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Preparation and thermal conductivity of tungsten coated diamond/copper composites

Shu-gang DAI[1,2], Jin-wang LI[1], Chang-ji WANG[1]

1. College of Astronautics, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, China;
2. Inst. 724 of China Shipbuilding Industry Corporation, Nanjing 211153, China

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Abstract: Tungsten was plated on the surface of diamond by using thermal diffusion method. Different process parameters were employed to prepare the composites with tungsten, diamond and copper. The micro morphology of different samples was observed, and the thermal conductivity of samples was measured by laser flash method. The optimal process parameters for preparing diamond/copper composites with high thermal conductivity were investigated. The results indicated that plating tungsten on diamond could modify the interface bonding. When the diamond was plated for 60 min, the coating appeared intact, uniform and flat, and the thermal conductivity of the sample could reach as high as 486 W/(m·K). The integrity and uniformity were more important than thickness for the coating. When the tungsten-plated diamond was further annealed, the metallurgical bonding between the coating and the diamond was enhanced, and the thermal conductivity rose to 559 W/(m·K).

Key words: diamond/copper composites; coating; thermal conductivity; interface bonding

1 Introduction

With the development of science and technology, the role of electronic devices is increasing, and the internal heat flux is growing. Traditional heat dissipation materials cannot meet the practical needs. Furthermore, it is necessary to consider the effect of temperature load on the thermal stress among packaging components under actual working conditions.

Theoretically, the thermal conductivity of diamond is as high as 2200−2600 W/(m·K), and the coefficient of thermal expansion is about $(0.86\pm0.1)\times10^{-6}\ \mathrm{K}^{-1}$ [1−4]. However, pure diamond is difficult and costly to obtain. The proper method is to use diamond as reinforcement to prepare metal matrix composites. Cu is a high cost-effective alternative, whose thermal conductivity could reach 398 W/(m·K). Although Cu has a higher thermal expansion coefficient, $17.5\times10^{-6}\ \mathrm{K}^{-1}$ [5], it can be adjusted by adding diamond [6]. Therefore, diamond/copper composite is a new type of thermal management material with great potential [7−10].

Many studies have focused on the thermal conductivity of the particle reinforced composites [11−15]. However, the thermal conductivity of diamond/copper composites is far beyond the theoretical value of most researches [16−18]. The measured value of thermal conductivity of the prepared samples was lower than the theoretical value, and the reason was that during the actual preparation process, the composites could not be completely dense. There were pores and defects in the interior, and there were also impurities and lattice defects in the raw materials. These factors led to the scattering of the electrons and phonons [14,19−22], which greatly increased the thermal resistance of the material and seriously damaged the thermal conductivity of the

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Corresponding author: Jin-wang LI, Tel: +86-13584023466, E-mail: ljw@nuaa.edu.cn
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composites [8,23]. If the above problems can be solved, the thermal conductivity of the composite will be greatly improved [24,25]. Therefore, it is necessary to strengthen the interface bonding between diamond and copper and to reduce the internal defects of the composites. Then the preparation condition of diamond/copper composite can be as ideal as possible, and its thermal conductivity can be closer to the theoretical value.

Most of the existing researches combined the two materials by adjusting the pressure and temperature [22−28], but there was rare research focused on the pressureless forming process. This study adopted innovative ways to prepare the diamond/copper composites by cold pressing sintering, pressureless infiltration and hot pressing sintering, respectively. Also the effects of different forming processes on the thermal conductivity of the composites had been studied.

For the interface modification, diamond surface plating had little damage to the copper matrix but also had a certain protective effect on the diamond [28]. However, the process of diamond surface modification was not mature. There were some uncertain elements in the experiments, such as the damage of the subsequent process to the coating, the actual reaction and diffusion between the coating, diamond and copper in the sintering process, and the improvement effect of diamond pre-coating on interfacial bonding. The relevant parameters were difficult to control in practice. Thus, to further explore the effect mechanism of coating on the thermal conductivity of composites, and to find a more conducive coating to improve the thermal conductivity of composites, the surface modification of diamond was selected to enhance the interface bonding. Tungsten was just the interface element which was insoluble in copper [29]. The effects of phase composition and micro morphology of the coating on the thermal conductivity of the composites were studied in this work. In addition, in order to explore the better preparation process of diamond/copper composites more comprehensively and systematically, two important parameters, diamond volume fraction and particle size, were also taken into consideration.

2 Experimental

Single crystal diamond of MBD 8 grade was used in the experiment. Tungsten was pre-plated on the diamond surface at 1000 °C by thermal diffusion method. The specific steps were as follows.

Washed diamond particles were put into the 15% sodium hydroxide solution and heated to boiling for 10 min. Then the sample were put into the 30% nitric acid solution and heated to boiling for 30 min. Finally, the diamond particles were washed and dried to obtain the surface-coarsened and activated diamond.

The diamond, high-purity tungsten powder and tungsten trioxide powder were put into the ball mill tank in a certain proportion. The planetary ball mill was used to mix the materials for 2 h at the rotation speed of 200 r/min. Then the mixed powder was poured into the corundum ark, and put into the vacuum tubular furnace. After vacuum pumping, the temperature was raised to 900−1100 °C at a certain speed and kept for a period. Vacuum was maintained in the tube furnace during electroplating. After all the above steps, the diamond particles coated with tungsten on the surface were finally obtained, as shown in Fig. 1.

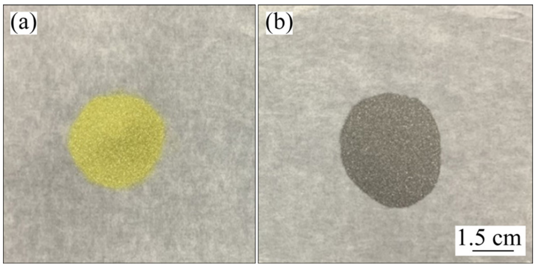

Fig. 1 Morphology of diamond powder before (a) and after (b) tungsten plating

Generally speaking, the increase of the thickness of the interface layer has a negative effect on the heat transfer of the interface. For this reason, it was expected to get a thinner coating to improve the thermal conductivity of the composite. Therefore, the coating thickness was controlled by adjusting the electroplating time. The diamond surface was modified with electroplating time of 15, 30, 60, 90 and 120 min, respectively.

Then the composite was prepared by cold pressing sintering, pressureless infiltration, and hot-pressing sintering, respectively. In the cold pressing sintering experiment, the mixture of diamond and copper powder was molded in a stainless-steel vessel with a pressure of 50 MPa, and put into a vacuum tube furnace to sinter at 1000 °C for 1 h, and then was cooled down to room temperature in the furnace. In the pressureless infiltration experiment, some of the coated diamond was mixed with PVA solution to get the diamond preform. A fixed amount of copper was placed on the diamond preform and heated to 1100 °C in a vacuum furnace to liquefy the copper and kept for 1 h. According to the mass of the diamond in preform and the preset diamond volume fraction of the composite, the mass of the placed copper could be calculated. When the diamond was preformed, the volume fraction of PVA solution was controlled to be the same as the preset volume fraction of copper to ensure the infiltration space of copper. The PVA in preform decomposed and disappeared at 200−300 °C, so that copper could penetrate the diamond to form the composite. In the hot pressing sintering experiment, the diamond copper mixed powder was put into the high-strength graphite mold. The composite was prepared in a vacuum hot pressing furnace under the pressure of 30 MPa and the temperature of 1050 °C lasting for 20 min, then the sample was cooled down to room temperature under the same pressure. The diamond particle size, volume fraction, and the plating time of tungsten coating were adjusted to obtain different samples in hot pressing experiments. By laser cutting the samples were made into discs with diameter of 12.7 mm and thickness of 3.5 mm.

In these experiments, a scanning electron microscope (SEM) was employed to observe the micro morphology of the diamond and the composites. The Archimedes drainage method was used to measure the density of the composites.

In this study, the thermal conductivity of composites was calculated as follows:

$$\lambda=\alpha\cdot\rho\cdot c_p \tag{1}$$

where λ is the thermal conductivity (W/(m·K)); α is the thermal diffusion coefficient (m^2/s); ρ is the density (kg/m^3); c_p is the specific heat capacity (J/(kg·K)).

The thermal diffusivity and specific heat capacity were measured by Netzsch LFA-467 thermal conductivity meter. Before the test, the upper and lower surfaces of the sample should be sprayed with carbon to make the heat of the surface transfer fast enough and to make the temperature of the surface keep stable. After the lower surface was hit by the laser, the temperature of the upper surface increased with time to the maximum value. Through a function of the empirical function curve of temperature and time, the time required for the temperature to rise to half of the maximum value could be calculated and then the thermal diffusion coefficient of the material could be figured out according to the empirical formula:

$$\alpha=0.1388d^2/t_{\mathrm{h}} \tag{2}$$

where d is the thickness of the sample (m), t_{h} is the time required for the temperature to rise to half of the maximum value (s).

In the test, a standard sample with known heat capacity and density was set. Under the same irradiation energy and detection area of the standard sample and the sample, the specific heat of the sample could be calculated by

$$c_p=\frac{c_{p\,\mathrm{std}}\rho_{\mathrm{std}}d_{\mathrm{std}}\Delta T_{\mathrm{std}}}{\rho d\Delta T} \tag{3}$$

where ΔT is the temperature rise of the upper surface(K), and the subscript “std” represents the standard sample.

3 Results and discussion

3.1 Effect of coating

3.1.1 Phase analysis

The phase analysis of the coating was carried out. The XRD patterns of tungsten-plated diamond particles prepared in 15, 30 and 60 min, are shown in Fig. 2. Theoretically, W can react with the diamond under the experimental conditions. The XRD results showed that the diffraction peak intensity of W was very high from the initial stage to the late stage of the coating, which was the main component in the coating. Moreover, there were no diffraction peaks of WC and W_2C in the 15 min pattern, which indicated that there was no carbide in the coating at the initial stage or the carbide content was too small to be detected. The coating mainly came from the reaction of WO_3 in the raw material with C after sublimation and vaporization to form a certain amount of W, and then gradually reacted with C to form W_2C and WC. The reason was that above 850 °C WO_3 sublimated significantly and

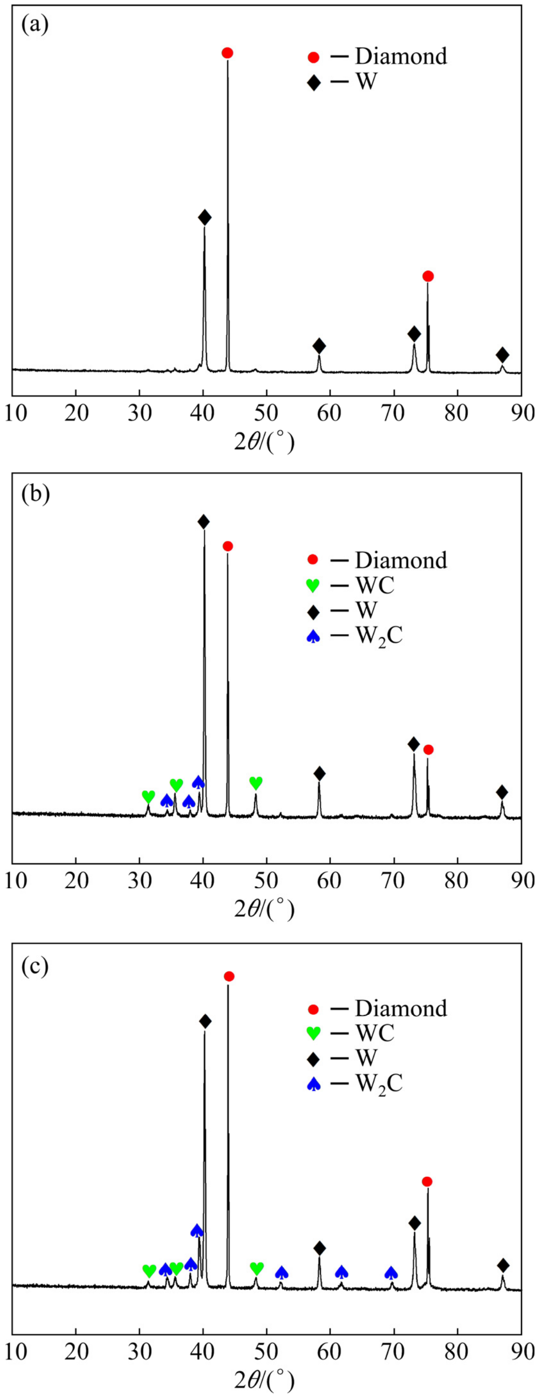

Fig. 2 XRD patterns of tungsten-coated diamond particles prepared for different plating time: (a) 15 min; (b) 30 min; (c) 60 min

contacted with diamond more fully. So its activation degree was much higher than the micro evaporation and diffusion of metal W, and it was easier for WO_3 to react with C.

Based on the results of XRD analysis, it was speculated that the following reactions may occur during the whole plating process:

$$WO_3+3C\rightarrow W+3CO \tag{4}$$

$$2W+C\rightarrow W_2C \tag{5}$$

$$W+C\rightarrow WC \tag{6}$$

$$W_2C+C\rightarrow 2WC \tag{7}$$

The Gibbs free energy of Reaction (5) was −43.9 kJ/mol, that of Reaction (6) was −11.4 kJ/mol, while that of Reaction (7) was −47.4 kJ/mol, at the same temperature of 1273 K. According to the calculated Gibbs free energy, when the plating temperature was 1273 K, W and C preferentially formed W_2C phase. During the high temperature plating process, C atoms in the diamond phase continued to diffuse to the coating, and W_2C formed WC phase with more C atoms, finally W formed WC phase with the surplus C atoms [30]. Therefore, with the increase of time, the intensity of W peak decreased, that of W_2C peak increased, and that of WC peak was always low.

3.1.2 Morphology

The microscopic morphology of the tungsten-coated diamond particles with different plating time was observed, as shown in Fig. 3. It can be seen that after plating obvious coating appeared on the surface of the diamond. The diamond basic shape remained unchanged, and the edges and corners were still clear. Among them, as shown in Fig. 3(a), the coating on the surface of the sample plated for 15 min was relatively uneven with obvious missing plating phenomenon. The local high-power observation was shown in Fig. 3(b). The coating had poor adhesion, which may be damaged in the subsequent sieving, cleaning and drying process. With the plating time increasing to 30 min, as shown in Fig. 3(c), the quality of the coating was gradually improved, and basically each crystal face of diamond had a relatively complete plating layer, but there were still a few defects. At the local high-power magnification, as shown in Fig. 3(d), after 30 min plating, the diamond surface was relatively rough. There were many irregular protrusions on the surface of the coating. The whole coating was uneven, and many areas of the coating had not fully grown longitudinally. Figures 3(e) and (f) showed that the diamond surface plated for 60 min was very complete and more even. As shown in Figs. 3(g) and (h), the coating plated for 90 min began to fall off at the edge of the diamond

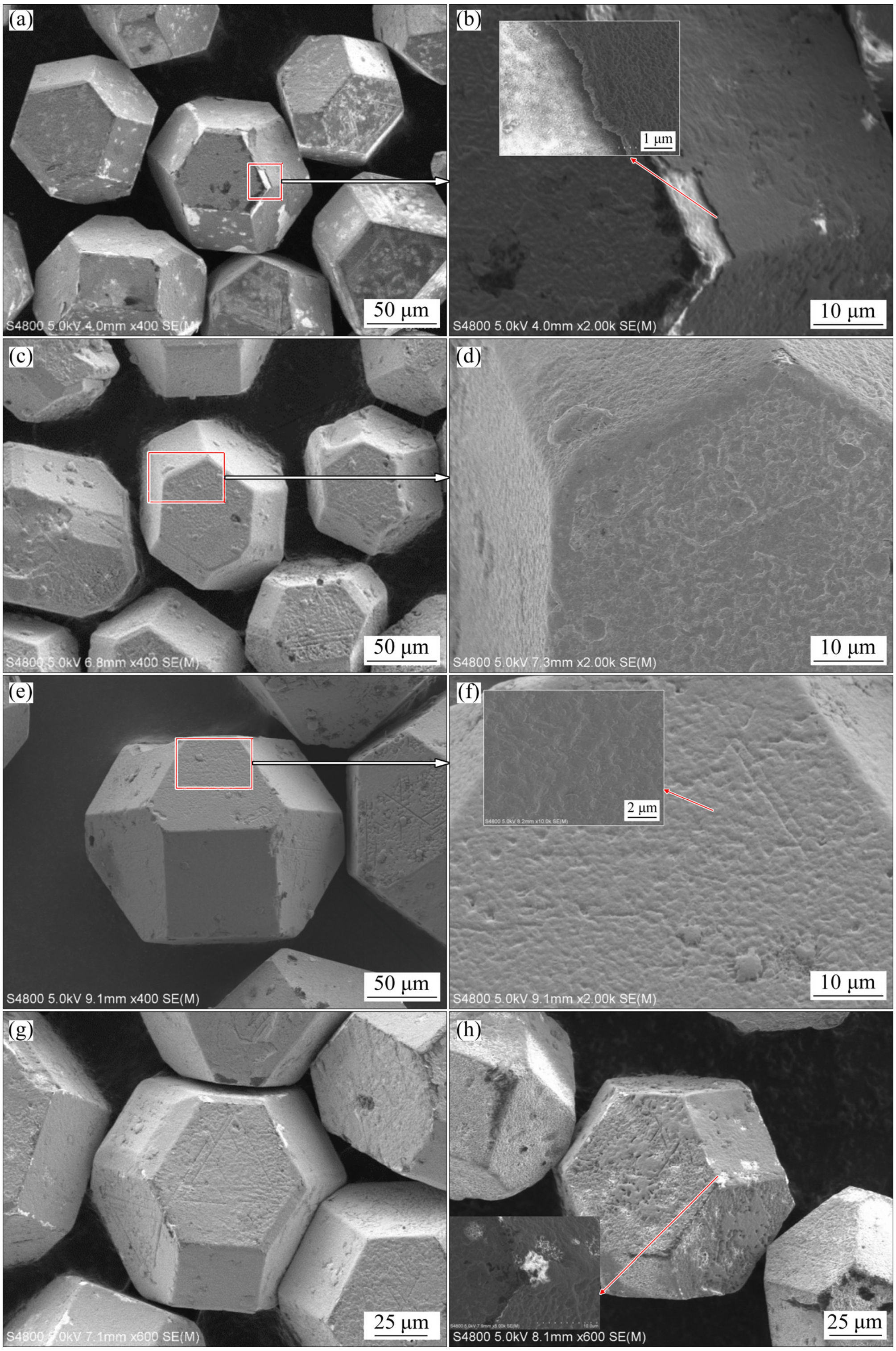

Fig. 3 SEM images of tungsten-coated diamond particles prepared for different plating time: (a, b) 15 min; (c, d) 30 min; (e, f) 60 min; (g) 90 min; (h) 120 min

crystal surface. The diamond coating plated for 120 min showed a large area of shedding and pitting, and the quality of the coating was greatly reduced.

Combined with the analysis of coating's phase composition in Section 3.1.1, the longer the plating time is, the more the carbides with metallurgical bonding with diamond in the coating is, and the better the interface bonding condition is. However, in the micro morphology of the particles, it was found that the coating quality of the particles plated for 90 and 120 min decreased, and the thermal conductivity of the obtained composite also became lower. In addition, it could be observed that the surface of particles coated for 90 and 120 min was rougher, which might be due to the formation of carbides with more large particles with the increase of plating time. Magnified observation of the surface of coated particles treated for 120 min was shown in Fig. 3(h). The surface morphology of particles plated for 120 min became rugged. Some areas were bonded with diamond, which might be carbides metallurgically bonded with diamond; some areas were raised, which may be the W not converted into carbides in the coating. There was no metallurgical bond between W and diamond, and the bonding force was too weak to resist the influence of thermal stress in the cooling process due to the difference of thermal expansion coefficient between W and diamond, resulting in detachment and deformation. When the plating time was short, most of the coating was still metal W. Although its bonding force with diamond was not as good as carbide, diamond was completely covered by the coating, which had strong thermal stress resistance. The surface of particles coated for 60 min was intact and even. With the increase of plating time and the amount of carbide, the W layer was gradually separated by carbide. When the W layer was dispersed, the weak bonding force between W and diamond was not strong enough to resist the thermal stress accumulated during the subsequent cooling process. Firstly, at the edge of the particles with concentrated thermal stress, shedding and destruction began to occur, and gradually spread to the W layer of the whole crystal surface. After 120 min, more coating fell off from the surface of coated particles.

Furthermore, the coated particles were ground and ultrasonically cleaned. After the coating was destroyed, the section morphology of the coating was observed by high-power SEM. As shown in Fig. 4, the nucleation points of the coating on the diamond grew along the longitudinal strip, then extended and accumulated horizontally, and combined with adjacent grains to form a dense coating.

The thickness of the coating was characterized by SEM. The change of the coating thickness with the plating time was shown in Fig. 5. Basically, with the prolongation of plating time, the coating thickness increased and had a high growth rate, especially during the first 60 min. In the last 60 min, the coating thickness changed little. With the increase of plating time, the trend of coating thickening slowed down or even stopped.

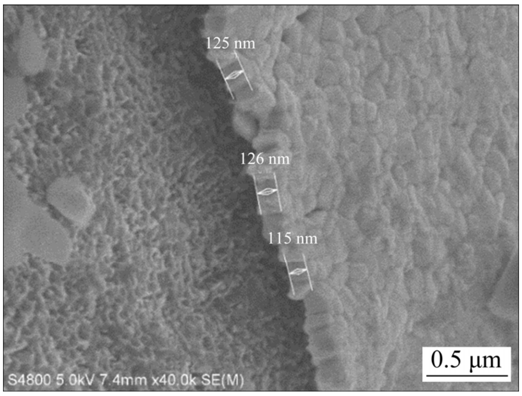

Fig. 4 Cross section morphology of coating after 15 min plating

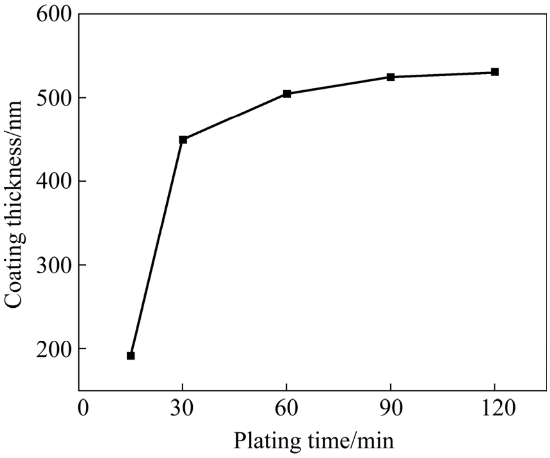

Fig. 5 Variation of coating thickness with coating time

There were two possible reasons for this phenomenon. The first one was that WO_3 had been completely consumed, so that the growth of coating thickness naturally slowed down to stop. The second reason might be that the coating process in this experiment mainly depended on the reaction between WO_3 and C atoms, after the chemical reaction took place, a coating layer gradually formed on the surface of the diamond. With the plating process being carried on, the coating gradually grew and extended, and the exposed area of diamond surface became less and less. As time went on, the coating gradually became complete. At this time, the reduction of tungsten mainly depended on C atoms diffused from diamond to coating, and the reaction efficiency was greatly reduced. With the increase of coating thickness, C atoms' diffusion to the surface got harder, the concentration of C atoms on the surface became lower, and the reaction appeared slower, resulting in a slower growth of the thickness of the coating. In addition, during the experiment, it was observed that the vacuum degree in the tubular furnace decreased rapidly when the plating time was less than 60 min, and the vacuum pump needed to be started frequently to maintain the vacuum degree. After 60 min, the change rate of vacuum degree decreased obviously, and after 80 min, there was little change in vacuum degree. The decrease of vacuum degree was mainly due to the sublimation of WO_3 and the formation of CO. The change of the decrease rate of vacuum degree in the plating process also reflected the change of the effective plating process with the plating time to a certain extent. The above results showed that the coating thickness was indeed affected by the coating time, but limited to the amount of coating materials or the mechanism of thermal diffusion plating, and the coating thickness increases slowly or no longer after reaching a certain value in this experiment. As mentioned above, the integrity of the coating was relatively high when the plating time was 60 min. On this premise, theoretically speaking, the duration of the plating reaction was limited and the coating thickness had an upper limit, which was conducive to control the thermal resistance of the interface layer.

As shown in Fig. 6, the thermal conductivity of the hot-pressed samples first increased and then decreased with the increase of plating time. The thermal conductivity of the sample depended more on the integrity and uniformity of the surface morphology than thickness of the coating. Although the coating of the sample plated for 60 min was thicker than that for 15 and 30 min, the surface could keep smooth and had no obvious damage, and the thermal conductivity of the composite was higher, which indicated that the micro gap and defects between the interfaces damage the thermal conductivity of the composite more than the thicker interface layer. The premise of obtaining thinner coating was to ensure the quality of the coating. Therefore, the plating layer with a thickness of about 505 nm obtained after 60 min plating was the best plating parameter.

3.1.3 Positive effects of heat treatment

As shown in Fig. 7, although a good surface coating was obtained, it was found that there was still a small gap between diamond and copper. Further observation of the composite cross section showed that, as shown in Fig. 8, the diamond crystal at the cross section was complete and separated from the copper phase. There were also many pits in the copper phase, in which the diamond may shed. The EDS surface scan analysis of the cross section showed that the W element was mainly distributed in the pits in the copper phase. Thus it was known that the coating fell off from the diamond, and the adhesion between the diamond and coating was not good enough. The joint between the coating and the diamond was the failure point of the whole interface.

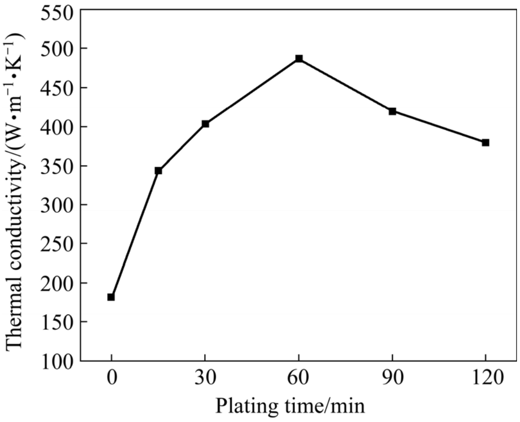

Fig. 6 Thermal conductivity of composites with different plating time

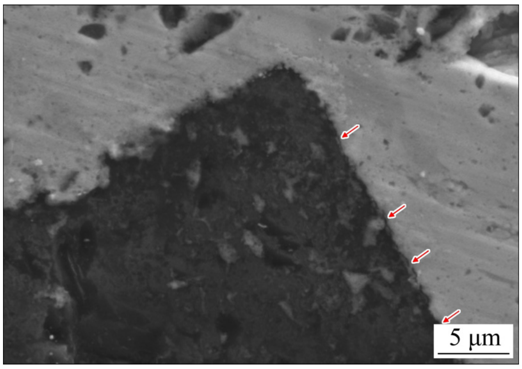

Fig. 7 Micro gap between diamond and copper

The reason for this situation was that there was not enough carbide metallurgical bonding with diamond in the coating. W, as the main component of the coating, could not bear the thermal stress effect of heating and cooling during sintering process, so that it was separated from diamond.

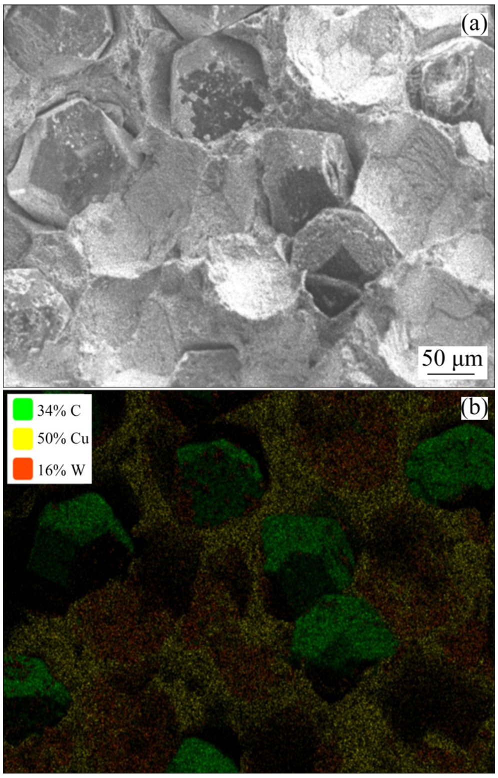

Fig. 8 EDS spectra of diamond/copper composites at cross section

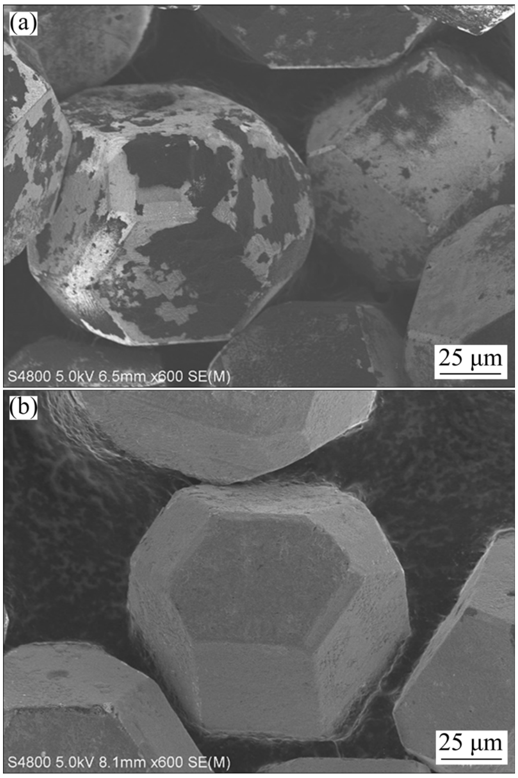

Fig. 9 SEM images of tungsten-plated diamond treated by different heat treatment processes: (a) Simulated sintering; (b) Slow heating and cooling sintering

There were two ways to solve this problem. One was to reduce the heating and cooling rate in the sintering process. According to the previous analysis, W reacted with C at high temperatures and gradually became carbide, so the other was to heat the coated particles again to increase the content of carbide in the coating and to enhance the interfacial adhesion.

Two different process parameters were used for the heat treatment of the coated particles. One was to raise the temperature of the coated particles to 1050 °C at the rate of 50 °C/min and to cool them in the furnace after holding the temperature for 20 min to simulate the previous sintering process. The other was to raise the temperature to 1000 °C at the rate of 10 °C/min and to cool them in the furnace after holding for 2 h at the rate of 10 °C/min to 300 °C. The micro morphology of the particles after heat treatment was shown in Fig. 9. It can be seen that the coating on the surface of the particles after heat treatment in the simulated sintering process had a large number of warping and shedding, which proved that the coating could not adapt to the previous sintering process. However, the coating of tungsten-coated diamond particles remained intact after slow heating and cooling.

Then, the element composition of the coating was analyzed after grinding and ultrasonic damage. As shown in Fig. 10, compared with the untreated particles, the C atom signal of the coating section after heat treatment was stable, and was equivalent to the W signal intensity. This result indicated that the composition of the coating was transformed into W carbide.

Furthermore, the heat-treated particles were used to prepare the composite, reducing the rising and falling speed of sintering temperature. The interface micro morphology of the composite was shown in Fig. 11. The combination of diamond and copper appeared very tight, with no gaps and defects. The thermal conductivity of the composite rose up to 559 W/(m·K). However, the thermal conductivity of the hot-pressed samples prepared with bare diamond was only 182 W/(m·K), which indicated that the process of pre-plating tungsten on diamond in this study had obvious effect on improving the thermal conductivity of the composite.

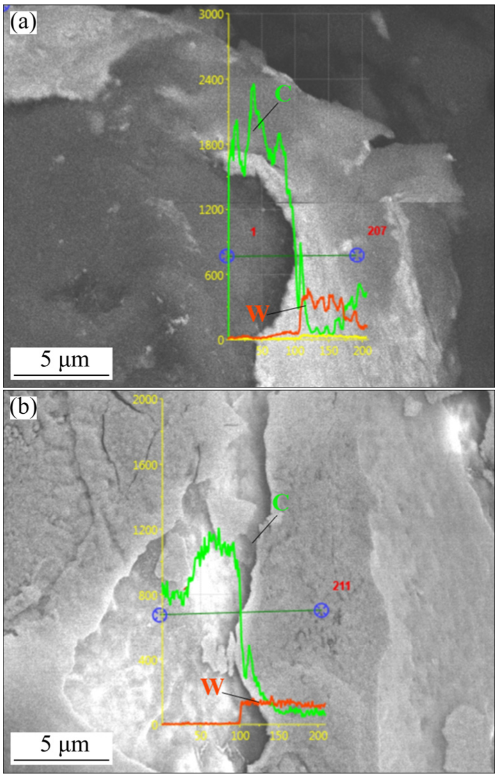

Fig. 10 EDS line scanning of coating before (a) and after (b) heat treatment

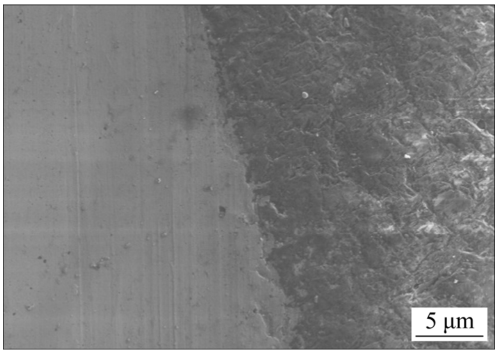

Fig. 11 Interface morphology of composites with tungsten-coated diamond after heat treatment

3.2 Effect of forming process

In the three forming processes, cold pressing sintering and pressureless infiltration equipments were generally used, and the cost was low. But no external force was applied to promoting sintering. Figure 12 showed the micro morphology of samples prepared respectively by cold pressing sintering, pressureless infiltration and hot pressing, with the diamond coated for 60 min without heat treatment. It can be seen from Fig. 12 that there were obvious gaps and defects on the surface of the samples prepared by cold pressing sintering and pressureless infiltration, and the samples prepared by hot pressing method were proved to be more complete and had fewer defects. The density and thermal conductivity of samples prepared by different forming methods under the conditions that diamond particle size was 90−116 μm and volume fraction was 50% were shown in Table 1. The porosity of the samples prepared by cold pressing sintering and pressureless infiltration were only 23% and 17%, which meant that there were a lot of pores and defects in the composite. Pores and defects caused the scattering of phonons and free electrons, and greatly reduced the thermal conductivity of the composites. The measurement results showed that

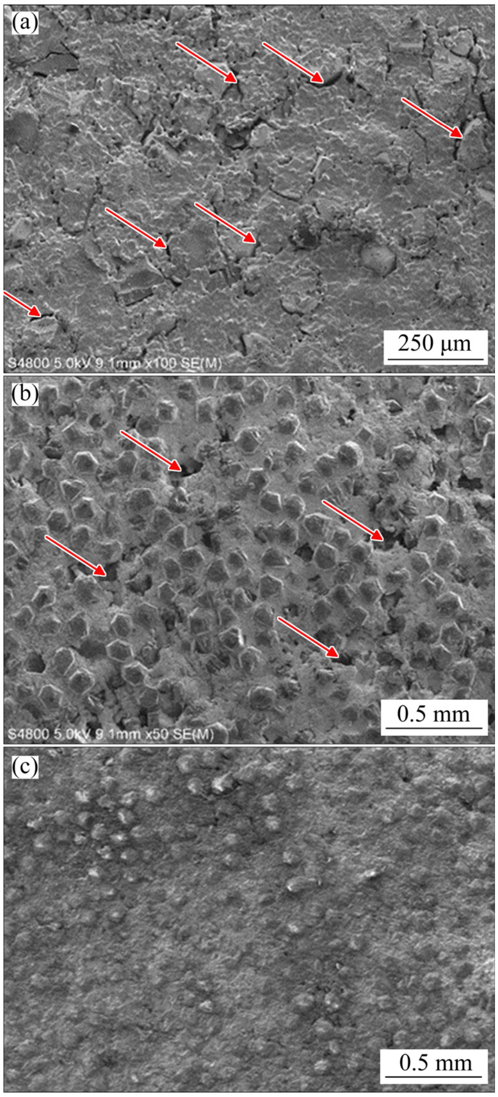

Fig. 12 SEM images of samples prepared by different forming processes: (a) Cold pressing sintering method; (b) Pressureless infiltration method; (c) Hot pressing sintering method

the thermal conductivity of the samples prepared by the two forming processes was less than 100 W/(m·K), much lower than that of copper. The strong thermal conductivity of diamond had not been reflected.

Table 1 Density and thermal conductivity of samples prepared by different forming processes

Forming process	Porosity/ %	Thermal conductivity/ ($\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$)
Cold pressing sintering	23	56
Pressureless infiltration	17	72
Hot pressing sintering	4	419

There was no external force in cold pressing sintering. Even if the diamond surface was coated, the interface bonding was weak. Moreover, the thermal expansion coefficient of diamond and copper was quite different, so the interface cannot bear the influence of the thermal stress during cooling [31]. The above factors led to the gaps and defects as shown in Fig. 12(a), which seriously damaged the thermal conductivity of the composite. Pressureless infiltration mainly depended on capillary force to make copper penetrate diamond, which required higher porosity of preformed diamond and better wettability between diamond and copper. When the preformed diamond was mixed unevenly in the manufacturing process and the binder decomposed and disappeared during sintering, direct contact between diamond particles would be inevitable. The copper phase was surplus at the low porosity area and was insufficient at the high porosity area. The agglomerated diamond hindered the free flow of copper, and the phenomenon of uneven infiltration occurred. Obvious defects could be observed on the surface of the sample. It is difficult to completely fill the pores between diamonds only by the flow of copper, which led to the poor thermal conductivity of the samples.

Powder metallurgy often needed temperature and pressure to provide sintering power. Diamond and copper did not react and the wettability between them was poor, which required external force to promote the combination of them [32−36]. In addition, the thermal expansion coefficient of diamond and copper was quite different, so it was necessary to have a strong interface bonding force to resist the influence of thermal stress in the sintering cooling process. The results showed that the samples prepared by the two pressureless sintering methods had more pore defects than those prepared by hot pressing sintering. The porosity was too high, and the thermal conductivity was far inferior. It was necessary to apply certain pressure during the sintering process to enhance the combination of diamond and copper, reduce porosity and defects, and improve the density and thermal conductivity of the composite.

3.3 Effect of particle size

Figure 13 showed the change of thermal conductivity of hot-pressed samples with different diamond particle sizes at 50% volume fraction of diamond.

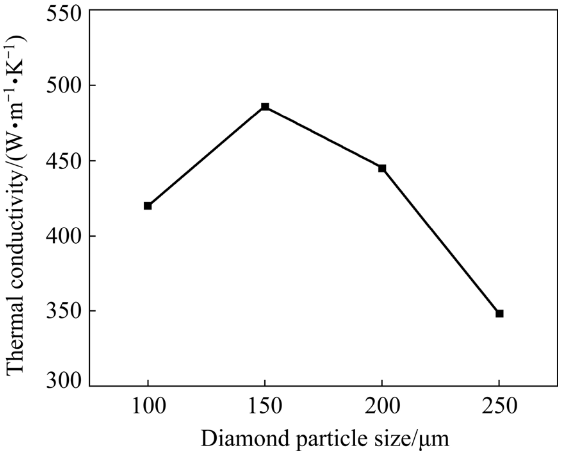

Fig. 13 Effect of diamond particle size on thermal conductivity of diamond/copper composites

The increase in particle size meant a decrease in the specific surface area of the diamond, a decrease in the number of interfaces, smaller thermal resistance of the interface, and higher final calculated thermal conductivity. However, in the actual preparation process, the larger particle size also led to a larger gap between the diamonds. Especially when the diamond agglomerated, it was difficult for copper phase to completely fill the space between the diamonds, resulting in the formation of internal defects in the composite. In addition, when the diamond particle size became larger, the particle size difference between diamond and copper powders was greater, the effect of ball milling mixture would be reduced, and the diamond agglomeration would be aggravated. Therefore, the thermal conductivity of diamond/copper composites increased first and then decreased with the increase of diamond particle size.

In addition, the ultrafine diamond powder with particle size of about 1μm was used for cold pressing sintering experiment. Figure 14 showed the micro morphology of the samples. It could be seen that there were a lot of pores on the surface of the samples, which will seriously damage the thermal conductivity of the composite. The results showed that the specific surface area of diamond was too large, the number of interfaces increased greatly and the interface thermal resistance also increased. In addition, it was difficult for the copper phase to completely and evenly fill the gap between diamonds in the actual preparation. A large amount of diamond was in direct contact, and the density of the composite was very low. Therefore, the measured thermal conductivity of the sample was only about 15 W/(m·K).

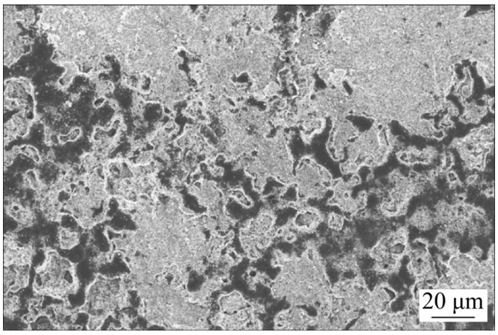

Fig. 14 SEM image of ultrafine diamond/copper composite

3.4 Effect of volume fraction of diamond

Figure 15 showed the change of thermal conductivity of hot-pressed samples with volume fraction of diamond under the condition of diamond particle size of 100 μm.

Under ideal theoretical calculation conditions, the higher the volume fraction of diamond with ultra-high thermal conductivity, the higher the thermal conductivity of the composite. However, in the actual preparation process, due to the obvious differences in particle size and density between the diamond powder and the copper powder, the ball milling mixture could not completely mix them. When the volume fraction of diamond increased, the diamond would inevitably agglomerate, resulting in the formation of internal defects and the decrease of thermal conductivity of the composite. The SEM images of the surfaces of samples with diamond volume fractions of 10%, 30%, 50%, and 60% are shown in Fig. 16. With the increase of diamond volume fraction, the distribution of diamond on the surface is incomplete and uneven. Especially for the sample with 60% of diamond volume fraction, diamond agglomeration and obvious defects could be found on the surface. The thermal conductivity dropped rapidly to 234 W/(m·K).

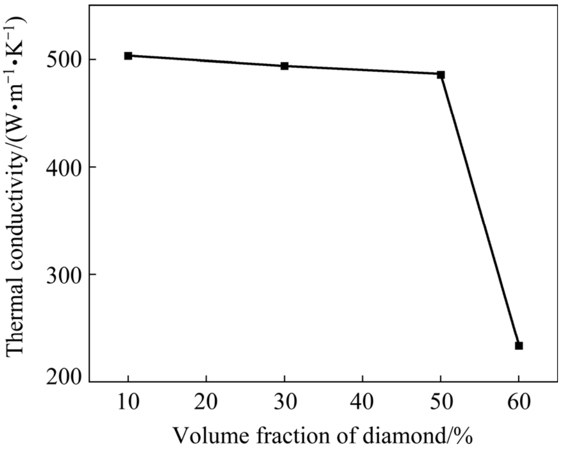

Fig. 15 Effect of diamond volume fraction on thermal conductivity of composites

In general, the experimental results showed that the volume fraction of the diamond should not be too large, and high-volume fraction meant high cost. Therefore, from the perspective of cost control and thermal conductivity improvement, it was meaningless to forcibly increase the volume fraction of the diamond if the influence of internal agglomeration and pore increase caused by high volume fraction could not be effectively reduced.

4 Conclusions

(1) XRD phase detection showed that the main composition of the coating was W. When the plating time was 60 min, the coating was the most complete and uniform. And the thickness of the coating could reach 505 nm, which was not the thinnest coating obtained in this study. But the thermal conductivity of the sample was the highest, which was 486 W/(m·K). The thermal conductivity of the composites depended on the integrity and uniformity of the coating rather than the thickness.

(2) After further annealing treatments, the coating transformed to carbide. There was more

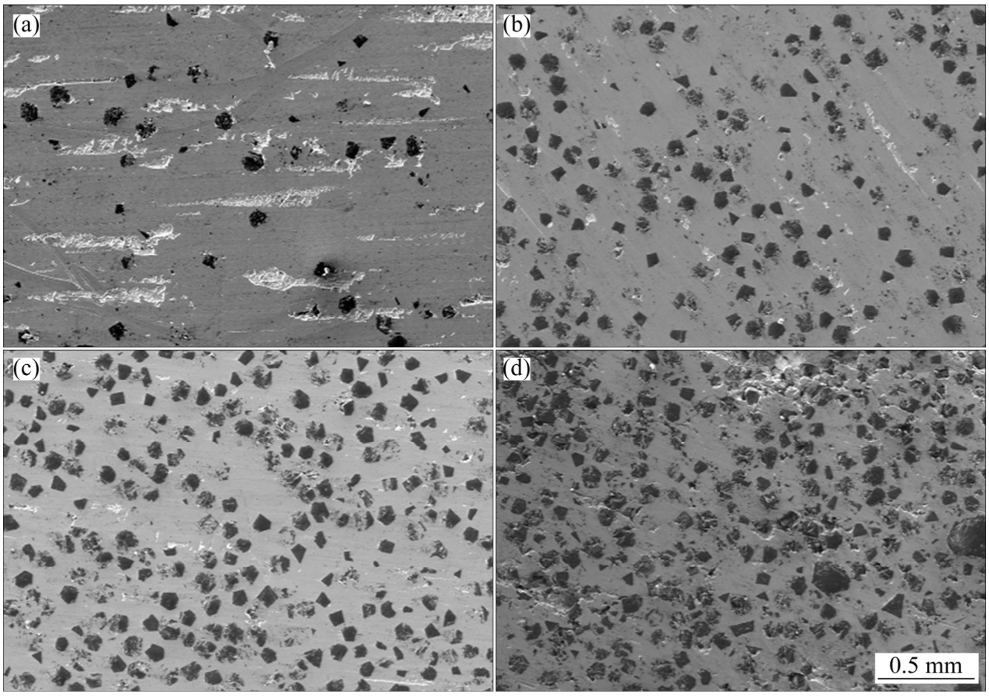

Fig. 16 Surface morphology of samples with different diamond volume fraction: (a)10%; (b)30%; (c) 50%; (d) 60%

metallurgical bonding between the coating and diamond, the interface of the composite became closer, and the thermal conductivity of the sample rose to 559 W/(m·K).

(3) In addition, the effect of pressureless forming was poor. And the thermal conductivity of the hot-pressed sample decreased with the increase of diamond volume fraction, and increased first and then decreased with the increase of diamond particle size.

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镀钨金刚石/铜复合材料的制备及导热性能

戴书刚[1,2]，李金旺[1]，王昌机[1]

1. 南京航空航天大学 航天学院，南京 211106；
2. 中国船舶重工集团第 724 研究所，南京 211153

摘　要：使用热扩散法在金刚石表面镀钨，并采用不同工艺参数制备镀钨金刚石/铜复合材料，观察不同样品的微观形貌，并使用激光闪射法测量样品的热导率，探索制备高热导率金刚石/铜复合材料的最佳工艺参数。研究结果表明，在金刚石表面镀钨可以改善界面结合，当镀覆时间为 60 min 时，镀层完整、均匀、平整，样品的热导率达到 486 W/(m·K)。镀层的完整性和均匀性比镀层厚度更为重要。进一步对镀钨金刚石进行退火处理后，镀层与金刚石之间的冶金结合增强，制备得到的复合材料的热导率提高到 559 W/(m·K)。

关键词：金刚石/铜复合材料；镀层；热导率；界面结合

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