Comparative study on the properties and microscopic mechanism of Ti coating and W coating diamond-copper composites

Shuhui Huang1,2, Hong Guo1,2,3, Zhen Zhang1,2, Ximin Zhang1,2, Haofeng Xie1,2, Zhongnan Xie1,2, Lijun Peng1,2 and Xujun Mi1,2

1 State Key Laboratory of Nonferrous Metals and Processes, GRINM Group Co., Ltd, Beijing, 100088, People’s Republic of China
2 GRIMAT Engineering Institute Co., Ltd, Beijing, 101407, People’s Republic of China
3 Author to whom any correspondence should be addressed.
E-mail: gh_grinm@126.com

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Abstract
Interface plays a decisive role in metal matrix composites, and the effects of Ti coating and W coating on the properties and microscopic mechanism of diamond-copper composites are compared in this paper. Ti-coated diamond with 50 nm, 100 nm and 150 nm plating thickness and W-coated diamond with 50 nm plating thickness are prepared by using magnetron sputtering. Then infiltration method is carried out to prepare diamond copper composites. SEM, EDS and XRD are used to material microstructure. Three-point bending experiment and flash method are used to test the bending strength and thermal conductivity of the composite material. The study found that, as the thickness of the Ti coating increases, the bending strength of the composites gradually increases, but the thermal conductivity first increases and then decreases. The thermal conductivity of W coated diamond copper composites is higher than that of Ti coated diamond copper composites with the same coating thickness. But bonding strength shows the opposite law. The reason for the above phenomenon is that the mechanism of action between the Ti coating and the W coating and the copper substrate is different at the micro interface of the composites. The research work has important reference value for the interface modification of diamond copper composites.

1. Introduction

With the continuous development of the modern microelectronics industry, electronic devices are gradually moving toward miniaturization of high power density, which brings about an exponential increase in power density and heat generation [1–4]. If the heat cannot be transmitted in time, it will be a threat of the electronic device on the work stability and reliability [2, 5–7]. Therefore, the ability of dissipating heat is critical for electronic packaging thermally conductive materials [8–12].

Diamond has excellent physical properties, especially with the highest thermal conductivity (1200 ~ 2000 W m\(^{-1}\) K\(^{-1}\)) and low thermal expansion coefficient (2.3 \(\times\) 10\(^{-6}\) K\(^{-1}\)) [13]. However, diamond is very expensive and difficult to prepare into large specification electronic packaging materials.

When using metals (copper, aluminum, silver, and their alloys) as electronic packaging materials, they can only be applied to the parts that do not directly contact the chip. Because the expansion coefficient of metal is much larger than that of the chip material, if the metal is directly connected to the chip as a heat sink, a large thermal stress will be generated at the connection, thereby reducing the life of the chip [5, 14, 15].

Diamond and metal (copper, aluminum, silver, and their alloys) composites have the characteristics of high thermal conductivity and low expansion, and can be machined into various shapes, which is the most advanced heat sink material currently used [16, 17].
When the diamond content is the same, the aluminum matrix composite has the lowest thermal conductivity and the highest expansion coefficient. Compared with silver-based composites, copper-based composites have slightly lower thermal conductivity and similar expansion coefficients, but at a significantly reduced cost [9, 18]. So diamond–copper composites have attracted extensive attention as a new generation of high-performance electronic package heat-dissipating materials [19].

However, due to the low chemical activity of diamond, it is difficult to achieve good interfacial bonding between diamond and copper matrix by the action of wetting during the preparation of the composites. It can be said that the interface between diamond and copper determines the performance of the composites, which is also the biggest challenge for the preparation of diamond copper composites [5, 12–15].

In recent years, many scholars have done a lot of work on the interface between diamond and copper. W, Cr, Zr, Ti, B and other elements have been used to improve the connection between diamond and copper. The results of these research work provide technical support for the industrial application of diamond copper materials, and this material system has been applied in the heat sink of high power electronic components [9, 16–19].

However, there are many interface solutions in diamond–copper composites, each with its own advantages and disadvantages. Ti and Cu easily form a solid solution, while W and Cu hardly form a solid solution. As the representative of two types of interface transition interface elements with different characteristics, Ti coating and W coating have different mechanisms for the interface modification of diamond–copper composites. At present, there is a lack of quantitative comparative research on the improvement of the properties of diamond–copper composites with two types of interface transition elements, as well as comparative research on microscopic mechanisms. In this paper, Ti coated diamond and W coated diamond are used as raw materials to prepare diamond-copper composites. The effects of coating thickness and type on the thermal conductivity and bending strength of the composite materials are mainly studied. It provides data support for constructing the standards of diamond copper composites system and further promoting industrial applications. And the mechanism by which Ti coating and W coating improve the performance of diamond-copper composites has also been studied. This provides theoretical support for the design of diamond-copper composites.

2. Materials and experimental

In this experiment, the particle size of diamond is about 30 μm (D50), and oxygen-free copper is used as matrix of composites. Diamond copper composites are prepared by pressure infiltration at 1373 ~ 1473 K with 20 ~ 30 MPa, and the volume fraction of diamond is about 55%.

Microstructure of diamond copper composites is analyzed by SEM (Hitachi s-4800 cold field emission scanning electron microscope) and the bending strength of composites is tested by a universal material testing machine of Instron5569. The sample used in bending strength test is 3 × 4 × 25 mm, and the loading rate is 0.5 mm min⁻¹. NETZSCH DSC 404 F3 is used to test the thermal conductivity of composites according to Chinese standard of GB/T 22588-2008. XRD (x-ray diffractometer) is carried out on a PANalytical X-Pert3 Powder equipment.

The properties of some elements and their carbides reported in the literature are shown in table 1. Among these elements, W carbide has the highest thermal conductivity, but the smallest wetting angle with copper. While the thermal conductivity of carbides of Ti or Zr is the same, and the wetting angle is larger that of W. In this paper, the surface of diamond is coated with W and Ti by magnetron sputtering, then the effect of the type and thickness of the coating on the properties of diamond copper composites is investigated.

The phase diagrams of Cu–Ti and Cu–W are shown in figure 1. Ti and Cu will form solid solution in the range of 1000 ~ 1300 K, but W will not. The thermal conductivity of copper and diamond are 400 W m⁻¹ K⁻¹ and 1300–2400 W m⁻¹ K⁻¹, respectively. And the thermal conductivity of all carbides in table 1 is lower than them.
3. Result

3.1. Ti coated diamond-copper composites
Magnetron sputtering is used to deposit 50 nm, 100 nm and 200 nm Ti layers on the surface of diamond particles with D50 of 30 μm through controlling time.

The diamond particles with different thickness of Ti coating are observed by SEM as shown in figure 2. The shape of diamond is irregular, and diamond particles are uniformly covered by Ti coating.

XRD patterns of the diamond particles with different thickness of Ti coating is shown in figure 3. The diffraction peaks of diamond, TiC and Ti can be seen in the diffraction pattern. As the thickness of the coating increases, the intensity of the diffraction peak of Ti also gradually increases. Magnetron sputtering is carried out at high temperature, and the surface temperature of the diamond can reach 973 K. At this temperature, a part of Ti reacts with diamond to form carbide.

Subsequently, pressure infiltration is performed at 1423 K to prepare Ti coated diamond-copper composites. During the infiltration process, most of Ti reacts with diamond to form carbides because of high temperature. But there is still a small amount of Ti and copper forming a solid solution near the interface after cooling.

Samples are taken from the three composites to test the bending strength and thermal conductivity, and the results are shown in table 2.

It can be seen that as the thickness of the Ti coating increases, the bending strength of the composites gradually increases, but the thermal conductivity first increases and then decreases. It is analyzed in the following.

SEM of the fracture of the composites after the three-point bending experiment are shown in figure 4. With the thickening of the Ti coating, the number of cleavage fractures of diamond in the fracture increases, which indicates that the interface bonding strength between diamond and copper gradually increases. This is consistent with the experimental results of the bending strength of the materials in table 2.

The thermal conductivity of TiC is significantly lower than that of diamond and copper, so its amount can evenly cover the diamond particles to produce a good connection effect. Excessive TiC will cause the thermal conductivity of the material to decrease. Diamond is distributed in the copper matrix as dispersion-strengthened particles, enhancing the strength of the composites. Copper and Ti solid solution has lower thermal conductivity than pure copper, so the remaining Ti after the conversion to carbide in the coating layer will reduce the thermal conductivity of the composites. But on the other hand, the diffusion of Ti in copper enhances the strength between copper and Ti carbide.

100 nm Ti coated diamond-copper composites is cut by laser and polished, and the SEM of the cut surface is shown in figure 5. Diamond is evenly distributed in the copper matrix, and no defects are observed in the
composites. It can be seen from the EDS spectrum analysis results that the Ti element is evenly distributed around the diamond particles and has penetrated into the copper matrix. The high magnification SEM of the interface of 100 nm Ti coated diamond-copper composites is shown in figure 6. The interface thickness is about 150 nm, and it also proves the diffusion of Ti at the interface.

Figure 2. SEM of the diamond particles with different thickness of Ti coating: (a) 50 nm, (b) 150 nm, (c) and (d) 100 nm.

Figure 3. XRD patterns of the diamond particles with different thickness of Ti coating.
3.2. W coated diamond-copper composites

It can be seen from the above that when the thickness of the coating exceeds 100 nm, the diamond can be substantially completely covered by magnetron sputtering. Therefore, a 100 nm W plating layer is also prepared.

Table 2. The result of bending strength and thermal conductivity of the three composites.

| Material | 50 nm Ti coating | 100 nm Ti coating | 150 nm Ti coating | Pure copper |
|----------|-----------------|-------------------|-------------------|-------------|
| Bending strength (MPa) | 511 | 602 | 624 | 230 |
| Thermal conductivity (W m\(^{-1}\) K\(^{-1}\)) | 350 | 412 | 391 | 401 |

Figure 4. SEM of the fracture of the different thickness Ti coated diamond-copper composites (a) 50 nm, (b) 100 nm, (c) 150 nm.

Figure 5. Laser cutting surface of 100 nm Ti coated diamond-copper composites: (a) SEM and (b) EDS.
on the diamond surface by magnetron sputtering, which is used to study the effect of different coating elements on the properties of composites.

It can be seen from table 1 that W reacts with C to form two compounds, W2C and WC are generated at about 1073 K and 1373 K respectively. The thermal conductivity of WC is much higher than W2C.

The composites is prepared by infiltration at 1373 ~ 1473 K, so the W plating layer on the surface of the diamond will be converted to WC instead of W2C. To verify the above reasoning, the W-coated diamond is heat treated at 1373 K. And then, The XRD analysis of the W coated diamond before and after heat treatment is carried out, and the results are shown in figure 7. It can be seen that the W coated layer on the diamond surface is completely converted to WC after heat treatment.

SEM and EDS are used to characterize the W coated diamond as shown in figure 8. The W element is evenly distributed on the surface of the diamond particles.

It can be seen in the high-magnification SEM shown in figure 9 that the W coated layer on the diamond surface before heat treatment is smooth, and the smooth W coated layer turns into a rough WC layer after heat treatment.

The rough surface of WC increases the area of the interface between diamond and copper substrate, which is helpful to improve the bending strength and thermal conductivity of the composites at the same time.

The bending strength and thermal conductivity of W coated diamond copper composites are also tested. SEM of the bending fracture of 100 nm W coated diamond copper composites is shown in figure 10.
Compared with 100 nm Ti coated diamond copper composites (figure 4(b)), the proportion of diamond cleavage fracture is lower in 100 nm W coated diamond copper composites. This indicates that the Ti coated diamond-copper composites have higher interface bonding strength.

The bending strength of the composites is consistent with the fracture characteristics. The bending strength of the W coated diamond copper composites is 524 MPa, which is about 15% lower than that of the Ti coated diamond-copper composites with the same coating thickness. But the thermal conductivity shows the opposite law. The thermal conductivity of W coated diamond copper composites reaches 530 W m$^{-1}$ K$^{-1}$, which is about 30% higher than that of Ti coated diamond copper composites with the same coating thickness.

### 4. Analysis and discussion

When carbide is used to connect diamond and copper, in order to obtain higher thermal conductivity of composites, the amount of carbide should be reduced as much as possible under the premise of completely wrapping diamond because of its lower thermal conductivity. But the relationship between the strength of composites and the amount of carbide is not like this, which is determined by the strength of the carbide and the strength of the contact interface.

Schematic diagram of the effect mechanism of coating thickness on the strength and thermal conductivity of composites is shown in figure 11. The ideal coating situation is shown in figure 11(a). Thermally conductive particles are covered by bonding layer evenly. If the bonding layer is continuous and intact, the thinner its thickness, the lower the thermal resistance. The actual situation is shown in figures 11(b)–(d), that the thermally conductive particles can be completely covered only when the bonding layer reaches a certain thickness. Then
when the bonding layer continues to thicken, it will cause the thermal conductivity of the composites to decrease.

Schematic diagram of the interface structure of (a) Ti or (b) W coated diamond-copper composites is shown in figure 12. The thermal conductivity of TiC is lower than that of WC, which is the main reason why the thermal conductivity of Ti coated diamond copper composites is lower than that of W coated diamond copper composites when the thickness of the coating is the same. The strength of interfacial bonding is enhanced, because Ti easily diffuses in copper to form a solid solution. The rough surface of WC is helpful to improve both the interface bonding strength and thermal conductivity of the composites.

Literature [15, 20–22] studied the micro-morphology of Ti coating and W coating as the transition layer between diamond and copper, as well as the effect of improving the performance of the composites. The experimental results of the above-mentioned literature show similar rules to this article. However, in terms of the microscopic morphological analysis of the interface, this paper found that Ti exists at the diamond-copper micro interface in addition to titanium carbide, but also in the form of titanium-copper solid solution. This is also one of the essential reasons that Ti coating and W coating modify the diamond-copper interface differently.
5. Conclusion

(1) Magnetron sputtering is used to deposit 100 nm of Ti and W on the diamond surface, respectively, and then pressure infiltration between 1373 and 1473 K is used to prepare the composites. The thermal conductivity and bonding strength of Ti coated diamond-copper composites are 412 W m\(^{-1}\) K\(^{-1}\) and 602 MPa, respectively, and the thermal conductivity and bonding strength of W coated diamond-copper composites are 530 W m\(^{-1}\) K\(^{-1}\) and 524 MPa, respectively. The thermal conductivity of W coated diamond copper composites is higher than that of Ti coated diamond copper composites with the same coating thickness. But bonding strength shows the opposite law.

(2) The reason why the Ti coating improves the performance of the diamond-copper composite material is the diffusion of Ti atoms in the copper matrix. While the reason why the W coating improves the performance of the diamond-copper composite material is that the rough surface of the carbide increases the contact area with the copper matrix.

(3) Both the thermal conductivity and strength are affected by the type of carbide, and the uniformly wrapped diamond carbide has a positive effect on the thermal conductivity and strength of the composites. The thickness of the carbide is inversely related to the thermal conductivity of the composites, and the strength of the composites is affected by the coupling effect of the type and thickness of the carbide.

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ORCID iDs

Shuhui Huang © https://orcid.org/0000-0003-3734-5427

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