

K e y   w o r d s: metal matrix composite, RVD diamond, MBD diamond, thermal conductivity, thermal expansion coefficient

1. Introduction

With the rapid development of the information age, electronic information technology has been widely used in high-tech fields such as national defense, aerospace, etc. It leads to higher and higher integration of electronic device chips and higher power [1, 2]. The heat dissipated by the chip during work has also increased significantly; if the temperature cannot be dissipated, it will seriously affect the stability and safety of electronic devices. It requires electronic packaging materials to have excellent heat dissipation performance [3, 4]. At the same time, to avoid the failure of electronic devices caused by excessive thermal stress, electronic packaging materials must maintain a similar coefficient of thermal expansion to that of electronic devices [5–7].

Due to the increasing power of electronic devices, the first and second generations of thermal manage-ment materials can no longer meet the requirements of high thermal conductivity. Diamond/copper composites are considered the next-generation thermal management materials because of their good thermal conductivity and low coefficient of thermal expansion [8–9]. Because the interface between diamond and copper is not wetted [10], the properties of the composites are very poor, and they are not suitable for use as packaging materials. For diamond/copper composites, diamond surface metallization can improve the interface bond between diamond particles and copper matrix. Carbide-forming elements such as W [11–13], Mo [14–16], Ti [17, 18], B [19], and Cr [20] offer an effective way to improve the wetting and interfacial bonding between diamond particles and copper matrix. Chemical plating [13], vacuum magnetron sputtering [21], molten salt [15], vacuum diffusion [22], sol-gel [6], and other methods are used to form a metal carbide coating on the surface of the diamond.

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Recently, many researchers have done a lot of research on MBD (Diamond grains for Metal Bond tool) diamond/copper composites, but little research has been seen on RVD (Diamond grains for Resinoid and Vitrified bond) diamond/copper composites. Therefore, in this work, a metal carbonization layer is obtained by plating chromium on the surface of MBD and RVD diamond using the molten salt method. On this basis, two kinds of diamond/copper composites were fabricated by vacuum hot pressing [13]. The microstructure, fracture morphology, relative density, thermal conductivity, and thermal expansion coefficient of the two composites were studied.

2. Experimental

2.1. Preparation of composites

Copper powder (99.99 % in purity) was used as the matrix material, and Synthetic MBD diamond particles and RVD diamond particles with an average particle size of 180–200 mesh (75–80 μm) were used as re-

inforcements, purchased from Henan Huanghe Whirlwind Co., China. Chromium powder with a purity of 99.99 wt.% was plated on the surface of a diamond by using the molten salt method, and a complete and uniform coating was covered on the surface of the diamond by controlling the heating temperature, heating time, and the chromium contents. Then, Cr-coated diamond powder and copper powder were loaded into a ball mill tank with a volume ratio of 55 : 45 and mixed. As the grinding ball causes damage to the coating, no grinding balls were used. The ball mill rotation speed was set to 120 rad min^{-1}, and the ball mill tank was put into the tumbling ball mill and mixed for 10 h. The mixed powder was loaded into the graphite mold after the powder was mixed uniformly. The surface of the powder was spread evenly and covered with graphite paper; then, the graphite indenter was placed on the graphite paper. The mold was put into the vacuum furnace and pressurized to 1.5 MPa for vacuum pumping. The temperature of the furnace was raised to 1100 ℃ and kept for 30 min, then the pressure to 15 MPa was supplemented when the liquid phase appeared. After the heat preservation was finished, the
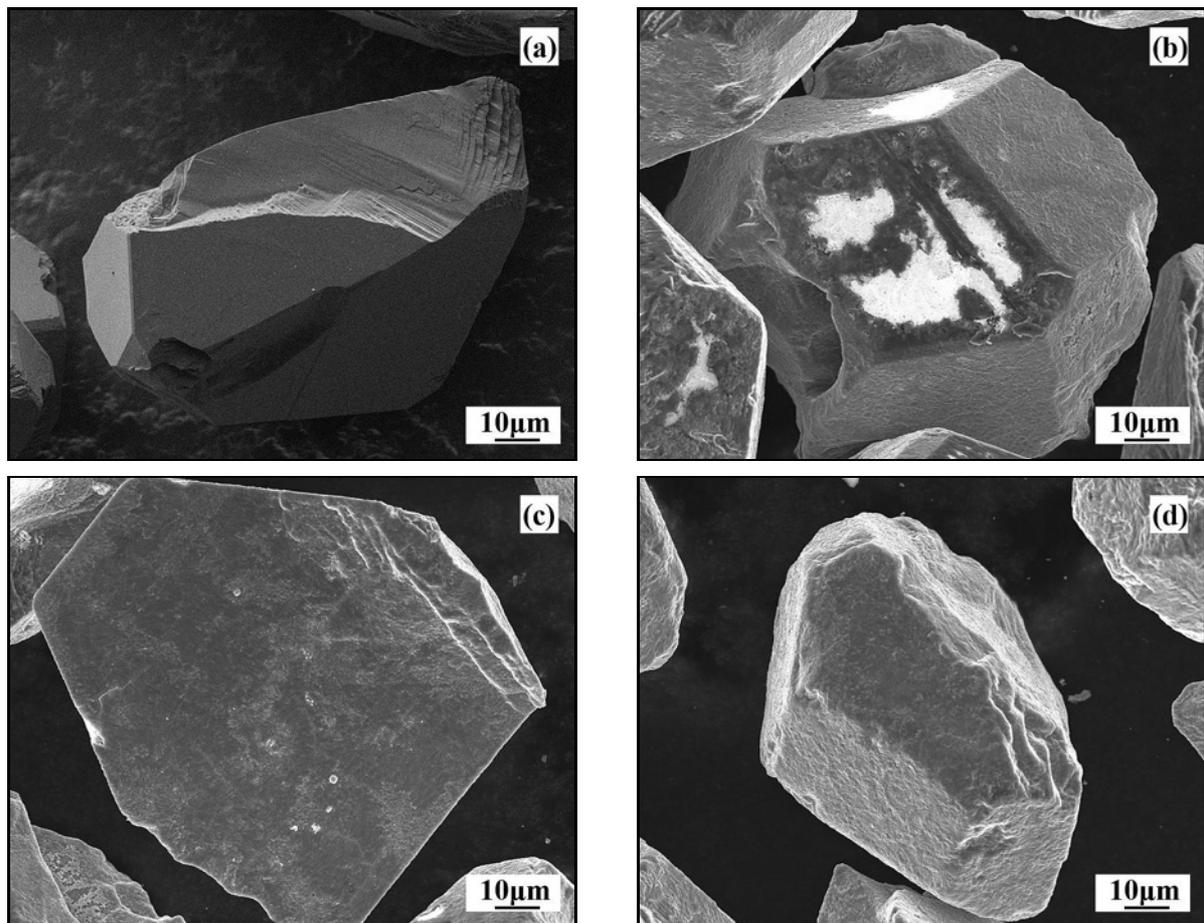
Fig. 1. RVD diamond particles plated with different content of chromium: (a) uncoated, (b) 6 %, (c) 8 %, and (d) 10 %.
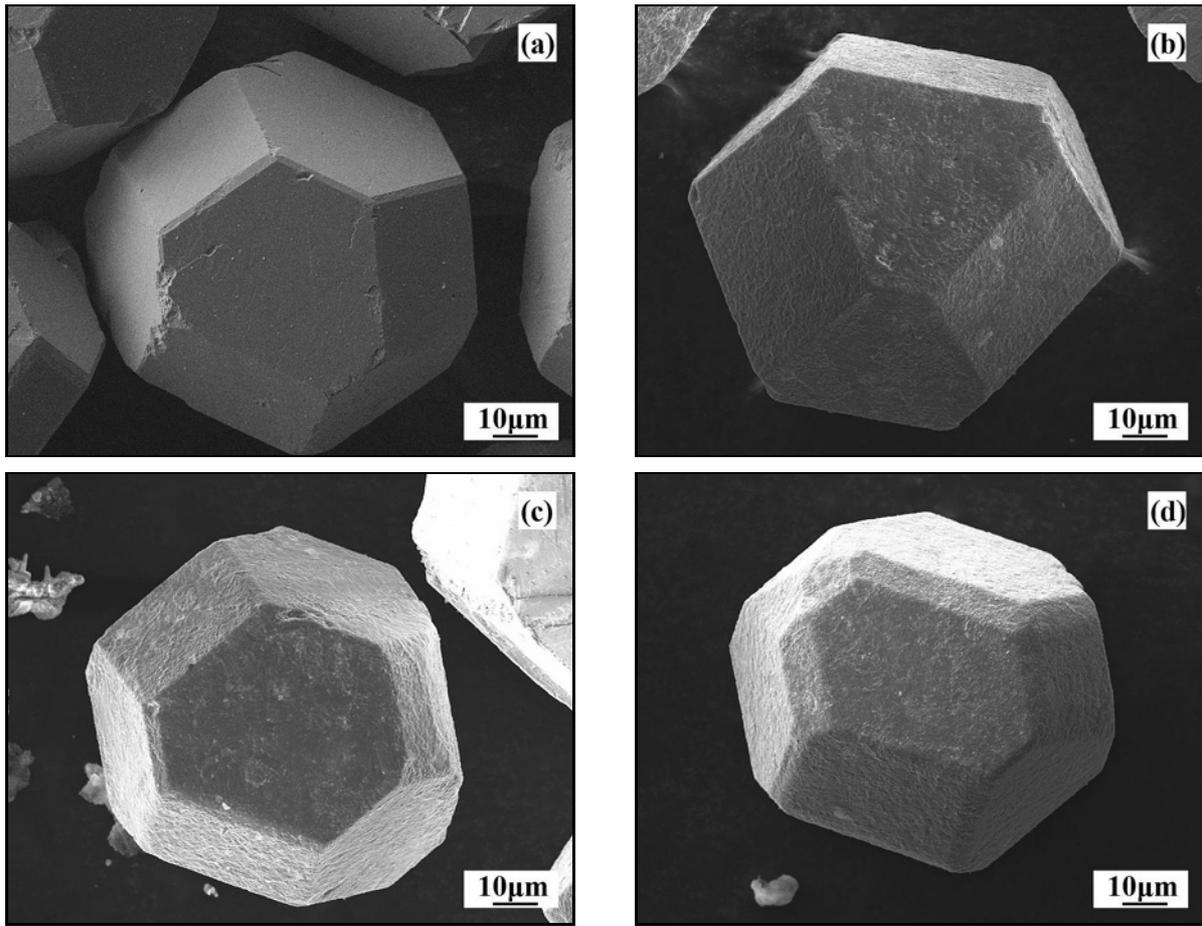
Fig. 2. MBD diamond particles plated with different content of chromium: (a) uncoated, (b) 6 %, (c) 8 %, and (d) 10 %.

sample was cooled down to room temperature, and the diamond/copper composite was obtained.

2.2. Characterization

The morphology of the two kinds of diamond particles and the fracture surface of the composite were characterized by field-emission scanning electron microscopy (ZEISS, Sigma-300, Germany). The density of the composites was measured by the Archimedes method, and the theoretical density of composites was calculated by the mixing rule:

$$\rho_c = \rho_d V_d + \rho_m V_m + \rho_i V_i, \qquad (1)$$

where ρ is density, and V is the volume fraction, the subscripts "c", "d", "m", and "i" refer to the composites, the diamond, the copper matrix, and the coating.

A disc sample with a diameter of 13 mm and a thickness of 2 mm was made, and the thermal diffusivity of the sample was measured by LFA 457 laser thermal conductivity analyzer. The thermal conductivity was calculated according to the formula:

$$\lambda = \alpha \times C_p \times \rho, \qquad (2)$$

where λ, α, and C_p are the thermal conductivity, the thermal diffusivity, and the specific heat capacity.

The specific heat capacity and the theoretical density of composites were calculated by the mixing rule:

$$C_p = \frac{C_d V_d \rho_d + C_m V_m \rho_m + C_i V_i \rho_i}{\rho_c}, \qquad (3)$$

where C is the specific heat capacity.

The thermal expansion coefficient of the sample was measured by a TMA402F3 thermal engine analyzer with a specimen of $2 \times 2 \times 30 \, \text{mm}^3$ in size, the heating rate was $5 \, ^\circ\text{C} \, \text{min}^{-1}$, and the test range was 25–300 $^\circ$C in vacuum (vacuum degree is less than 10^{-2} mbar).

3. Results and discussion

3.1. Microstructure of Cr-coated diamond particles

Figure 1 shows an SEM image of RVD diamond particles plated with different chromium content after heat treatment at 950 $^\circ$C for 60 min. When the content
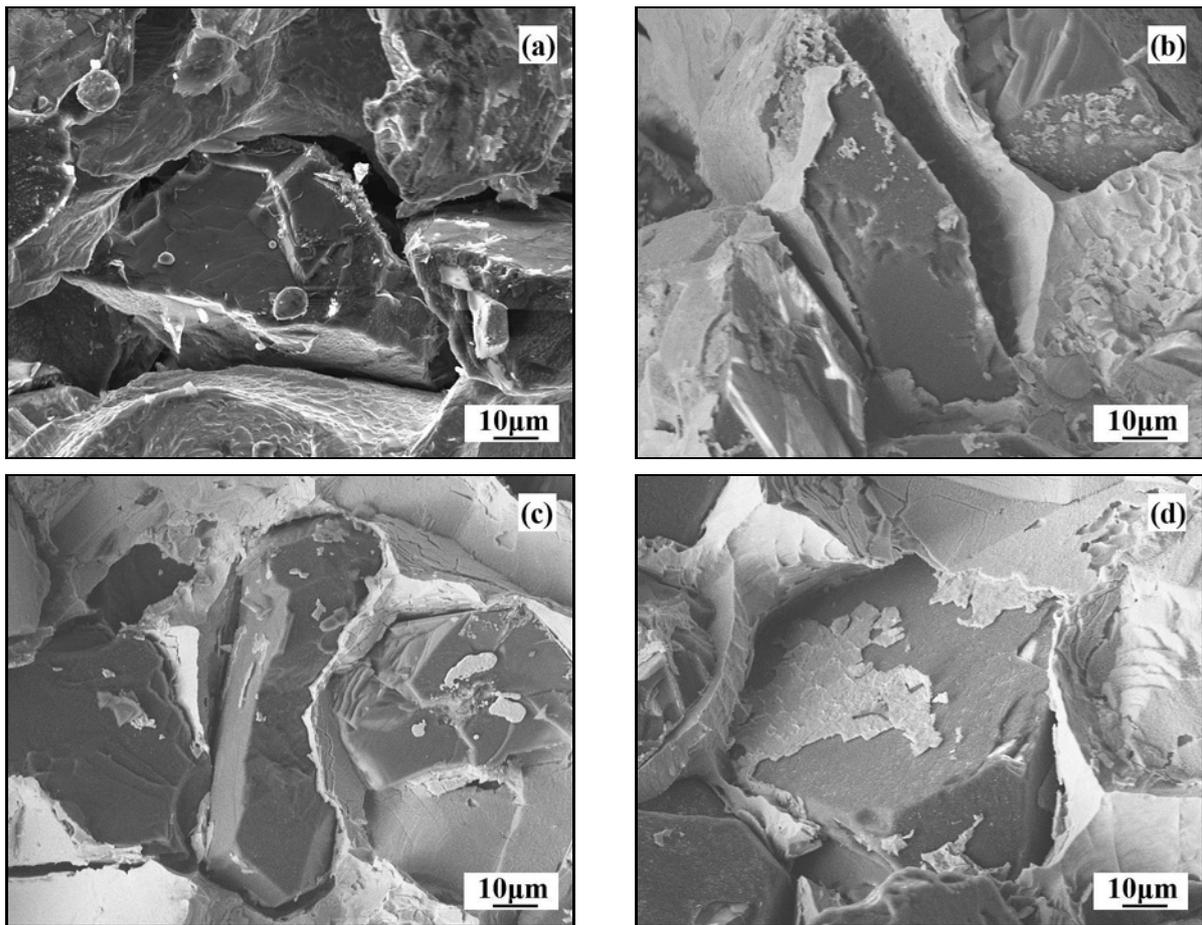
Fig. 3. The fracture surface of RVD diamond/copper composites with uncoated and Cr-coated diamond particles: (a) uncoated, (b) 6%Cr-coated, (c) 8%Cr-coated, and (d) 10%Cr-coated.

of chromium is 6 %, there is leakage of plating in some areas of RVD diamond particles. With the increase of chromium content, a complete and uniform coating is formed on the surface of diamond particles. Figure 2 shows an SEM image of MBD diamond particles coated with different content of chromium. It can be seen from the figure that when the chromium content is 6, 8, and 10 %, a complete coating can be formed on the surface of the diamond particles, and there is no leakage of plating. When using the molten salt method, the chloride becomes a molten state under high temperature, providing a fluid reaction medium for diamond particles and chromium. The presence of molten salt improves the wettability between diamond particles and chromium, and chromium dissolves in the molten salt, which makes it easier to react with diamond particles to form chromium carbide. With the increased chromium content, more chromium can react with the diamond and finally form a complete coating on the surface of the diamond.

3.2. Microstructure of Cr-coated diamond/copper composites

Figure 3 shows the SEM image of the fracture surface of RVD diamond/copper composite with uncoated and Cr-coated diamond particles. When diamond particles are directly combined with the copper matrix, due to the poor wettability between diamond particles and copper matrix, diamond particles are not combined with the copper matrix. A large gap between diamond particles and copper matrix indicates that the interface bonding is weak. The bonding between diamond particles and copper matrix depends on mechanical force, which significantly reduces the thermal conductivity and flexural strength of the composites. It can be seen that the bonding between the diamond particles and the copper matrix becomes tight after plating chromium on the surface of diamond particles. When the content of chromium is 6 %, there is leakage of plating in some areas of RVD diamond particles, which causes the diamond particles and the copper matrix not to be closely connected. When the chromium content is 8 %, the diamond particles break,
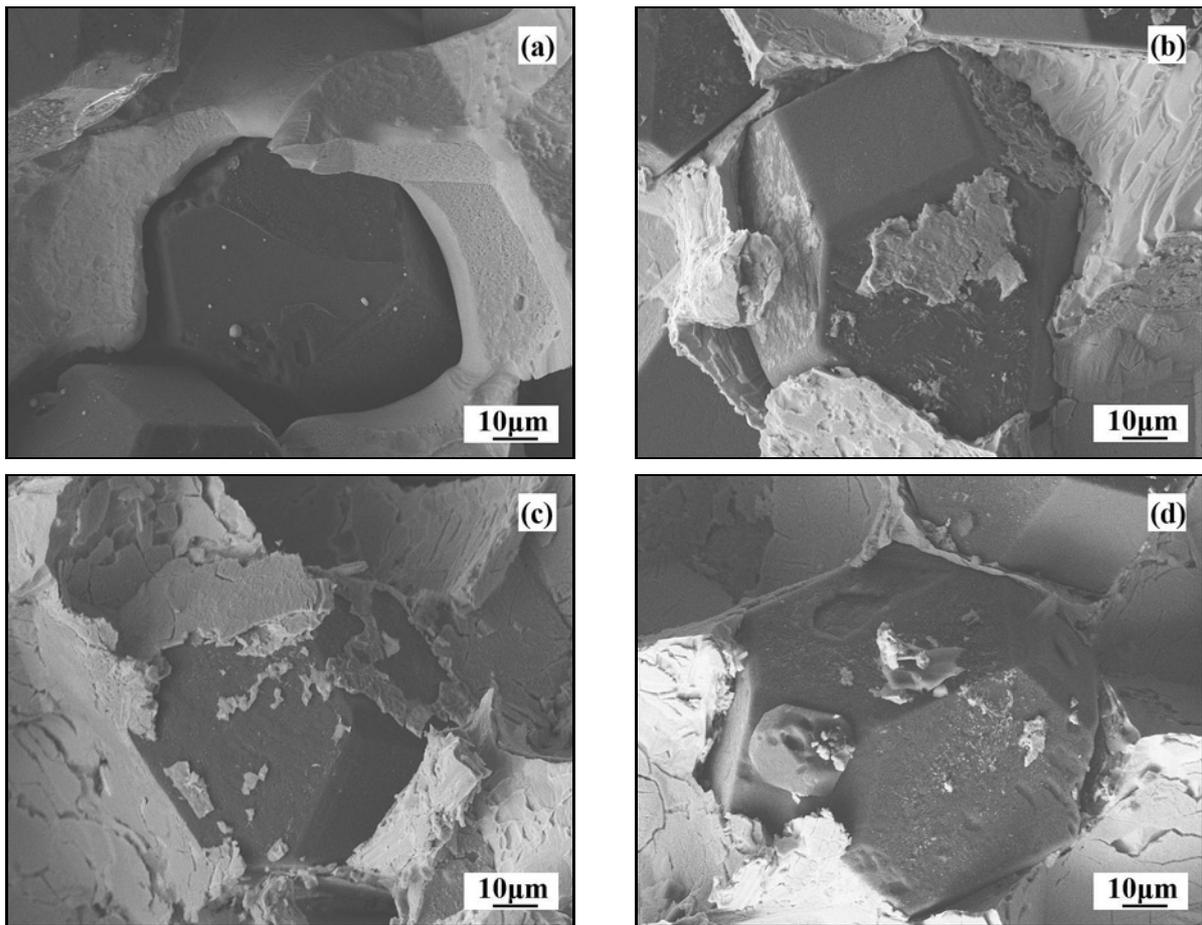
Fig. 4. The fracture surface of MBD diamond/copper composites with uncoated and Cr-coated diamond particles: (a) uncoated, (b) 6%Cr-coated, (c) 8%Cr-coated, and (d) 10%Cr-coated.

which indicates that the interfacial bonding strength is higher than the fracture stress of the diamond. When the chromium content is 10 %, the coating warps and falls off, indicating poor bonding between the coating and the diamond. Figure 4 shows the SEM image of the fracture surface of MBD diamond/copper composite. Like RVD diamond/copper composite, with increased chromium content, the bonding between diamond particles and copper matrix becomes closer, and the gap becomes smaller. Figures 3 and 4 show that chromium carbide layers promoted the wettability and interface bonding between diamond particles and copper matrix. The interfacial bonding between the diamond particles and copper matrix can be improved, which improves the performance of composite materials.

Figure 5 shows EDS images of the fracture surface of two kinds of composites. In the figure, red represents element C, green represents element Cr, and blue represents element Cu. It can be seen that the coating on the diamond surface falls off with the fracture of the composites, and only a small part remains on the diamond surface; some diamond peels off with the fracture of the composites and leaves pits. Many Cr and

C elements are found in some pits, which is due to the peeling off of diamond, and the coating falls off and remains in the pit, which indicates that the bonding between the coating and diamond is poor and easy to peel off, which will lead to the decrease of the thermal conductivity of diamond/copper composites.

3.3. Relative density of diamond/copper composites

The relative density of the composites was calculated according to the formula:

$$R = \frac{\rho_0}{\rho_c} \times 100\%, \qquad (4)$$

where R is relative density and ρ_0 is the actual density of the composites.

Figure 6 shows the relative density of two kinds of diamond/copper with different chromium content. When diamond particles are directly combined with copper matrix, the relative density of the composite material is the lowest; this is because there is no wetting between diamond and copper, and the interface
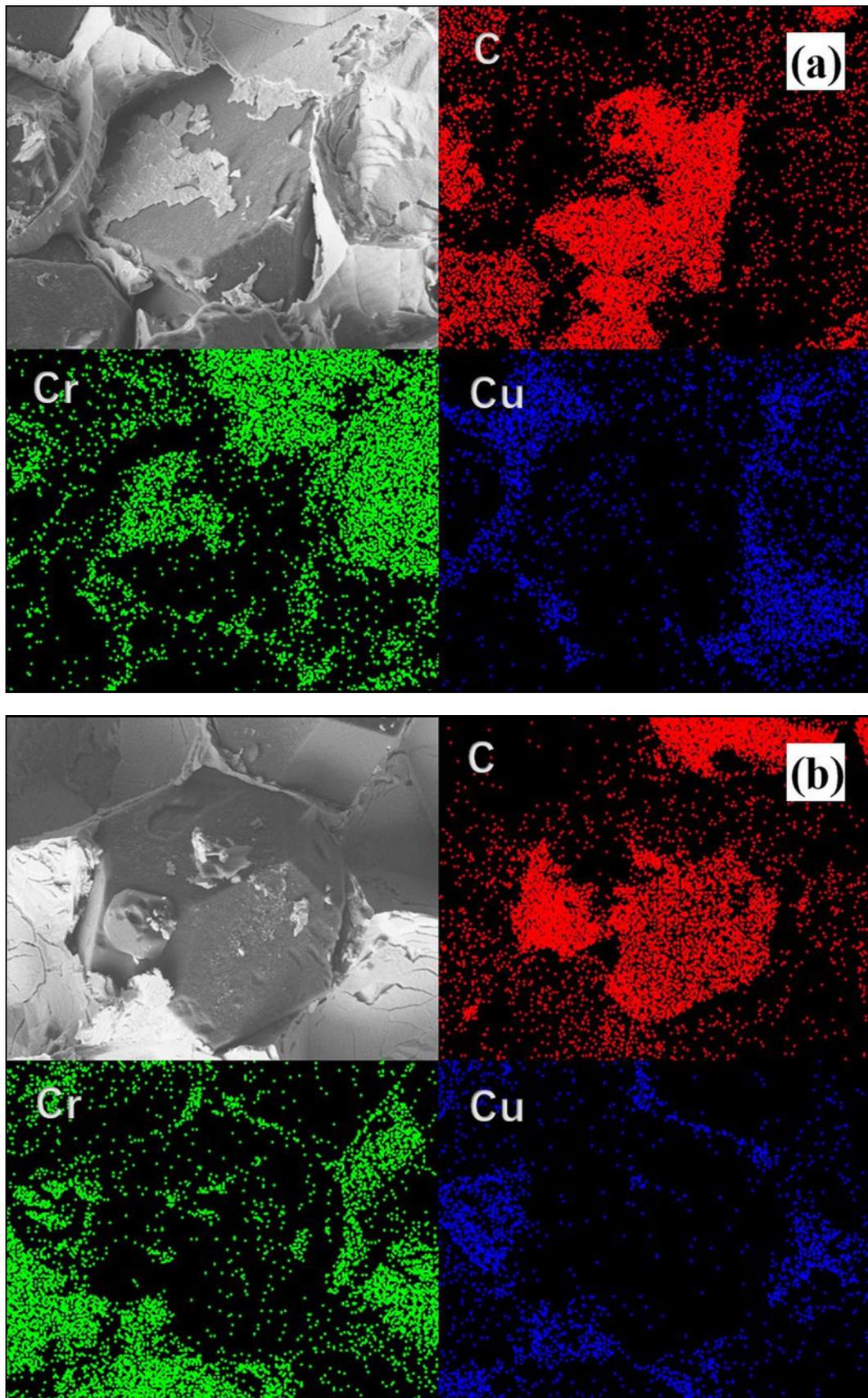
Fig. 5. EDS images of the fracture surface of diamond/copper composites: (a) 10%Cr-coated RVD diamond/copper and (b)10%Cr-coated MBD diamond/copper.
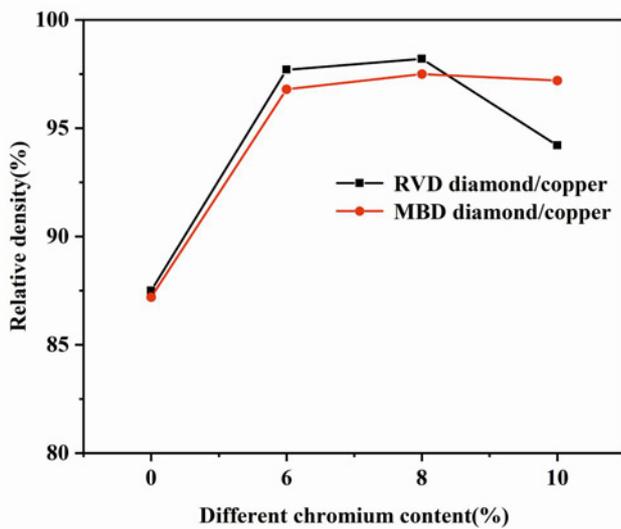
Fig. 6. The relative density of RVD diamond/copper and MBD diamond/copper composites with different chromium content.

Fig. 7. Thermal conductivity of RVD diamond/copper and MBD diamond/copper composites with different chromium content.

spacing between diamond and copper is large. After chromium plating on the diamond particles, the relative density of the composite increases significantly. When the content of chromium increases from 0 to 8 %, the density of both composites increases, and the relative density of RVD diamond/copper composites is higher than that of MBD diamond/copper composites. When the content of chromium is 8 %, the density of both composites reaches the maximum value. When chromium content is 10 %, the density of MBD diamond/copper composites changes little, and the relative density of RVD diamond/copper composites is significantly reduced. Due to the irregular shape of the RVD diamond, it is easier to fall off when the coating is too thick at a high temperature, the falling off of the coating will deteriorate the combination of diamond particles and copper matrix.

3.4. Thermal conductivity of diamond/copper composites

It can be seen from Fig. 7 that the thermal conductivity of diamond/copper composites is greatly improved by plating chromium on the surface of the diamond. With increased chromium content, the thermal conductivity of the composites prepared by the two kinds of the diamond increases first and then decreases. When the chromium content increases from 6 to 8 %, the thickness of the coating increases with the chromium content, and the coating is more complete and uniform. The bonding between diamond particles and the copper matrix is more closely, and the thermal conductivity of the two composites increases. This is similar to the changing trend of relative den-

sity. When the chromium content increases from 8 to 10 %, the thermal conductivity of both composites decreases, and the thermal conductivity of RVD diamond/copper composites decreases sharply. As the chromium content increases, the thickness of the diamond surface coating is also increasing. The coating is thicker, and the thermal resistance of the interface gradually increases. Chromium and diamond react to form Cr_7C_3 and Cr_3C_2. The thermal conductivity of Cr_7C_3 is $19.1\,\mathrm{W\,m^{-1}\,K^{-1}}$, and the thermal conductivity of Cr_3C_2 is $19\,\mathrm{W\,m^{-1}\,K^{-1}}$ [23], which has a more significant impact on the thermal conductivity of composite, resulting in a decrease in the thermal conductivity of the composite material. It can also be seen in the figure that the thermal conductivity of RVD diamond composites decreases faster than that of MBD diamond composites. This is because composites are prepared by vacuum hot pressing when the temperature is too high, the accumulation of thermal stress in the coating causes its peeling, and the shape of the RVD diamond is irregular. It is easier to fall off when the coating is too thick; falling off the coating deteriorates the combination of diamond particles and copper matrix. It reduces the thermal conductivity of the composites. Comparing the thermal conductivity of the two composites, the thermal conductivity of RVD diamond/copper composites is higher than that of MBD diamond/copper composites. In the preparation of diamond/copper composites using vacuum hot pressing, due to the irregular shape of RVD diamonds, the RVD diamonds are more densely packed in the composites. The volume percentage of diamonds in the composites is higher, which results in the thermal conductivity of the prepared RVD dia-
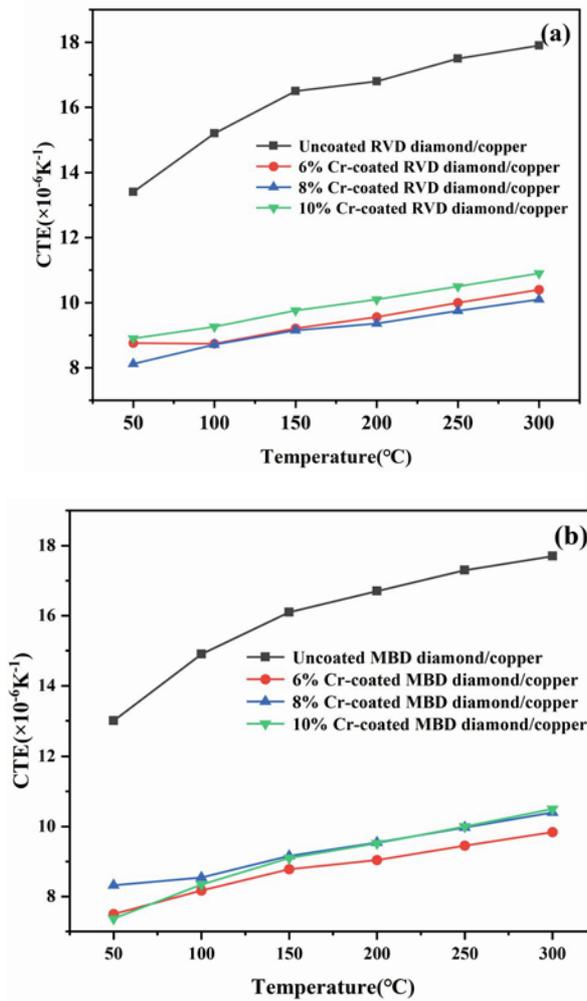
Fig. 8. Variation curve of thermal expansion coefficient of diamond/copper composites with temperature: (a) RVD diamond/copper composites and (b) MBD diamond/copper composites.

Fig. 9. Comparison of thermal expansion coefficient and theoretical calculation value of diamond/copper composites.

mond/copper composites being generally higher than that of MBD diamond/copper composites.

3.4. The CTE of diamond/copper composites

Figure 8 shows the CTE of two kinds of diamond/copper composites at different temperatures. It can be seen from the figure that the CTE of uncoated diamond/copper composites is much higher than that of Cr-coated diamond/copper composites. Chromium carbide can play a buffering role when the composite material is heated and expanded, thereby reducing the CTE of the composites. As the temperature increases, the CTE of the composites shows an upward trend, which is due to the positive temperature effect of the CTE of the diamond/copper composite. When the temperature increases, the CTE of the uncoated diamond/copper composites increases faster,

and the interfacial bonding strength determines the restraint degree of diamond particles on the expansion of matrix copper; the stronger the interface bonding, the smaller the CTE changes with temperature. Because of the poor wettability between diamond particles and copper matrix, the interfacial bonding is weak, so the CTE increases rapidly with temperature; with chromium plating on the surface of the diamond, the interfacial bonding can be improved, so the CTE changes slowly with temperature. The CTE of Cr-coated RVD diamond/copper composites is greater than that of Cr-coated MBD diamond/copper composites, which indicates that MBD diamond has a better inhibition effect on matrix expansion. Figure 9 shows the comparison curve between the measured and theoretical values of the CTE of diamond/copper composites. There are mainly two models for the theoretical calculation of the CTE of composites. The first

is the Turner model [24]. Turner model assumes that the stress inside and outside the particle reinforcement in the composite is evenly distributed and ignores the influence of shear stress. The expression is as follows:

$$\alpha = \frac{\alpha_m V_m K_m + \alpha_d V_d K_d}{V_m K_m + V_d K_d}. \qquad (5)$$

The second model is the Kerner model [25]. The Kerner model assumes that the reinforcement is in the form of spherical particles, and the shear force is considered. The expression for the composite CTE is obtained as:

$$\alpha_c = \alpha_d V_d + \alpha_m V_m + (\alpha_d - \alpha_m) V_d V_m \cdot$$
$$\cdot \frac{K_d - K_m}{V_d K_d + V_m K_m + \left(\dfrac{3 K_d K_m}{4 G_m}\right)}, \qquad (6)$$

where α_c, α_d, and α_m are the CTE of the composites, reinforcement, and matrix ($\alpha_{diamond} = 2.3 \times 10^{-6}\,K^{-1}$; $\alpha_{copper} = 17 \times 10^{-6}\,K^{-1}$), V_d and V_m are the volume fractions of the reinforcement and the matrix, K_d and K_m are the bulk moduli of the reinforcement and the matrix ($K_{diamond} = 580\,GPa$, $K_{copper} = 140\,GPa$), and G_m is the shear modulus of the matrix ($G_{copper} = 49\,GPa$).

Comparing the CTE of the composites at 50 ℃ with the two models, it can be seen from Fig. 9 that the CTE of the uncoated diamond/copper composites is much higher than the theoretical value, which indicates that the diamond particles cannot hinder the expansion of the copper matrix.

The actual CTE of Cr-coated MBD diamond/copper composites is closer to the theoretical value, while the actual thermal expansion coefficient of Cr-coated RVD diamond/copper composites is slightly larger than the theoretical value. This is because the shape of RVD diamond particles is irregular, MBD diamond particles are regular cuboctahedrons, and MBD diamond particles are closer to spherical, so the CTE of Cr-coated MBD diamond particles is closer to the theoretical value.

4. Conclusions

The molten salt method was used for chromium plating on the surface of diamond particles, and a complete and uniform coating was obtained on the surface of both diamond particles. Chromium plating on the surface of a diamond improves the wettability between diamond particles and copper matrix, the interface bonding becomes stronger, and the thermal conductivity of the diamond/copper composites prepared was significantly increased. The highest thermal conductivity of RVD diamond copper is 483 W m^{-1} K^{-1}, and

of MBD diamond/copper is 450 W m^{-1} K^{-1}, which is much higher than for the composites directly prepared by diamond particles and copper matrix, and the thermal conductivity of RVD diamond-copper composites is generally higher than that of MBD diamond/copper composites. Moreover, the CTE of the composite prepared by chromium plated diamond is significantly reduced, and the CTE of the RVD diamond/copper composites is slightly higher than MBD diamond/copper composites; the CTE of Cr-coated MBD diamond/copper composites is closer to the theoretical value.

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